

CO on Pt(335): Electric field screening on a stepped surface

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We compare CO's response to electric fields at edge and terrace sites on the stepped Pt(335) surface. The comparison is made at zero frequency and at the frequency of the C–O stretch vibration. Atop-bonded CO is observed with reflection–absorption ir spectroscopy (RAIRS), electroreflectance vibrational spectroscopy (EVS), and high-resolution electron energy loss spectroscopy (HREELS). Coadsorbed H or O is used to control the CO adsorption site. With both RAIRS and HREELS the measured vibrational cross-section of atop CO at the step edge is 2.0 ± 0.2 times greater than for CO on the terrace. The vibrational Stark effect—the change of CO's vibrational frequency with externally applied electrostatic field—is also a factor 2.0 ± 0.2 larger for atop CO at the step edge than it is for atop CO on the terrace. Because the vibrational cross section varies as the square of the field while the Stark effect is linear, a model in which CO responds to the screened local field at a single point cannot simultaneously explain the observed site dependence of both the vibrational Stark effect and the vibrational cross section. The most plausible explanation is that CO's response to electric fields is nonlocal. A simple model is presented that can account for our data. © 1995 American Institute of Physics.

I. INTRODUCTION

Vibrational spectroscopy is used to study CO on stepped Pt surfaces to better understand exhaust gas catalysis,¹ gas sensors, and electrochemical applications.² On stepped Pt, CO can adsorb at edge or terrace sites, and at each it has a characteristic vibrational frequency. At each site, CO responds to the induced local electric field E . To obtain site occupancies from the spectra, the ratio of E at the edge vs terrace sites must be understood. Besides site-to-site variation, at a particular site the component of E that interacts with the molecule varies strongly with distance z from the surface. The need to consider the z dependence of the field in models of the *electronic* response of metal surfaces is widely recognized. However, it is ignored in the standard model³ of adsorbate vibrational response on a metal, which assumes that a point dipole interacts with the local E field at only one point.

We have used three different types of vibrational spectroscopy to study atop-bonded CO on a stepped Pt surface. We compare CO at the step edges with CO on the terrace, for both ir and static fields. We find that CO's vibrational cross-section and Stark tuning rate—the shift of the vibrational frequency in a static E field—are both twice as large on the step edge as on the flat terraces. The experimental results cannot be explained by *any* model that expresses the molecu-

lar response in terms of E at a single point: the response is *nonlocal*. Our experiment shows that the strong z dependence of the E field at a metal surface significantly affects CO's vibrational properties. A simple nonlocal model that agrees with our observations is also presented.

As shown in Fig. 1, the surface we use is Pt(335): Pt(S)[4(111)×(100)] in step–terrace notation. We compare the vibrational intensity of atop-bonded CO at step edge and terrace sites using reflection–absorption infrared spectroscopy (RAIRS) and high-resolution electron energy loss spectroscopy (HREELS). We also compare the effect of an applied electrostatic field on CO's vibrational frequency (the Stark tuning rate) between the two sites, using electroreflectance vibrational spectroscopy (EVS).^{4–6} We manipulate the CO so it is either all on the edge or all on the terrace using coadsorbed H or O. This allows us to compare CO at the two sites with total CO coverage θ_{CO} held constant.

Previous ir studies of CO on stepped Pt have encountered some apparent contradictions. In a beautiful experiment,^{7,8} Reutt-Robey *et al.* used time-resolved RAIRS to observe CO as it diffused from sites on the terrace to the step edge of Pt(S)[28(111)×(1 $\bar{1}$ 0)] and Pt(S)[12(111)×(1 $\bar{1}$ 0)]. They found that on these surfaces the integrated ir absorption S stayed constant within 5% as the CO moved from terrace sites to the edge. Since $S \propto E^2$, this implies that at the ir frequency, E changes by no more than 2.5% between terrace sites and edge sites. However, a very different picture emerged from a RAIRS experiment with CO on Pt(335) reported by Hayden *et al.*⁹ They monitored S as θ_{CO} increased. At low θ_{CO} , as edge sites are being filled, $(dS/d\theta_{\text{CO}})$ is 2.7

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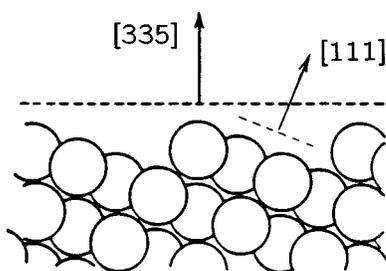


