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Infrared spectroscopy of physisorbed and chemisorbed N$_2$ in the Pt(111)(3×3)N$_2$ structure

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Using infrared spectroscopy and low electron energy diffraction, we have investigated the adsorption of N$_2$, at 30 K, on the Pt(111) and the Pt(111)(1×1)H surfaces. At monolayer coverage, N$_2$ orders in commensurate (3×3) structures on both surfaces, and we propose that the unit cells contain four molecules in each case. The infrared spectra reveal that N$_2$ exclusively physisorbs on the Pt(111)(1×1)H surface, while both physisorbed and chemisorbed N$_2$ is detected on the Pt(111) surface. Physisorbed N$_2$ is the majority species in the latter case, and the two adsorption states show an almost identical uptake behavior, which indicates that they are intrinsic constituents of the growing (3×3) N$_2$ islands. An analysis of the infrared absorbance data, based on a simple scaling concept suggested by density functional theory calculations, supports a model in which the (3×3) unit cell contains one chemisorbed molecule in end-on atop configuration and three physisorbed molecules. We note that a classic "pinwheel" structure on a hexagonal lattice, with the end-on chemisorbed N$_2$ molecules acting as "pins," is compatible with this composition. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2804869]

I. INTRODUCTION

Experimental and theoretical studies show that N$_2$ interacts weakly with Pt surfaces. Recent infrared spectroscopic measurements have revealed that N$_2$ does not adsorb at 90 K on the defect-free Pt(111) surface[1] or on the terraces of the stepped Pt(779) and Pt(335) surfaces.[2] However, N$_2$ chemisorbs readily at the step sites of the stepped crystals[2] and at similar defects on the Pt(111) surface[1,3] with a characteristic spectroscopic signature, an infrared absorption peak around 2230 cm^{-1}, i.e. ~100 cm^{-1} lower than the gas phase N$_2$ internal vibration at 2331 cm^{-1}. These observations are supported by density functional theory (DFT) calculations,[2] which identify an end-on atop chemisorbed N$_2$ configuration at the Pt surface step sites. The N$_2$–Pt binding energy is ~0.5 eV. The calculations also show that N$_2$ may chemisorb very weakly (~0.15 eV binding energy, end-on atop configuration) at the Pt(111) terrace sites, but this adsorption state may also be nonexisting depending on the calculational approach and conditions. This raises an obvious experimental question regarding whether a weakly chemisorbed N$_2$ state may be populated at lower temperatures.

At a surface temperature below 45 K, N$_2$ physisorbs readily on Pt(111), as shown by x-ray photoemission spectroscopy (XPS) measurements.[3] He-diffraction experiments[4] reveal the formation of a commensurate (4×4)N$_2$ overlayer at 40 K and a commensurate (3×3)N$_2$ overlayer at 30 K

and below. Both these investigations observe, below 30 K, a two-dimensional (2D) gas phase N$_2$ adsorbate at low coverage, which at a critical density nucleates to form condensed 2D islands. For larger N$_2$ exposures, the He-diffraction experiments show that additional molecules are incorporated in the growing (3×3) N$_2$ islands, and according to the XPS measurements,[3] physisorbed N$_2$ is the majority species in the full monolayer at a surface coverage $\Theta \sim 0.4$. The physisorbed N$_2$ was not detected in the concomitant infrared spectroscopic measurements.[3] However, N$_2$ chemisorbed at steplike surface defects was readily detected, and the highly mobile N$_2$ molecules were found to saturate the steps at very small gas exposures. Most interesting though is the observation at low temperature of a new chemisorbed N$_2$ state with a vibrational frequency of 2266 cm^{-1}. The population of this state increases linearly with increasing N$_2$ coverage up to saturation of the N$_2$ monolayer, i.e., an entirely different behavior from that observed for N$_2$ chemisorbed at the steplike defects. Consequently, this new N$_2$ chemisorption state, with a binding energy around 0.15 eV, was assigned to correspond to N$_2$ chemisorbed at the terraces of the Pt(111) surface in an end-on atop configuration.[3] A nagging point in this context is the lack of a distinct XPS signal. Are these molecules simply very few, and if so why? Can only sufficiently energetic molecules enter this state or is a peculiar defect related mechanism involved? A possible explanation is that the N1s XPS line of this weakly chemisorbed state is so little shifted relative to the physisorption signal that only a single slightly distorted XPS peak results.

