DTU Library

Molecular N-2 chemisorption-specific adsorption on step defect sites on Pt surfaces

Tripa, C. Emil; Zubkov, T.S.; Yates, John T.; Mavrikakis, Manos; Nørskov, Jens Kehlet

Link back to DTU Orbit

Molecular N_2 chemisorption—specific adsorption on step defect sites on Pt surfaces

C. Emil Tripa, Tykhon S. Zubkov, and John T. Yates, Jr.[a]
Surface Science Center, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Manos Mavrikakis[b] and Jens K. Nørskov
Center for Atomic-scale Materials Physics (CAMP), Department of Physics,
Technical University of Denmark, DK-2800 Lyngby, Denmark

Infrared reflection-absorption spectroscopy and density functional theory, within the generalized gradient approximation, were used to investigate both experimentally and theoretically N_2 chemisorption on stepped and smooth Pt surfaces. N_2 chemisorption was observed to occur only on the edge atoms of step defect sites in atop configuration by both methods. The calculated vibrational frequency of N_2 chemisorbed on Pt(112) step sites (2244 cm^{-1}) is in good agreement with the frequency observed experimentally (2231–2234 cm^{-1}) at saturation coverage on Pt(335) and Pt(779). The predicted small N_2 binding energy confirmed its weak chemisorption on Pt surfaces claimed in previous studies. The calculations indicate that N_2 decreases and CO increases the work function of the Pt(112) surface. N_2 could be coadsorbed with CO below saturation coverage of the steps with CO and there is a charge transfer between the two adspecies through the substrate. © *1999 American Institute of Physics.* [S0021-9606(99)71141-4]

I. INTRODUCTION

The detection of surface defect sites by spectroscopic means using a test molecule that specifically adsorbs at such sites can form a useful basis for understanding heterogeneous catalysis. Since the first postulate by Taylor[1] that catalytic processes may occur preferentially at defect sites, measurements of the catalytic activity of surfaces have focused on the role the defect sites may play. Van Hardeveld and Van Montfoort[2] studied high surface-area dispersed Pt catalysts by nitrogen adsorption, proposing a special surface defect site, designated as the B_5 site, which adsorbed molecular nitrogen. The existence of this adsorption site was seriously questioned by later studies of N_2 adsorption on silica-supported Pt catalysts and Pt(111) foil.[3,4] It has recently been proposed that molecular nitrogen is a specific sensor for vacancy defect sites on the Pt(111) surface, and that N_2 does not chemisorb on the nondefective Pt(111) surface.[5] These defects were produced by controlled ion bombardment of the Pt(111) surface, and were capable of adsorbing N_2 molecules that exhibit a frequency in the 2222–2244 cm^{-1} range. In a recent paper, we have compared the infrared (IR) spectra of N_2 adsorbed on different Pt substrates. This paper compares highly dispersed oxide-supported Pt catalysts, and Pt(335), Pt(779), sputtered and smooth Pt(111) surfaces, as model catalyst surfaces.[6] We have shown that the IR frequencies on all these substrates are virtually identical, indicating that the adsorption sites are the step defect sites.

In this work, adsorption of N_2 on two single-crystal Pt surfaces has been examined experimentally by reflection-absorption IR (RAIR) spectroscopy. Each surface contains periodic step defect sites made by cutting and polishing the crystal at different angles from the vector normal to the Pt(111) plane. The Pt(335) surface exposes four-atom wide Pt(111) terraces, separated by Pt(100) monoatomic steps. The Pt(779) surface exposes eight-atom wide Pt(111) terraces, also separated by single Pt(100) steps. Since the crystal planes are present on the opposing faces of the same Pt(111) crystal, highly controlled comparisons between the two faces are possible under identical conditions of temperature, pressure, vacuum quality, and optical geometry within the reflection infrared spectrometer. The RAIR spectroscopic data from these two stepped Pt surfaces as a function of coverage show that N_2 adsorption occurs at step sites only. Our experiments show that N_2 adsorption is blocked by chemisorbed CO molecules which occupy step sites, further supporting our proposal for the specific chemisorption of N_2 at the step sites.

Theoretical analysis of the chemisorption of N_2 on the smooth Pt(111) and on the Pt(112) stepped surface [which also exposes (100) step sites] has focused on the thermodynamics of N_2 adsorption on all possible sites. The results of self-consistent density functional theory (DFT) calculations clearly suggest that N_2 adsorbs on step sites only. In addition, the question of whether adsorption occurs on the top or bottom Pt atom at a (100) step defect has been examined, finding that the top of the step is the favorable site for end-on bonding of the N_2 molecule. The vibrational frequency and work function change for N_2 bound at step defect sites has been deduced theoretically, showing that the bound N_2 molecule is electropositive outward, and that its frequency is shifted downward from its gas phase value by about 147 cm^{-1} upon chemisorption, reasonably matching the experimental observations presented in this paper. These results

---

[a]Electronic mail: jyates@vms.cis.pitt.edu
[b]Current address: Department of Chemical Engineering, University of Wisconsin–Madison, 1415 Engineering Drive, Madison, Wisconsin 53706-1691.

will now allow defect sites on high area catalytic Pt surfaces to be investigated by infrared methods with confidence, based on these controlled studies on model defective Pt surfaces.