FIG. 1. Side view of the ideal Pt(335) surface.

times higher than at high θ_{CO} where the adsorption sites being occupied are primarily on the terrace. This suggests that at the ir frequency, E increases by a factor 1.64 on going from sites on the terrace to the edge; however, the change in θ_{CO} and the strong dipole coupling between the two species complicate the analysis.^{10–12} A similar experiment was reported by Lambert and Tobin¹³ but their analysis suggested that the ir cross sections for CO at edge and terrace sites on Pt(335) are almost equal. This appeared to confirm the observations of Reutt-Robey *et al.* [When the experiments in Refs. 9 and 13 were performed, all of the CO on Pt(335) was believed to be atop bonded. Actually, as seen with EELS,^{14,15} a significant and coverage-dependent fraction is bridge bonded.]

An independent estimate of the screening of static E is obtained with EVS.^{4–6} Here, externally applied E changes an adsorbate's vibrational frequency ν . The measured $(d\nu/dE)$ is proportional to the local E that acts on the molecule. For CO on Pt(111), $(d\nu/dE)$ is reported in Ref. 16; for edge CO on Pt(335) in Refs. 13 and 17. In the limit of low θ_{CO} , the measured $(d\nu/dE)$ for CO on Pt(335) is a factor 1.30 ± 0.20 larger than for CO on Pt(111). To the extent that CO on Pt(111) is like CO on the (111) terraces of Pt(335), this compares E at the two sites. At higher θ_{CO} , Lambert and Tobin¹³ found that $(d\nu/dE)$ of edge atop CO on Pt(335) was as expected, but it was much smaller for terrace atop CO—at most 13% of the edge CO value. (Different results are reported in Sec. III A of the present work.) In water, for CO on a Pt(335) electrode, Kim *et al.*^{18,19} used IRAS to measure CO's ν as a function of electrode potential Φ . They found that $(d\nu/d\Phi)$ of edge CO is a factor 2.4 larger than for terrace CO.

These and other experiments indicate that our understanding of the electrostatic screening associated with steps on Pt is incomplete. The local work function (measured with photoemission from adsorbed Xe) at the step edge is 1 eV smaller than at sites on the terrace.^{20,21} This is a larger difference than for any other metal. The measured effect of step density on the work function ϕ of Pt(S)[$m(111) \times (100)$] surfaces²² is also larger than for any other metal—a factor 12 larger than calculated from a jellium model.²³ This discrepancy has been attributed to Pt's d electrons, but it has also been argued²⁴ that since the d electrons are near the nucleus they should have little effect on ϕ or screening.

To estimate the local E at a stepped Pt surface, one approach has been to simply treat the Pt as an ideal conductor

and use classical electrostatics. In this way, Greenler *et al.*²⁵ estimated that for CO on Pt(335), E is a factor 1.48 ± 0.07 larger at the edge site than the average for the terrace sites. In the approximation that the screening of static and ir fields is the same, this implies that the ir cross section for CO at an edge site should be a factor 2.2 ± 0.2 times that of CO at a terrace site. A similar calculation has been performed by Wang,²⁶ both for Pt(335) and for the Pt(S)[$28(111) \times (1\bar{1}0)$] surface studied by Reutt-Robey *et al.*^{7,8} The results for Pt(335) agree with those of Ref. 25. For the surface with wider terraces, E at the edge is estimated to be 1.2 ± 0.04 times larger than on the terrace, leading to a predicted cross section ratio of 1.4 ± 0.1 , smaller than for Pt(335), but still too large to be consistent with experiment.

At a more fundamental level, Lang and Kohn²⁷ calculated the screening of static E at a plane jellium surface. Jellium calculations of screening near a step have been reported.^{22,28,29} There have also been *ab initio* calculations of screening at the Al(100),³⁰ Ag(100),³¹ and Ag(110)³² surfaces. These show that near the top layer of surface atoms, screening is a function of lateral position. We are not aware of an *ab initio* calculation of screening at a stepped surface. However, an *ab initio* calculation of the structure of the stepped Al(331) surface has been reported.³³

Electrodynamic effects at plane metal surfaces were reviewed³⁴ by Feibelman in 1982. Since then, second-harmonic generation at metal surfaces has become a powerful tool³⁵ and this has motivated theoretical investigations.^{36–40} However, even for a simple metal like Al, the observed effect of step density on second-harmonic intensity⁴¹ is much larger than present (jellium) theories predict.⁴² Nonlocal electrodynamic effects on the vibrational frequency⁴³ and damping⁴⁴ of adsorbed molecules (modeled as point dipoles) have also been considered, but we are not aware of any application of these ideas to the vibrational intensity of adsorbates on metals. Another focus of theoretical work has been cluster calculations. In principle, if a cluster is large enough, E is screened the same at its surface as at the surface of a bulk metal. *Ab initio* calculations of the vibrational Stark effect and intensity of CO on clusters of metal atoms have been reported,^{45–48} but no attempt has been made to relate these to surface screening.