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Here, we report measurements using infrared reflection absorption spectroscopy (IRAS) and low-energy electron diffraction (LEED) of N_2 adsorption at 30 K on the Pt(111) surface and the hydrogen saturated Pt(111)(1×1)H surface. Our LEED observations show that the adsorbed N_2 monolayers form ordered commensurate (3×3) structures on both surfaces. The infrared spectra reveal that only physisorbed N_2 populates the Pt(111)(1×1)H surface characterized by a narrow infrared absorption peak at 2324 cm^{-1}. A physisorbed N_2 state also populates the Pt(111) surface, characterized by a sharp peak at 2322 cm^{-1}. Most notable though is the observation of a weakly chemisorbed N_2 state at 2265 cm^{-1}, i.e., identical to the state reported in Ref. 3 and discussed above. Our measured integrated infrared absorbance of this N_2 state is also in good agreement with these data. This close correspondence between the observations from two different experiments strongly supports the proposal that this N_2 chemisorption state is characteristic of the Pt(111) terraces. N_2 adsorption at defects behaves differently and reflects the status of the specific substrate surface investigated. For N_2 chemisorbed at the Pt(111) step sites, we observe an infrared absorption peak at 2232 cm^{-1}, which is more than an order of magnitude weaker than the corresponding signal at 2234 cm^{-1} reported in Ref. 3.

The infrared spectra show that the physisorbed N_2 state is the majority species on Pt(111). This state and the terrace chemisorbed state have an almost identical uptake behavior, which indicates that both species are intrinsic constituents of the growing (3×3) N_2 islands. An analysis of the infrared absorbance data, based on a simple scaling concept suggested by DFT calculations, supports a model in which the (3×3) unit cell contains one chemisorbed molecule in an end-on atop configuration and three physisorbed molecules. We note that a classic "pinwheel" structure on a hexagonal lattice is compatible with this composition. Every end-on bonded chemisorbed N_2 "pin" would then be surrounded by six physisorbed N_2 each attached to two pin molecules.

II. EXPERIMENTAL

The IRAS measurements were performed with the use of an evacuated Bruker IFS 120 HR Fourier transform infrared spectrometer connected to an ion pumped ultrahigh vacuum (UHV) chamber with a base pressure in the 10^{-10} Torr range. The UHV chamber was equipped with LEED optics and a quadrupole mass spectrometer. In order to obtain optimal sensitivity in the spectral range of interest, 2100–2500 cm^{-1}, a spectrometer setup with a glowbar light source, a potassium bromide beam splitter, and an indium antimonide (InSb) detector was used. A more detailed description of the apparatus is presented in Ref. 5.

The Pt(111) single crystal, oriented to within 0.3° of the (111) face by Laue backreflection, was mounted on a manipulator equipped for resistive heating, LN_2 or LHe cooling, and temperature measurements using a platinel thermocouple clamped to the crystal surface. The specimen was cleaned *in situ* by heating at 1150 K for 15 min followed by oxidation at 1000 K for 1 h and subsequently sputtered with Ar ions

(250 eV, 1 $\mu A/cm^2$) at room temperature, and finally annealed at 1000 K.

The crystal was exposed to gases from the background via a manifold system with leak valves. All gas exposures were measured in langmuirs (1 L=1×10^{-6} Torr s) based on the ionization gauge pressure readings. Before IRAS measurements, the hydrogen and nitrogen adsorptions were monitored by work function measurements. The N_2 adsorption and the IRAS measurements were performed at 30 K. The surface was cleaned between consecutive measurements by flash heating to 1000 K. In the Pt(111)(1×1)H experiments, the hydrogen exposure was performed before the background spectrum was recorded. IR absorbance spectra were obtained by taking the ratio of consecutive normalized background and sample spectra. All IRAS data were collected with 2 cm^{-1} resolution, Blackman-Harris three-term apodization function, and zero filling factor of 4.[6] LEED observations of ordered structure formation were performed after IRAS measurements and also in separate experiments with a low primary current in order to avoid possible electron-beam-induced effects in the N_2 overlayer.

The DFT calculations are performed using DACAPO,[7] a plane-wave implementation[8,9] employing ultrasoft pseudopotentials to represent the ionic cores.[10] For the exchange and correlation functional, the RPBE functional was used.[11] The Brillouin zone was sampled using a Monkhorst-Pack scheme with a temperature smearing of the Fermi surface. An energy cutoff of 26 Ry was employed. The Pt(111) surface was represented using a periodically repeated four layer slab of platinum atoms in a 2×2 surface symmetry with a PRBE lattice constant of 4.02 Å. The slabs were separated by 12 Å of vacuum. The two topmost layers were allowed to relax, while the lower layers were kept fixed at the bulk positions. The N_2 molecule was adsorbed in an end-on atop configuration.