II. EXPERIMENT

A. Apparatus

The measurements were performed in an ultrahigh vacuum chamber (UHV) with a base pressure $\sim 1 \times 10^{-10}$ mbar, which has been described in detail elsewhere.[7] The chamber is equipped with low energy electron diffraction (LEED) optics, a single-pass cylindrical mirror analyzer for Auger electron spectroscopy (AES), a Fourier transform infrared (FTIR) spectrometer, and an absolutely calibrated and collimated capillary array gas doser delivering a flux of $1.7 \times 10^{12} N_2 \, \mathrm{Torr}^{-1} \mathrm{s}^{-1} \mathrm{cm}^{-2}$ for our crystal geometry.[8]

The two stepped Pt surfaces used here, (335) and (779), were prepared on a Pt(111) monocrystal (15 mm diam) with two faces oriented at different angles relative to the $\langle 111 \rangle$ axis. This double-faced crystal permits accurate comparisons of chemisorption on the two faces under identical conditions of cooling, heating, and background vacuum. The crystal was oriented, cut, and polished within $0.5°$ of the desired orientations by conventional methods.[9,10] The crystal was mounted on two 1.0 mm W wires through which heating and cooling are accomplished. A chromel-alumel thermocouple was spotweleded to the rim of the crystal. The surfaces were cleaned in the conventional procedure by cycles of 600 eV Ar^+ sputtering, followed by 1000 K O_2 cleaning and annealing to 1200 K. In the early cleaning stages, the surfaces displayed significant amounts of Ca, Si, C, and O as evidenced by the Auger spectroscopy. It is known that Si segregates efficiently to the surfaces at about 900 K, while for CaO the higher the temperature the larger the surface segregation rate for temperatures below 1200 K.[11,12] We, therefore, annealed the crystal at 1200 K during the sputtering step, subsequently reducing slowly the temperature to 900 K toward the end of the sputtering schedule. The carbon impurity was removed mainly by oxidation in a molecular O_2 beam produced from the collimated capillary array doser; no surface reconstruction was noted in the LEED patterns under these cleaning conditions.

Special attention was paid to the surface order and cleanliness. Figure 1 shows the Auger spectra of the two surfaces when these no longer exhibited impurity segregation after annealing at 1200 K for ~ 1 h. The presence of two well-resolved Pt peaks at 150 and 158 eV (sulphur test), the absence of peaks at 121 eV (phosphorus), 292 eV (calcium), and 510 eV (oxygen), along with a 94/236 eV peak-to-peak ratio of 0.25 (silicon test) indicate the presence of clean surfaces within the limits of Auger spectroscopy.[11,12] Occasionally, traces of C (272 eV) and O (510 eV) were noticed as a result of background CO decomposition on the surface by the primary electron beam used for AES and oxygen cleaning removed the carbon in this case. The step structure, confirmed by LEED measurements, was in excellent agreement with patterns characteristic of four-atom wide and eight-atom
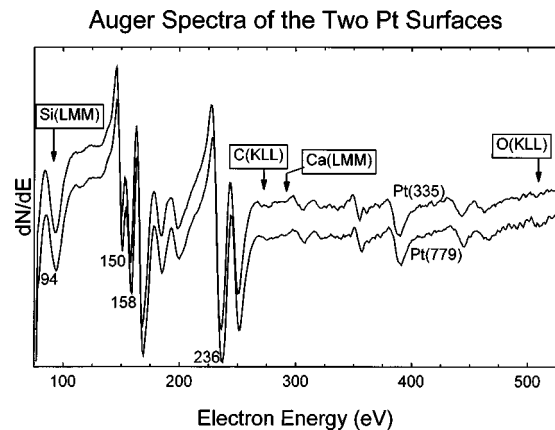

FIG. 1. Auger spectra of the clean Pt(335) and Pt(779) surfaces. The arrows point to the energies where the impurity elements, if present, would show their Auger transitions.

wide (111) terraces of Pt(335) and Pt(779), respectively (Fig. 2).

Measurements of the slight curvature of the stepped crystal surfaces used in this work indicate that inadvertent step sites due to crystal curvature cannot exceed 1 step/1500 Å for the Pt(335) surface and 1 step/2300 Å for the Pt(779) surface.[10]

The reflection-absorption infrared (RAIR) spectroscopy measurements were made with a N_2-purged double-beam FTIR spectrometer described elsewhere.[13] All IR spectra were collected with 2 cm^{-1} resolution and were averaged over 2000 scans. The angle of incidence of the IR beam is about $85°$.

$^{14}N_2$ used in the present work (99.9999%; natural isotopic abundance) was always dosed through the molecular
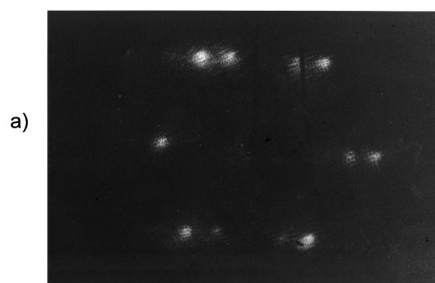
FIG. 2. Low energy electron diffraction (LEED) patterns of cleaned stepped Pt surfaces: (a) Pt(335) or Pt(S)-[4(111)×(001)], 145 eV; (b) Pt(779) or Pt(S)-[8(111)×(001)], 145 eV.

beam doser to achieve N$_2$ adsorption mainly on only one of the monocrystal faces.