The experimental results described here clearly establish that the vibrational cross section and Stark tuning rate of atop CO are both enhanced *by the same factor* at edge sites as compared with terrace sites. Because the vibrational cross section varies as the square of the field while the Stark effect is linear, we conclude that CO's vibrational response to E is nonlocal. A simple model is presented that gives the screening ratios seen in our experiment.

II. EXPERIMENT

Details of the spectroscopy techniques and sample preparation procedures are given elsewhere.^{5,17,49,50} The ir source for both RAIRS and EVS was a lead-salt diode laser, with a spectral range of 1947 to 2022 cm^{-1} . The ir study used $^{13}\text{C}^{18}\text{O}$. This allowed atop CO to be seen with the laser, but not bridge CO. Since we use the EVS data only to determine *ratios* of Stark tuning rates, we omitted the calibration

steps needed for quantitative accuracy.⁵ Consequently, the EVS spectra we display have arbitrary, but consistent units. The HREEL spectra went from 300 to 5000 cm^{-1} with 60 to 70 cm^{-1} resolution. All of our measurements were repeated several times and were reproducible.

As CO builds up on clean Pt(335), it first occupies edge sites, and the edge sites remain occupied at the higher coverages at which terrace CO is present.^{9,13} If only CO is used, the vibrational spectrum of terrace CO is always strongly affected by dipole coupling to the edge CO modes.^{9,13} To make a direct comparison of equal amounts of CO on the edge and the terrace, we block the edge sites with O or H before dosing with CO. Predosing with O or H is done at about 100 K. Subsequent heating of a H-predosed surface to 420 K causes the H to desorb and the CO to move to edge sites. Heating the O-predosed surface to 260 K causes the O to move to the terrace while the CO moves to the edge. Our use of coadsorbed O to manipulate CO's site occupancy on stepped Pt follows Szabó *et al.*⁵¹ Likewise, Hahn *et al.*⁵² have used H on stepped Pt to prevent CO adsorption.

The sample temperature was 95–105 K during all the spectroscopic measurements. In the ir experiments, CO and H₂ were dosed by background filling while O₂ was dosed by an effusive doser placed one sample diameter away from the sample. The doser enhanced the effective pressure at the sample by about a factor of 20. In the HREELS experiments, each gas was dosed through an individual doser, with enhancement factors of about 100 over background dosing. The H and CO coverages were determined by temperature-programmed desorption (TPD). For CO the saturation coverage was assumed to be 0.63 monolayer (ML);¹³ for H it was assumed to be 1 ML.¹⁷ (Here, one ML corresponds to one adsorbate per surface Pt atom.) Our TPD results for all three adsorbates are in agreement with previous measurements on stepped Pt.^{9,13,15,51,53–55} To avoid the presence of terrace CO after the sample was heated, we kept θ_{CO} below 0.2 ML; at such low coverages terrace sites are not populated on the clean surface.^{15,55}

For the H coadsorption experiments, the surface was first dosed with H₂ near 100 K, (0.72 ML for the ir experiments; 0.25 ML for HREELS) and then with CO. Infrared (RAIR and EV) or EEL spectra were next measured, and the sample was heated to 420 K. A TPD spectrum that was taken as the sample temperature was raised showed that this desorbed all the H, but 95% of the CO remained. After the sample cooled back to 100 K, one more set of ir spectra was acquired. Finally the sample was heated enough to desorb all the CO. During this desorption θ_{CO} was determined with TPD.