III. RESULTS AND DISCUSSION

Here, we present and discuss IRAS and LEED observations of molecular nitrogen adsorption on the clean Pt(111) surface and the Pt(111)(1×1)H surface at low temperatures.

A. N_2 adsorption: Vibrational spectra

Figure 1 shows IRAS spectra recorded for several different N_2 exposures, ranging from 0.6 to 8 L, of the Pt(111) surface at 30 K. Three infrared absorption peaks related to the intramolecular stretch vibration of adsorbed N_2 are observed at 2232, 2265, and 2322 cm^{-1}, respectively.

The sharp peak at 2322 cm^{-1} is only marginally downshifted, $\Delta\nu=9$ cm^{-1}, relative to the gas phase value, 2231 cm^{-1}, of the internal N_2 vibration,[12] and the observed linewidth, ~3 cm^{-1}, is essentially given by the instrumental resolution of 2 cm^{-1}. Both features are characteristic signs of the weak electronic interaction between the adsorbate and the substrate for a physisorbed molecular state. However, the physisorption interaction is responsible for the observed dipole activity of the N_2 stretch vibration. This mode is not dipole active for the homonuclear N_2 molecule, but the physisorption interaction induces a dipole moment in the ad-
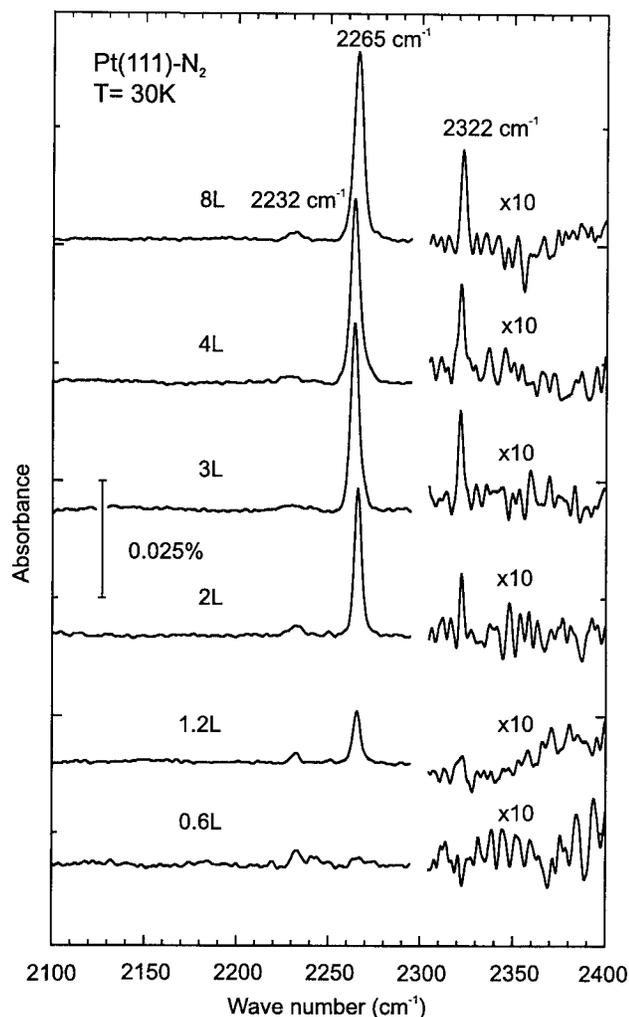
FIG. 1. IRAS spectra recorded for different nitrogen exposures, ranging from 0.6 to 8 L, of the Pt(111) surface at 30 K. The amplitude in the interval 2300–2400 cm^{-1} has been magnified with a factor of 10.