B. Computational details

The adsorption of nitrogen molecules on a flat (111) and a stepped Pt(112) surface was investigated using periodic slab DFT calculations. The flat surface was simulated by a four atomic layer slab (total thickness ~6.9 Å), whereas for the much more open stepped surface a slab with nine atomic layers was used (total thickness ~ 6.5 Å). Six (or fourteen) equivalent layers of vacuum were used to separate any two successive metal (111) [or (112)] slabs. Adsorption was allowed on only one of the two surfaces exposed per slab, and the electrostatic potential was adjusted accordingly. N$_2$ adsorption on the Pt(111) surface was studied within a 2×2 unit cell, whereas a 3×2 unit cell was used for the (112) surface. Modeling adsorption of N$_2$ on a Pt(335) or Pt(779) stepped surface, as studied in the experiments described herein, would require considerably larger unit cells, resulting in much more expensive calculations than the ones performed here.

The topmost surface 2(4) atomic layers of the Pt(111) [Pt(112)] slab were allowed to relax during adsorption, respectively. Ionic cores were described by ultrasoft pseudopotentials,[14] and the Kohn–Sham one-electron valence states were expanded in a basis of plane waves with kinetic energies below 25 Ry. The surface Brillouin zone was sampled at 18 special k-points for the (111) slab and 16 k-points for the (112) slab. The exchange-correlation energy and potential were described by the generalized gradient approximation (GGA-PW91).[15,16] Results are also reported for the RPBE functional describing the exchange-correlation energy, which has been generally shown to give better adsorption energies.[17] The calculated PW91 lattice constant for bulk Pt was found to be 4.00Å, in reasonable agreement with the experimental value of 3.92 Å.[18] The self-consistent PW91 density is determined by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi population of the Kohn–Sham states ($k_B T = 0.1$ eV), and Pulay mixing of the resulting electronic density.[19] All total energies have been extrapolated to $k_B T = 0$ eV. The vibrational frequencies reported here were all calculated for the relaxed molecules adsorbed on relaxed surfaces.

III. RESULTS

A. IR spectroscopic observation of N$_2$ adsorption on Pt(335) and Pt(779)

Molecular nitrogen adsorbs on Pt(335) at 88 K in a configuration that is active in RAIR spectroscopy, as shown in Fig. 3. The set of RAIR spectra in Fig. 3 displays bands situated within the 2231–2244 cm^{-1} range, previously assigned to the N≡N stretching mode adsorbed on Pt defect sites.[5] The bottom four spectra in Fig. 3 show that two bands (2244 and 2236 cm^{-1}) develop and grow simultaneously upon increasing the N$_2$ exposure, shifting downward in frequency. At higher exposures, only the low-frequency band (2231 cm^{-1}) is visible, for exposures as high as 3.8
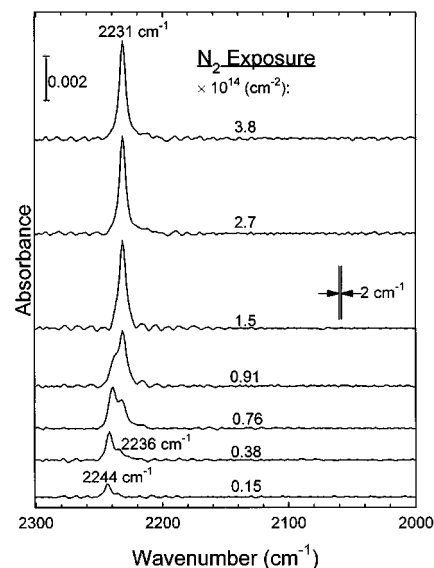
FIG. 3. RAIR spectra of N$_2$(a) on Pt(335) at 88 K.

×10^{14} N$_2$ cm^{-2}. The full width at half maximum (FWHM) of the 2231 cm^{-1} band is only 5 cm^{-1} (including the instrumental resolution of 2 cm^{-1}).

The adsorption of N$_2$ on Pt(779) at 88 K follows a similar RAIR trend (see Fig. 4) as that on Pt(335). The spectral development begins with two singleton N≡N stretching modes (2245 and 2236 cm^{-1}) at very low exposures, then passes through an intermediate stage where both bands are present, towards the high exposure range where only the low-frequency band (2234 cm^{-1}) is visible. The 5 cm^{-1} FWHM of the 2234 cm^{-1} band is the same as the 2231 cm^{-1} band recorded on the Pt(335) surface.

In Fig. 5, the integrated RAIR band intensity in each spectrum is plotted versus N$_2$ exposure. Both curves follow
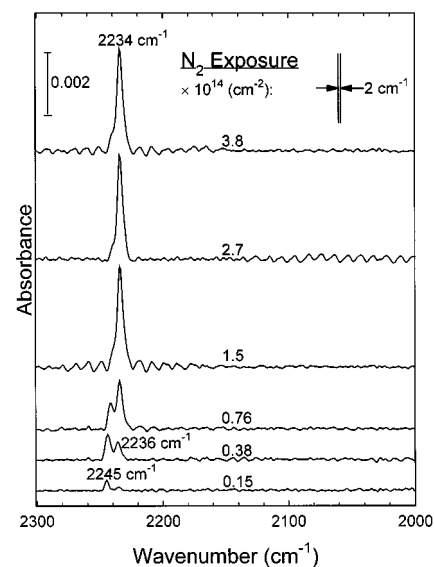
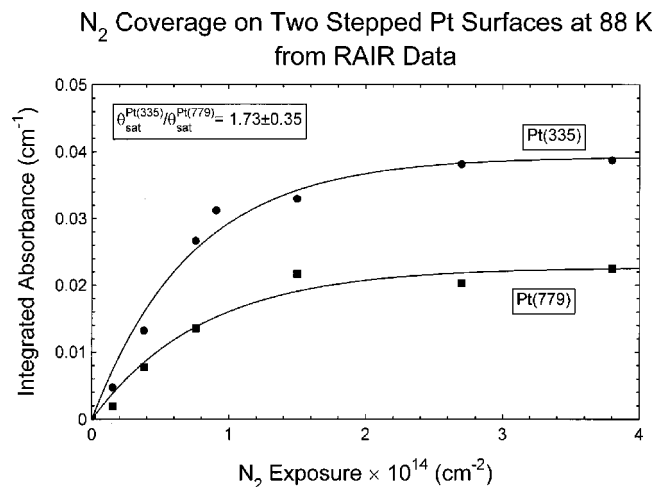FIG. 4. RAIR spectra of N$_2$(a) on Pt(779) at 88 K.