FIG. 2. The integrated absorbance vs nitrogen exposure of Pt(111) at 30 K for (a) the 2322 cm^{-1} physisorbed state, (b) the 2265 cm^{-1} chemisorbed state, and (c) the 2232 cm^{-1} defect site state.

sorbed molecule, which depends on the molecular polarizability and hence varies with the internuclear distance. The vibrating molecule will accordingly be associated with a dynamic dipole moment, and the $n=0 \rightarrow 1$ transition will be dipole active. We have discussed this process in more detail elsewhere[13] and only remark here that the physisorption induced dynamic dipole moment is weak compared to the moments associated with chemisorbed molecules. We note that this physisorbed N$_2$ state on Pt(111) around 30 K has previously been identified with x-ray photoelectron spectroscopy.[3]

The relatively intense infrared absorption peak located at about 2265 cm^{-1} is significantly downshifted from the N$_2$ gas phase frequency, $\Delta \nu = 66$ cm^{-1}, with an enhanced linewidth around 5 cm^{-1}, i.e., properties characteristic of a chemisorbed molecular state. This N$_2$ state was observed previously in IRAS measurements[3] and was tentatively assigned to N$_2$ weakly chemisorbed at the terrace sites of the Pt(111) surface. We will make a more detailed comparison below. The physisorbed and the weakly chemisorbed N$_2$ states experience similar adsorption energies, and both desorb around 45 K.[3,4] Our IRAS data in Fig. 1 reveal that the N$_2$ vibration frequency of these two adsorption states is essentially independent of the N$_2$ exposure below 4 L.
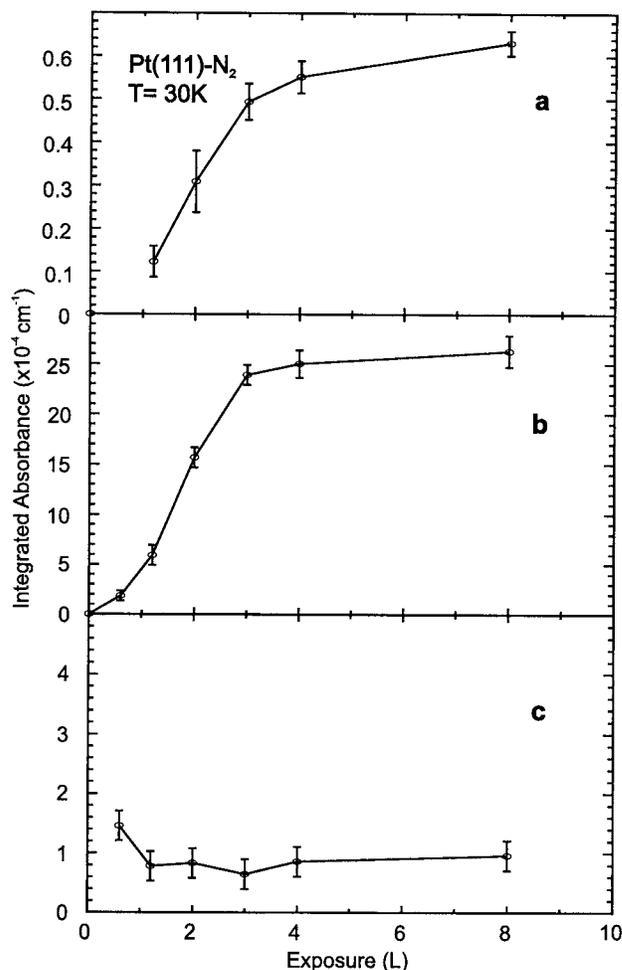
The weak infrared peak at about 2232 cm^{-1} in Fig. 1 is within the interval 2230–2245 cm^{-1}, which is characteristic of N$_2$ chemisorption at defect/step sites on Pt(111) at temperatures below 90 K.[1–3] The integrated absorbance varies with surface preparation, as expected for species chemisorbed at such sites. In our measurements, the defect site adsorption is weak and completed already for our lowest N$_2$ exposure.

Figure 2 shows integrated absorbance data versus N$_2$ exposure at 30 K obtained from the spectra shown in Fig. 1. Panels (a), (b), and (c) display such data for the 2322 cm^{-1} physisorbed state, the 2265 cm^{-1} chemisorbed terrace state, and the 2232 cm^{-1} defect/step site state, respectively. A striking observation in Fig. 2 is the similar evolution of the N$_2$ uptake in the physisorbed and terrace chemisorbed states, which increases rapidly up to the formation of an ordered (3×3) N$_2$ overlayer at an exposure around 3 L. The subsequent compression and saturation of the overlayer proceeds slowly. Helium-diffraction experiments[4] show that N$_2$ initially adsorbs in a 2D gas phase, which nucleates to form 2D islands at an exposure of ~0.15 L. Additional N$_2$ molecules contribute to the island growth. Hence, a natural explanation of the similar uptake is that the physisorbed and chemisorbed N$_2$ states are intrinsic constituents of the ordered 2D islands

of the condensing N_2 overlayer. The weak coverage dependence of the vibrational frequencies of the two terrace adsorption states is compatible with this idea since molecules incorporated in an ordered structure experience an equivalent local environment.

Our spectroscopic data strongly support the tentative proposal of Ref. 3 that the weakly adsorbed 2265 cm^{-1} N_2 species corresponds to a terrace chemisorbed state. It is instructive to compare the integrated absorbance data in Fig. 2 with the corresponding data in Ref. 3. The integrated absorbance is given by[14]

$$I = \int d\omega \Delta(\omega) = \frac{16\pi^2}{\hbar c} n_s (\mu_1^s)^2 \Omega G(\alpha), \qquad (1)$$

where n_s is the number of adsorbed molecules per unit area, μ_1^s is the vibrational dipole matrix element at this coverage, and Ω is the frequency of the internal stretch vibration. The factor $G(\alpha)$ is determined by the optical incidence conditions and the dielectric properties of the metal substrate. $G(\alpha)$ may differ slightly between different setups due to different incidence conditions [$G(\alpha)=11.5$ in our case]. Apart from that, we expect that well-defined adsorption states should give equal values of I in different experiments performed at otherwise equal experimental conditions, while defect related adsorption states may give completely different signals depending on surface preparation. The IRAS data in the two investigations reflect these aspects well. (i) The defect related N_2 chemisorption state saturates at low N_2 exposure but give very different I values of $\sim 0.1 \times 10^{-3}$ cm^{-1} in our case and $\sim 3 \times 10^{-3}$ cm^{-1} in Ref. 3. (ii) The terrace chemisorbed N_2 signal increases smoothly up to a coverage around 0.4 corresponding approximately to the (3×3) N_2 structure. The observed infrared absorbances are very similar $I \sim 2.5 \times 10^{-3}$ cm^{-1} in our work and $I \sim 3.5 \times 10^{-3}$ cm^{-1} in Ref. 3, a marginal difference which may be related to different $G(\alpha)$ values.

We have found that the chemisorbed N_2 states are completely eliminated if the Pt(111) surface is precovered with a $p(1 \times 1)$H overlayer. This was formed by an 80 L H_2 dose at 90 K prior to N_2 adsorption at 30 K. The spectra shown in Fig. 3 were recorded subsequent to a 3 L nitrogen exposure of the clean Pt(111) surface and the hydrogen saturated Pt(111)(1×1)H surface resulting in a $(3 \times 3)N_2$ overlayer in both cases. On the Pt(111)(1×1)H surface, the nitrogen chemisorption peaks are extinct and the internal vibration of the physisorbed molecule is upshifted to 2324 cm^{-1}. These observations agree well with our previous findings regarding O_2 adsorption on Pt(111)(1×1)H: blocked chemisorption and a slightly upshifted internal vibration frequency of the physisorbed O_2 state.[15] The physisorbed nitrogen molecules desorb at about 45 K. The infrared absorbance of the physisorption peaks at 2322 and 2324 cm^{-1} in Fig. 3 is $\sim 0.5 \times 10^{-4}$ cm^{-1} in both cases, which indicates, as we discussed already, that the physisorbed molecules are majority species in the Pt(111)(3×3)N_2 structure.
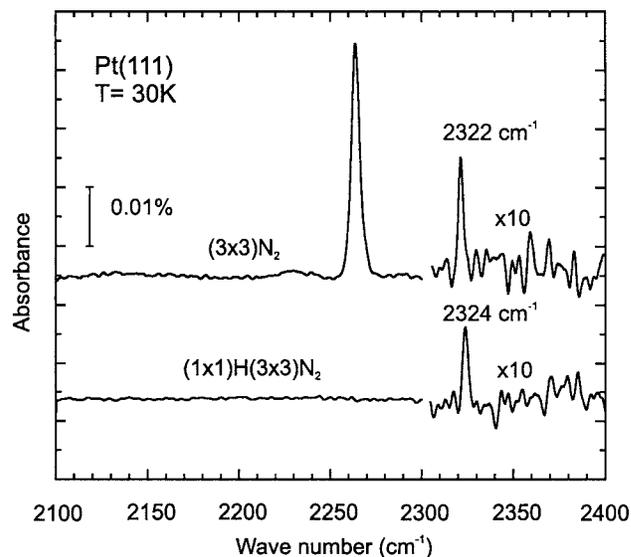

FIG. 3. Spectra recorded for a 3 L N_2 exposure at 30 K of the clean Pt(111) and the Pt(111)(1×1)H surface.