FIG. 5. N_2 coverage vs exposure on two stepped Pt surfaces. The ratio of the N_2 saturation coverage on the two surfaces calculated from this plot is 1.73 ± 0.35. The theoretical ratio is 2, based on the step site densities.

the expected behavior, displaying an asymptotic approach to a final intensity at high exposures. The ratio of the integrated absorbances corresponding to saturation coverage on the two stepped surfaces is calculated to be 1.73 ± 0.35 (error bar defined as $\pm 2\sigma$) from exponential fits to the two curves. The integrated IR intensity for N_2 on both surfaces reaches a maximum at an exposure of about 2.0×10^{14} cm^{-2}. This limiting exposure is in excellent agreement with that measured by gas-phase adsorption uptake experiments.[20]

B. RAIR spectroscopy of N_2 coadsorption with CO on Pt(335): Identification of the adsorption site

It was found that the adsorption of $^{13}C^{18}O$ on Pt(335) monotonically reduces to zero the infrared intensity for saturation coverage of N_2, in agreement with previous studies.[3,4] Figure 6 shows RAIR spectral developments where $^{13}C^{18}O$ is adsorbed only on the step sites to increasing coverage, followed by saturation of the surface by N_2. The $^{13}C^{18}O$ initially produces an IR band at 1970–1987 cm^{-1}, corresponding to CO exclusively on step sites.[21–23] Upon subsequent N_2 adsorption, conversion of some of the preadsorbed $^{13}C^{18}O$ to a new form of CO (1950–1960 cm^{-1}), still bonded to the step atoms, occurs. The low intensity band at 2012 cm^{-1}, seen in the highest CO coverage spectrum, is due to a small amount of the isotopic impurity, $^{13}C^{16}O$. The location of the $^{13}C^{18}O$ band for adsorption on the terrace sites of Pt(335) is indicated in the lower spectrum of Fig. 6.

C. Modeling N_2 adsorption on flat and stepped Pt surfaces

The adsorption of N_2 on Pt(111) was studied theoretically for a $\frac{1}{4}$ ML coverage. All four possible high symmetry sites for end-on adsorption available on the Pt(111) facet were examined. As shown in Table I, from these sites only the atop configuration gave a small binding energy of -0.16 eV within the PW91 description of the exchange-correlation energy. However, the same molecular state calculated within the RPBE functional appears to be unstable by 0.17 eV. The
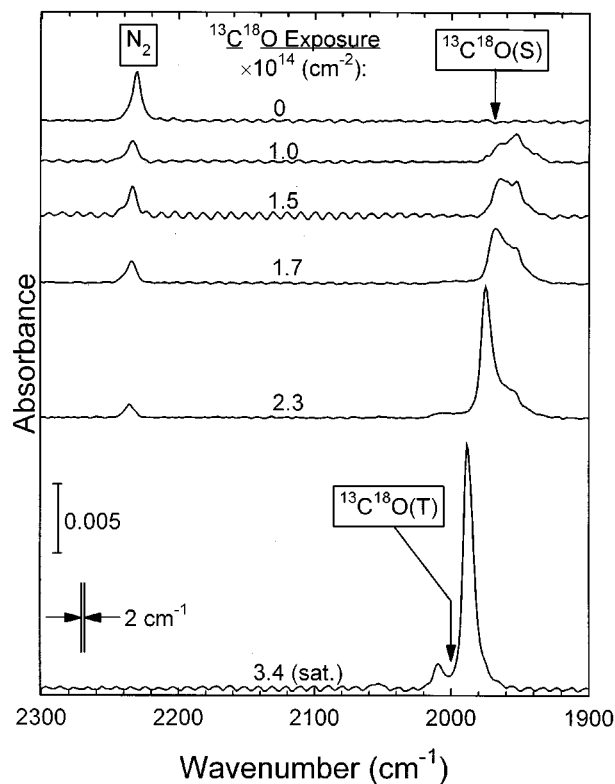

FIG. 6. RAIR spectra of N_2 coadsorption with preadsorbed $^{13}C^{18}O$ on Pt(335). The $^{13}C^{18}O(T)$ band due to terrace-adsorbed species, if it were present, should be seen at ~ 2000 cm^{-1}. The arrow points to the frequency where a terrace CO band should develop, if it were present. The 2011 cm^{-1} band is produced by the $^{13}C^{16}O(S)$ impurity. The saturation condition in the lower spectrum refers to saturation of the step sites by $^{13}C^{18}O$.

latter result is derived from the minimum energy structure calculated self-consistently in PW91, not in RPBE. Geometry optimization in RPBE may result either in lack of a local minimum (desorption of N_2) or the existence of a very shallow minimum further away from the surface. The remaining three possible molecular configurations examined are clearly unstable. No stable side-on molecularly adsorbed state on Pt(111) was found either.