B. N_2 adsorption: Structure

Our LEED observations show that nitrogen adsorption on Pt(111) at 30 K results in an adsorbed commensurate (3 ×3)N_2 overlayer, which for nitrogen exposures larger than 3 L distorts rotationally when the overlayer density is increased. These observations agree well with the results from a previous helium scattering experiment.[4] As discussed above, we also observe the formation of a $(3 \times 3)N_2$ overlayer for a 3 L N_2 exposure of the Pt(111)(1×1)H surface at 30 K. This structure contains only physisorbed N_2 molecules, and we note that also monolayers of Ar and O_2 adsorbed on Pt(111)(1×1)H at 30 K grow azimuthally aligned (3×3) structures.[13] In the Ar case, the simplest interpretation of this structure is a commensurate overlayer with two Ar unit lengths matching three Pt(111)(1×1)H unit lengths and with four adparticles in each (3×3) unit cell. We propose the same structure model for the Pt(111)(1×1)H(3×3)N_2 system. The coverage of physisorbed N_2 is then $\Theta=0.44$, and the adsorbate density is 6.7×10^{14} molecules/cm^2. This structure model is compatible with the (3×3) structure of a physisorbed N_2 monolayer on the Pt(111) surface found in molecular dynamics simulations,[4] and the molecules exhibit in this case an in-plane herringbone orientational order.

The experimental information regarding the Pt(111)(3 ×3)N_2 structure suggests a more complicated situation. The IRAS data discussed above indicate that the unit cell involves both physisorbed and chemisorbed N_2 molecules and that physisorbed N_2 constitutes the majority species, observations corroborated by previous XPS and IRAS measurements.[3] A structure model similar to the Pt(111)(1 ×1)H(3×3)N_2 system, discussed above, but with one chemisorbed and three physisorbed N_2 molecules, as shown in Fig. 4, is compatible with the experimental observations. The chemisorbed N_2 molecules is assumed to occupy an end-on configuration on top of a Pt atom, which is reasonable considering the relatively small downshift, 66 cm^{-1}, of the N–N vibrational frequency and also in accordance with
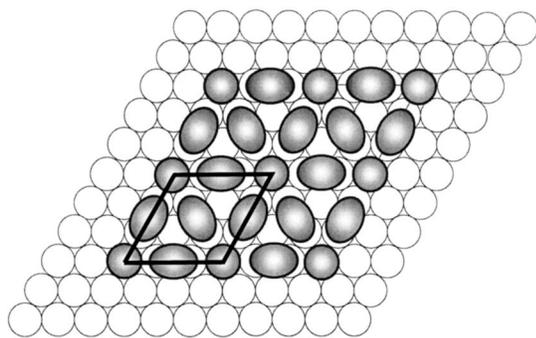
FIG. 4. Proposed model of commensurate (3×3) structure of molecular nitrogen formed at 30 K on Pt(111) with one chemisorbed and three physisorbed molecules per unit cell.
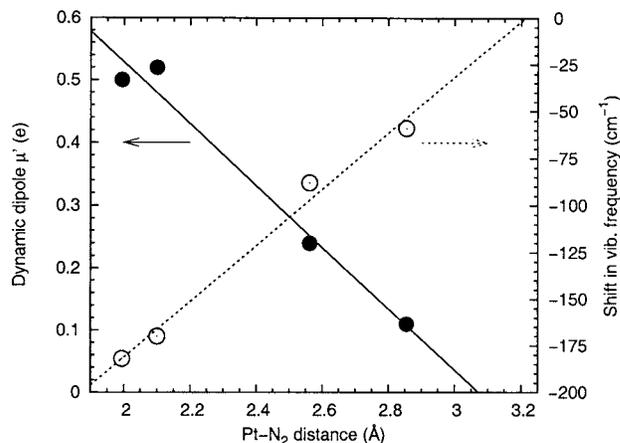

FIG. 5. Dynamic dipole and shift in vibrational frequency vs the Pt−N₂ distance as given by DFT calculations. The Pt−N₂ distance is the vertical distance from the center of mass of the N₂ molecule to the center of the first layer of Pt atoms. The Pt−N₂ distance was varied by fixing the distance of the N atom closest to the Pt surface (the N1 atom) and then allowing for the system to relax. After relaxation, both the N₂ bond and the Pt surface were optimized for the given N1 distance. The actual Pt−N₂ distance was read off after the relaxation. The smallest Pt−N₂ distance corresponds to the relaxation optimum without constraints.

observations for N₂ adsorbed on stepped Pt surfaces.[2] The physisorbed N₂ molecules are simply placed in symmetry positions in the unit cell. The N₂ coverage in this structure is $\Theta=0.44$, which agrees well with the reported saturation coverage 0.41 ± 0.04 of N₂ on Pt(111) below 40 K.[3] An interesting feature of the model in Fig. 4 is the adsorbate arrangement with an end-on chemisorbed N₂ molecule surrounded by six physisorbed N₂ molecules at a distance of 4.16, as seen in the center of Fig. 4. This is a well known pinwheel configuration,[16] with four molecules in the unit cell and each wheel molecule linked to two pin molecules. A different kind of pinwheel arrangement has been reported for N₂ physisorbed on the Cu(110) surface.[16] In this case, every wheel molecule belongs to a single pin molecule.

The structure model in Fig. 4 is compatible with the infrared spectroscopic data, the uptake behavior of chemisorbed and physisorbed molecules, the N₂ coverage, and the LEED observations. However, precise data regarding the relative abundance of chemisorbed and physisorbed N₂ would be most valuable. Neither the thermal desorption data nor the XPS data of Ref. 3 reveal distinct separate signals from the two species. We have investigated the possibility to obtain quantitative information about the surface density of chemisorbed N₂ from the infrared data.

As mentioned in the Introduction, DFT calculations show that the chemisorption bond for N₂ in the end-on atop configuration on Pt(111) is weak, ~0.1 eV, or absent. Considering an accuracy of ~0.1 eV in the calculations, this picture agrees with the measured small adsorption energy of 0.15 eV.[3,4] Frequency shifts of the internal N–N stretch vibration and induced dipole moments can also be obtained from the DFT calculations. The frequency shift is accurately measured in the experiment, and we decided to tune the calculation to the measured shift by varying the Pt−N₂ distance over a suitable range in order to obtain a theoretical estimate of the induced dynamic dipole and the related N₂ density. The calculated data for the shift $\Delta\nu$ and the dynamic dipole μ' versus the Pt−N₂ distance are shown in Fig. 5. The dashed and solid lines are linear fits to the calculated data points and give $\mu'=0$ and $\Delta\nu=0$ at about the same Pt−N₂ distance, 3.1 and 3.2 Å, respectively, in fact close to the estimated distance of 3.1 Å for physisorbed N₂. The adsorption energy is small, ±0.1 eV, over the distance range. The

measured frequency shift is $\Delta\nu=66$ cm^{-1}, which, from the linear fits in Fig. 5, corresponds to a Pt−N₂ distance of 2.78 Å and a dynamic dipole moment $\mu'=0.15e$ at this distance.

We can now estimate the surface density of chemisorbed N₂ molecules from Eq. (1) using the measured integrated infrared absorbance $I=25\times10^{-4}$ cm^{-1}, the measured vibrational frequency $\Omega=2265$ cm^{-1}, and the calculated dipole matrix element μ_1, given by

$$\mu_1 = \mu'\sqrt{\langle r^2\rangle}. \qquad (2)$$

Here, $\sqrt{\langle r^2\rangle}=\sqrt{\hbar/(2m\Omega)}$ is the rms displacement of the internal molecular bond in the harmonic oscillator approximation, where m is the reduced mass of the oscillator, which gives $\mu_1=0.023$ D. $G(\alpha)=11.5$ at our optical conditions, and we obtain 3.6×10^{13} chemisorbed N₂/cm² . This is ~5% of the total density 6.7×10^{14} N₂/cm² in the (3×3)N₂ overlayer, which indicates that chemisorbed N₂ is a characteristic adsorption state of the N₂ overlayer and not just a small contamination ~0.05% like the N₂ molecules chemisorbed at the step edges of our Pt(111) crystal.