The adsorption of N_2 on Pt(112) was studied for coverages between $\frac{1}{6}$ and $\frac{1}{2}$ ML. All possible sites available on this stepped surface were investigated for the adsorption of one to three nitrogen molecules per unit-cell. The results are summarized in Table I. For one molecule per unit-cell ($\theta = \frac{1}{6}$) corresponding to half coverage of the step edge, three stable states were found per PW91, all of which represent adsorption on the step-edge. No stable state was identified for terrace sites of the stepped surface. Of the stable—per PW91—molecular states, the one corresponding to the bridged, end-on configuration on the step edge appears to be marginally unstable per RPBE, and therefore, we did not calculate its stretch frequency. The most stable molecular state is an end-on configuration, on top of a step edge Pt atom, with a binding energy of -0.67 eV per PW91 (-0.34 eV per RPBE). The second stable molecular state calculated

TABLE I. Comparison between calculated and experimental coverages and vibrational frequencies; theoretical predictions of binding energies and work function changes for N$_2$ on Pt(112), Pt(335), Pt(779), and Pt(111). Negative values in the PW91 and RPBE columns correspond to thermodynamically stable states. $\Delta\phi$ is reported with respect to the clean surface. N$_2$ (gas phase): ω_{exp}=2356 cm^{-1}, ω_{calc}=2391 cm^{-1}.

State	$\theta_{N_2}^{step}$ calc	$\theta_{N_2}^{step}$ exp	PW91 (eV/N$_2$)	RPBE[a] (eV/N$_2$)	$\Delta\phi$ (eV/N$_2$)	ω(N$_2$) (cm^{-1}) calc	ω(N$_2$) (cm^{-1}) exp
Step N$_2$, $\perp$ atop	0.5	0.41[b] 0.56[b]	−0.67	−0.34	−0.28	2244	2231/Pt(335) 2234/Pt(779)
Step N$_2$, $\perp$ atop	1.0	---	−0.46	−0.09	−0.09	2251/2227[c]	---
Step N$_2$, $\parallel$ bridged	0.5		−0.57	−0.14	+0.07	1895	
Step N$_2$, $\perp$ bridged	0.5		−0.35	+0.03			
(111) N$_2$, $\perp$ atop	0.25[d]	N.A.[e]	−0.16	+0.17			N.A.[e]

[a]Geometry not optimized. Positive values mean that the interaction is repulsive at the PW91 minimum energy configuration, and that N$_2$ will move further away from the surface.
[b]The experimental *saturation coverage* on Pt(335) and Pt(779), respectively, from Ref. 20.
[c]The two ω values correspond to in-phase/out-of-phase modes, respectively.
[d]Global coverage.
[e]Not applicable. See Ref. 5.

for N$_2$ on Pt(112) corresponds to a side-on configuration with the N$_2$ molecule anchored on two adjacent step Pt atoms. The corresponding binding energy is −0.57 eV per PW91 (−0.14 eV per RPBE).

The possibility of adsorbing two N$_2$ molecules per unit cell of the Pt(112) slab ($\theta=\frac{1}{3}$) was examined next. All possible combinations were investigated, including sites on the step edge or terrace and end-on or side-on molecular configurations. The only stable state we found is listed in Table I and corresponds to both molecules adsorbed end-on, on top of adjacent Pt atoms on the step edge. This configuration implies full coverage of the Pt(112) step edge by nitrogen molecules, with a per molecule binding energy of −0.46 eV in PW91 (−0.09 eV in RPBE).

The calculated work function changes due to adsorption of N$_2$ on Pt(112) for the different stable configurations identified are given in Table I. The atop state causes a net decrease in the clean surface's work function, for all coverages up to the step edge saturation limit. On the contrary, the side-on stable molecular state is predicted to slightly increase the surface work function.

Further attempts to accommodate more than two nitrogen molecules per unit-cell for the Pt(112) surface for all possible combinations of different adsorption sites and molecular configurations all failed, implying that it is impossible to have stable molecular N$_2$ states elsewhere but on the edges of the Pt step sites.

D. Modeling N$_2$ coadsorption with CO on Pt(112)

The results of the calculations for CO chemisorption prior to N$_2$ adsorption on Pt(112), in a 1:1 mixture, are summarized in Table II. All possible sites were investigated, and the most energetically favorable configuration for different coverages is given. CO, similarly to N$_2$, prefers binding on top of the step-edge Pt atoms with its C-end closer to the surface. CO is also stable on the terraces of the Pt(211) surface, with a binding energy smaller than that on the step edge.[24] However, this case was not examined here, since the primary objective is to study the coadsorption of CO and N$_2$

on sites where N$_2$ can adsorb as well. A simple comparison of the calculated binding energies for CO and N$_2$ at corresponding coverages clearly indicates that CO forms a much stronger bond to the surface (2.11 eV for CO versus 0.67 eV for N$_2$, for the half-covered step edge). Thus, preadsorbed CO cannot be displaced by N$_2$, and CO blocks Pt sites from N$_2$ adsorption. As for the case with pure N$_2$, CO can also populate all step-edge sites, with only a small decrease in its binding energy per molecule ($\sim$ 0.30 eV) due to repulsive interactions between neighboring CO molecules. According to the calculations, CO chemisorption induces a small increase in the surface work function.

Table II includes the results of a calculation where half the step edge on each step site is covered with CO, and the rest of the step edge is then filled with N$_2$. The total energy gain for the CO half-covered step edge surface increases by $\sim$0.2 eV upon filling the step edge with N$_2$, indicating that nitrogen molecules can still weakly adsorb on the empty sites of the partially CO covered step edge. The C–O stretch frequency is calculated to be down-shifted by $\sim$ 31 cm^{-1} due to the filling of the step edge with an equal amount of N$_2$.

Figure 7 summarizes the theoretical results of the surface work function changes for pure CO, pure N$_2$, and a 1:1 mixture of CO:N$_2$ adsorbed on the Pt(112) surface, as a function of the step-edge coverage. Clearly, for the case of pure CO adsorption there is a net increase in the work function for the whole range of coverages examined. In contrast, for the case

TABLE II. Calculated binding energies, vibrational frequencies, and work function changes ($\Delta\phi$) for CO and CO+N$_2$ on Pt(112). Negative values in the binding energy (PW91) column correspond to thermodynamically stable states. $\Delta\phi$ is reported with respect to the clean surface. CO (gas phase): ω_{exp}=2143 cm^{-1}, ω_{calc}=2188 cm^{-1}.

State	$\theta_{N_2}^{step}$	PW91 (eV/CO)	ω(CO) (cm^{-1})	$\Delta\phi$ (eV/CO)
Step CO, $\perp$ atop	0.5	−2.11	2107	+0.07
Step CO, $\perp$ atop	1.0	−1.84		+0.07
Step CO+N$_2$, $\perp$ atop	1.0	−2.30[a]	2076	−0.04

[a]Total binding energy for CO+N$_2$ molecules.

Calculated Work Function Changes on Pt(112) Induced by Adsorption of N$_2$ and CO
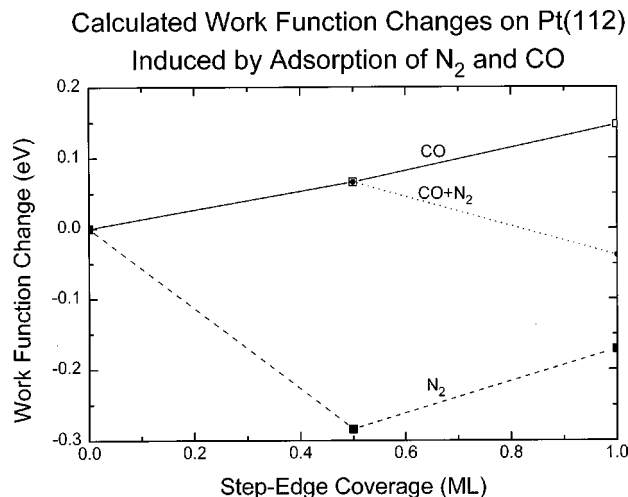

FIG. 7. Calculated changes in the work function of the clean Pt(211) surface as a function of the step edge coverage. The solid and dashed lines correspond to adsorption of pure CO and N$_2$, respectively. The dotted line corresponds to a 1:1 mixture of CO+N$_2$, with CO adsorbed first.

of pure N$_2$ adsorption, the work function initially decreases and then increases as a function of coverage, but always remains below the value of the clean surface. Finally, initial adsorption of CO up to half coverage of the step edge increases the work function, but this increase is overcompensated by the subsequent filling of the step edge with nitrogen molecules. The work function of the fully saturated, with a 1:1 mixture of CO:N$_2$, step edge surface is slightly lower (~0.04 eV) than the work function of the clean surface.

IV. DISCUSSION

The main result of this experimental and theoretical study is that localized adsorption of N$_2$ on Pt surfaces can only occur on step defect sites. This conclusion is supported by the following observations: (1) lack of N$_2$ adsorption on the defect-free Pt(111) surface;[5] (2) reasonably high binding energy of N$_2$ on step sites in atop configuration, compared to other possible sites and configurations; (3) the integrated N≡N absorbance saturation coverage of N$_2$ on the Pt(335) surface which is 1.73 ± 0.35 times greater than on the Pt(779) surface, close to the ideal ratio of two representing the step density ratio on the two surfaces (see Fig. 5); and (4) strong reduction or lack of N$_2$ coadsorption with CO which is specifically localized at step sites, confirmed both experimentally and theoretically.

Preferential atop N$_2$ adsorption on metal surface atoms has been established, both experimentally and theoretically, for several transition metal surfaces under various experimental conditions (see, for example, Ref. 25 and references therein). Therefore, our observation of N$_2$ adsorption on stepped Pt(112), Pt(335), and Pt(779) surfaces is in agreement with this general trend. However, no N$_2$ chemisorption on the defect-free Pt(111) surface was detected experimentally in previous studies, and the desorption energy of the physisorbed N$_2$ from the same surface was estimated to be -0.11 eV.[5] The atop molecular state found on the flat Pt(111) surface per PW91, when calculated within the RPBE

description of the exchange-correlation energy, appears to be unstable by 0.17 eV. The theoretical data suggest that N$_2$ at most physisorbs on Pt(111). This however cannot be captured with our calculations since van der Waals type forces are not included. Based on these data we propose that there can be no molecular chemisorption of nitrogen on the Pt(111) surface.