Arguing along the lines presented above, we may obtain estimates of the physisorbed and chemisorbed N₂ densities in the Pt(111)(3×3)N₂ structure using the Pt(111)(1×1)H(3×3)N₂ system as a gauge. The latter structure contains only physisorbed N₂; the adsorption energy is ~0.15 eV, i.e., the same as for physisorbed and chemisorbed N₂ on Pt(111).[3,4] The N₂ vibrational frequency is 2324 cm^{-1}, downshifted $\Delta\nu=7$ cm^{-1} relative to the gas phase; the infrared absorbance is 0.45×10^{-4} cm^{-1}, the surface density is 6.7×10^{14} physisorbed N₂ molecules/cm², as proposed above, and the corresponding dipole matrix element is 7.0×10^{-4} D. The XPS data[3] and our IRAS data show that physisorbed N₂ is the majority species on Pt(111), which means that dipole screening will be similar for the physisorbed molecules in the two systems. The vibrational frequency shift and dynamic dipole

moment are zero for the free N_2 molecule, and we simply use a linear scaling of the vibrational frequency shifts and the dynamic dipole moment to obtain the dipole matrix element and density of physisorbed N_2 on Pt(111). In this case, the vibrational frequency is 2322 cm^{-1}, i.e., $\Delta\nu=9$ cm^{-1}, and the dynamic dipole moment is, accordingly, 9/7 times the value for our gauge system. From Eq. (2), we then obtain the dipole matrix element $\mu_1=9.0\times10^{-4}$ D, which from the integrated absorbance and Eq. (1) gives a surface density of 4.6×10^{14} physisorbed N_2 molecules/cm^2 in the $(3\times3)N_2$ structure on Pt(111). This is about 70% of the N_2 surface coverage of 6.7×10^{14}/cm^2, close to 75%, which corresponds to three physisorbed N_2 molecules in the (3×3) unit cell of Fig. 4.

We have also used this scaling idea to obtain an estimate of the surface density of chemisorbed N_2 on Pt(111). This is the minority species, and dipole screening should be weak; we have used the screening corrected value of 1.0×10^{-3} D (Ref. 13) for the Pt(111)(1×1)H(3×3)N_2 reference system.[17] The vibrational frequency for the chemisorbed N_2 is 2265 cm^{-1}, i.e., $\Delta\nu=66$ cm^{-1}, and the infrared absorbance is 25×10^{-4} cm^{-1}. The dynamical dipole is, accordingly, 66/7 times larger than for the N_2 reference. From Eq. (2) and the reference dipole matrix element, 1.0×10^{-3} D, we obtain for chemisorbed N_2 the dipole matrix element $\mu_1=9.5\times10^{-3}$ D, which from the integrated absorbance and Eq. (1) gives a surface density of 2.1×10^{14} chemisorbed N_2 molecules/cm^2 in the Pt(111)(3×3)N_2 structure. This density is $\sim30\%$ of the total N_2 surface density and is also in this case close to the expected 25% corresponding to one chemisorbed N_2 molecule in the (3×3) unit cell.

Our simple analysis of the measured infrared data evidently gives support for the $(3\times3)N_2$ structure model in Fig. 4. The idea of scaling the vibrational frequency shifts and the dynamic dipole moments derives empirically from the DFT calculations. The N_2 adsorption states of concern have low adsorption energies reflected in small values of $\Delta\nu$ and μ' corresponding to small perturbations of the adsorbed molecules. It is conceivable that a linear scaling of $\Delta\nu$ and μ' in this limit is a reasonable approximation.

IV. CONCLUSION

Our LEED and IRAS measurements show that N_2 adsorption at 30 K on the Pt(111) and Pt(111)(1×1)H surface results in commensurate (3×3) overlayers. We propose that the unit cell contain four N_2 molecules in both cases, at a surface coverage of $\Theta=0.44$, with the distinction that only physisorbed N_2 populates the hydrogen covered Pt surface,

while both physisorbed and chemisorbed molecules appear on the bare surface. In the latter case, the two species show a similar uptake behavior at constant vibrational frequencies, which suggest that both adsorption states are intrinsic constituents of the growing $(3\times3)N_2$ islands. The IRAS intensities show that physisorbed N_2 is the majority species, and estimated surface densities of adsorbed N_2 suggest that the unit cell contains three physisorbed and one chemisorbed molecules. The small vibrational frequency shift of the chemisorbed N_2 relative to the gas phase indicates, in accordance with N_2 chemisorption on stepped Pt surfaces, that the molecule is bonded in an end-on atop configuration. We propose a simple structure model for this system with each chemisorbed molecule acting as a pin surrounded in a symmetric arrangement by six physisorbed wheel molecules each (shared by two pin molecules). This is a well-known pin-wheel configuration and is compatible with the experimental information available.

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