A necessary common term for comparing the theoretical and the experimental results is the N$_2$ absolute coverage. Experimentally, this information is not readily available from RAIR data. In another set of experiments, which will be described in a future paper,[20] we measured a 0.41 monolayer (ML) local saturation coverage on the step sites of the Pt(335) surface, using the adsorption uptake method. The same method gave a 0.56 ML N$_2$ local saturation coverage on the step sites of the Pt(779) surface. Given the limitations of the uptake method, it can be concluded that the N$_2$ step saturation coverage on a stepped Pt surface does not exceed ~0.5 ML, and only the calculated data for this particular coverage are relevant for comparison with the experimental data. The particularly small binding energies shown in RPBE (Table I) for all states but $\theta_{\text{step}} = \frac{1}{2}$, suggest that higher coverages would not be experimentally achievable, at least within the temperature range of our experiments in ultra high vacuum. Indeed, higher coverages could not be accomplished experimentally, whereas lower coverages have not been examined in this theoretical study because of their extremely high computational cost.

The N≡N stretch frequency for the most stable molecular state (atop configuration) for the half-covered step edge of the Pt(112) surface, calculated as 2244 cm^{-1}, corresponds to a down-shift of 147 cm^{-1} with respect to the calculated gas-phase value (2391 cm^{-1}). The high-coverage RAIRS experiments on Pt(335) and (779) described here show bands at 2231 and 2234 cm^{-1}, respectively, yielding a down-shift of ~125 cm^{-1} with respect to the experimentally determined gas phase value (2356 cm^{-1}). Given the different surfaces treated by experiment and theory, the agreement in the frequency shift is quite reasonable.

At very low coverages of N$_2$, a higher frequency band is observed experimentally, whose origin could not be captured in the calculations described here. Additional RAIRS experiments, not shown here, have revealed that the high-frequency band is associated with a nonequilibrated state, which upon thermal activation converts into the low-frequency N$_2$ state.[26] At high coverages of N$_2$, the nonequilibrated state is not observed.

The calculations predict that N$_2$ could also adsorb on the step sites in a bridged, side-on configuration, although the binding energy predicted by the RPBE functional (-0.14 eV) places this state in the limit of very weak chemisorption. The N–N stretch frequency for this state was calculated to be 1895 cm^{-1}, suggesting a decrease in the bonding order of N$_2$ in this configuration, as is usually the case. This state is less stable than the end-on state and thus it will be more difficult to observe experimentally, let alone the fact that the N–N stretch of the side-on state may correspond to an IR inactive mode if the intramolecular axis is strictly parallel to the surface. Side-on states are dominant for molecules such as O$_2$

chemisorbed on transition metal surfaces [for example, on Pt(111)] and there is good agreement between experiment [high-resolution electron energy-loss spectra (HREELS)] and theory (DFT periodic slab calculations) for their stretching frequency.[27] However, we have no experimental evidence for the existence of this parallel, bridged configuration, for N_2 on Pt(335) and Pt(779).

As the local coverage of N_2 at the step edge ($\theta_{N_2}^{step}$) is increased from $\frac{1}{2}$ to 1, no appreciable tilting of the molecules is determined in our fully relaxed calculations. The moderate repulsive interaction between adjacent nitrogen molecules on the step edge is also illustrated by the modest decrease in binding energy per molecule with coverage (-0.67 eV for $\theta_{N_2}^{step}=0.5, -0.46$ eV for $\theta_{N_2}^{step}=1.0$, both per PW91). Both the in-phase (2251 cm^{-1}) and out-of-phase (2227 cm^{-1}) modes of adjacent N_2 adsorbed molecules were calculated suggesting an upper and lower bound for the coverage-dependent vibrational spectra. However, the low RPBE binding energy determined for the PW91 optimized structure indicates that geometry optimization in RPBE may result in a shallow minimum or that there is no minimum at all for the fully covered step edge and, therefore, that structure may be difficult or impossible to realize and observe experimentally. Indeed, the RAIRS data failed to show evidence for the in-phase 2251 cm^{-1} band, the only active mode assuming a quasi-parallel alignment of the dynamic dipole moments of all the oscillators on a given step site.

The heat of adsorption for an experimental saturation coverage (0.5 ML) of N_2 on a Pt(112) surface is predicted theoretically to be -0.34 eV within the RPBE approximation. Previous experimental determinations of the adsorption heat by the isosteric equilibrium method[3] and the kinetic analysis of the temperature-programmed desorption curves[28] place it around -0.15 eV. The experimental values cannot account for the localized N_2 adsorption observed by us and must, therefore, be underestimations. The calculated binding energy is in agreement with the low N_2 desorption temperature from stepped Pt surfaces (~ 150 K).[20]

The calculations suggest that the atop N_2 state leads to a net decrease in the surface work function, implying charge transfer from the N_2 molecules to the surface, for all coverages up to the step edge saturation limit. However, the calculated work function change for the experimental saturation coverage (-0.28 eV) is lower than that reported in the literature for Pt surfaces with a high density of defect sites ($-0.5 \cdots -0.7$ eV).[28] An interesting difference identified through the calculations is that the side-on molecular state slightly increases the surface work function, suggesting that the charge transfer is in the opposite direction for this configuration. Similarly, as shown in Table II, CO chemisorption causes a small increase in the surface work function, which was calculated to be almost linear with coverage, indicating a net charge transfer to the CO molecules. This result agrees very well with previous work function change measurements of CO adsorbed on Pt(210).[29] In another study, however, adsorption of CO on Pt(112) up to 50% step saturation coverage (or 0.17 ML total coverage) induced no measurable change in the surface work function.[30]

The calculation performed for the case of coadsorbed

CO and N_2 corresponds to a final state where the step edge is fully saturated. There is a mere increase of 0.2 eV (PW91) in the total binding energy of this state compared to the binding energy of CO, for half a monolayer coverage of the step edge. Therefore, a weakening of the Pt–CO bond upon N_2 coadsorption may occur, due to a net charge transfer from N_2 to CO through the substrate, as suggested by the work function change. It is remarkable that the experimentally observed down-shift of the C–O stretch on Pt(335) and (779) was predicted reasonably well by our calculations on the 1:1 CO:N_2 mixture on Pt(211) (20 versus 31 cm^{-1}, respectively). We can interpret the CO bands in Fig. 6 as essentially an overlap between the high and the low-frequency bands. Based on the theoretical predictions shown here, the high-frequency CO band can be associated with compact one-dimensional CO islands on the step sites, while the low-frequency CO band originates from compact one-dimensional domains where N_2 alternates with CO.

The initial adsorption of CO leads to a net charge transfer from the surface increasing its work function. Further adsorption of N_2 reverses this trend, and there is a net charge transfer from N_2 towards the surface. The work function of the surface with its step edge fully saturated by a 1:1 mixture of CO:N_2 is slightly lower (~ 0.04 eV) than the work function of the clean surface, effectively resulting in a charge transfer from N_2 to CO molecules through the metal substrate.

V. CONCLUSIONS

In this study, we have investigated both experimentally and theoretically the chemisorption of N_2 on Pt surfaces with and without step defect sites. We have found that:

(1) The chemisorption sites are the edge atoms on the step defect sites;

(2) The calculated IR vibrational frequency of the N_2 molecule chemisorbed on step sites is in very good agreement with that observed experimentally;

(3) In agreement with TPD (temperature programmed desorption) data, the predicted binding energy of N_2 on these sites is small, which explains why other adsorbates with higher binding energy displace N_2;

(4) The calculated work function change of the Pt(112) surface is negative both when pure N_2 adsorbs on it, and when N_2 coadsorbs with electron-withdrawing adspecies such as CO.

[1] H. S. Taylor, Proc. R. Soc. London, Ser. A **108**, 105 (1925).
[2] R. Van Hardeveld and A. Van Montfoort, Surf. Sci. **4**, 396 (1966).

[3] T. A. Egerton and N. Sheppard, J. Chem. Soc., Faraday Trans. 1 **70**, 1357 (1974).

[4] R. A. Shigeishi and D. A. King, Surf. Sci. **62**, 379 (1977).

[5] C. R. Arumainayagam, C. E. Tripa, J. Xu, and J. T. Yates, Jr., Surf. Sci. **360**, 121 (1996).

[6] C. E. Tripa and J. T. Yates, Jr., ''Step Defect Sites: The Sites Responsible for Molecular Nitrogen Chemisorption on Pt Surfaces,'' Rev. Roum. Chim. (in press).

[7] M. Trenary, K. Uram, and J. T. Yates, Jr., Surf. Sci. **157**, 512 (1985).

[8] A. Winkler and J. T. Yates, Jr., J. Vac. Sci. Technol. A **6**, 2929 (1988).

[9] J. T. Yates, Jr., *Experimental Innovations in Surface Science—A Guide to Practical Laboratory Methods and Instruments* (AIP, Springer-Verlag, New York, 1998), pp. 230–235.

[10] C. E. Tripa and J. T. Yates, Jr., J. Vac. Sci. Technol. A **14**, 2544 (1996).

[11] M. Mundschau and R. Vanselow, Surf. Sci. **157**, 87 (1985).

[12] H. P. Bonzel, A. M. Franken, and G. Pirug, Surf. Sci. **104**, 625 (1981).

[13] Z. Xu and J. T. Yates, Jr., J. Vac. Sci. Technol. A **8**, 3666 (1990).

[14] D. H. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[15] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[16] J. A. White and D. M. Bird, Phys. Rev. B **50**, 4954 (1994).

[17] B. Hammer, L. B. Hansen, and J. K. Nørskov, Phys. Rev. B **59**, 7413 (1999).

[18] *Structure Data of Elements and Intermetallic Phases, Landolt-Börnstein, New Series Vol. III, b* (Springer-Verlag, Berlin, Heidelberg, 1971).

[19] G. Kresse and J. Forthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[20] C. E. Tripa, T. S. Zubkov, and J. T. Yates, Jr. (unpublished).

[21] J. Xu, P. Henriksen, and J. T. Yates, Jr., J. Chem. Phys. **97**, 5250 (1992).

[22] H. J. Jänsch, J. Xu, and J. T. Yates, Jr., J. Chem. Phys. **99**, 721 (1993).

[23] C. E. Tripa and J. T. Yates, Jr., Nature **398**, 591 (1999).

[24] B. Hammer, O. H. Nielsen, and J. K. Nørskov, Catal. Lett. **46**, 31 (1997).

[25] J. J. Mortensen, B. Hammer, and J. K. Nørskov, Phys. Rev. Lett. **80**, 4333 (1998).

[26] T. S. Zubkov, C. E. Tripa, and J. T. Yates, Jr. (unpublished).

[27] A. Eichler and J. Hafner, Phys. Rev. Lett. **79**, 4481 (1997).

[28] B. E. Nieuwenhuys and W. M. H. Sachtler, Surf. Sci. **34**, 317 (1973).

[29] M. Ehsasi, S. Rezaie-Serej, J. H. Block, and K. Christmann, J. Chem. Phys. **92**, 7596 (1990).

[30] M. A. Henderson, A. Szabó, and J. T. Yates, Jr., J. Chem. Phys. **91**, 7255 (1989).