The procedure for the O coadsorption was similar. The initial O₂ dose was 0.1 L (1 L = 10⁻⁶ Torr s) and the sample temperature was 190 K. This saturated the edge sites with O and ensured that the O₂ all dissociated.⁵⁶ Next, 3.0 L of CO was dosed at 150 K, giving θ_{CO} = 0.19 ML. This overlayer was studied. To get the CO to migrate to edge sites, the overlayer was annealed for five minutes at 260 K. On Pt(112),⁵¹ terrace CO and edge O switch position at 230 K. On Pt(335), only part of the CO moved to the edge at 230 K; but the exchange was complete at 260 K. This 260 K anneal caused about 15% of the CO to react with O to form CO₂. A

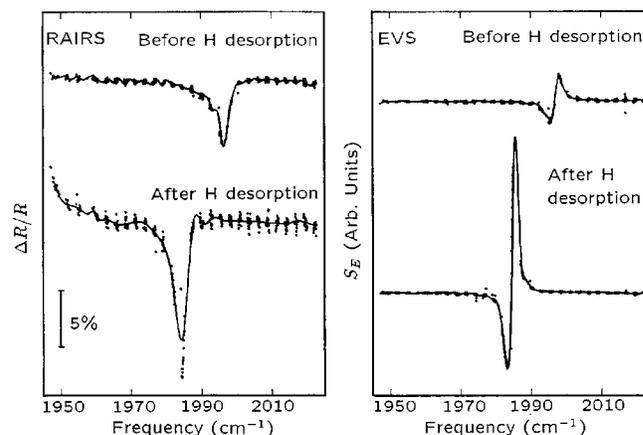


FIG. 2. RAIR and EV spectra for 0.16 ML of CO on a Pt(335) surface precovered with 0.72 ML of H, before and after heating the sample to 420 K. Upon H desorption, the CO moves to edge sites. The lines are spline fits to the data after smoothing.

TPD scan that monitored product CO₂ showed a minor peak at 180 K, with about 10% of the total area, and additional desorption near 260 K as a precursor to the main peak at 320 K.

In addition to these spectra, intended to compare CO at edge and terrace sites, we also obtained RAIR and EV spectra at higher θ_{CO} , with just CO on the surface, to test the reproducibility of the results in Ref. 13. We found some differences, as described below.

III. RESULTS

A. RAIRS and EVS

Figure 2 shows RAIR and EV spectra of 0.16 ML of CO, first for a sample precovered with 0.72 ML of H, and again after the sample had been heated to 420 K to desorb the H. Desorbing the H decreases the CO band's peak frequency ν and increases its intensity. With coadsorbed H, $\nu=1995 \text{ cm}^{-1}$; after the H is desorbed, $\nu=1984 \text{ cm}^{-1}$. It is well established^{9,13,17,55} that on Pt(335), for ¹³C¹⁸O on the edge, $1975 < \nu < 1985 \text{ cm}^{-1}$ and on the terrace $1987 < \nu < 2000 \text{ cm}^{-1}$. We therefore attribute the frequency shift to the movement of CO from terrace to edge sites. Annealing increases the integrated area S of the RAIRS band by a factor of 1.6 ± 0.2 . Any loss of CO would reduce S . We estimate that $< 0.003 \text{ ML}$ of background ¹³C¹⁸O adsorbed during the annealing and cooling. The increase in S is therefore not due to a change in θ_{CO} , but to CO's site shift.

The EV spectra are proportional to the static E field and to $d(\Delta R/R)/d\nu$, where $\Delta R/R$ is the RAIRS signal and ν is the frequency.^{4–6} The Stark tuning rate ($d\nu/dE$) is proportional to the ratio of the integrated EV spectrum to the RAIR spectrum, and can be estimated by comparing either peak heights or integrated areas. The two methods are averaged for the values given here. It is evident from Fig. 2 that desorbing the H increases the EV signal by a larger factor than the RAIR signal, indicating an enhanced Stark tuning rate. Moreover, since ($d\nu/dE$) is obtained from a ratio of an EV to an RAIR spectrum, it is largely insensitive to changes in

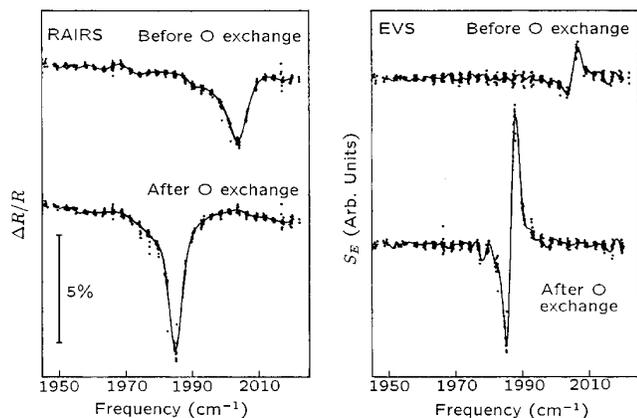


FIG. 3. RAIR and EV spectra for 0.19 ML of CO on a Pt(335) surface predosed with 0.1 L oxygen, before and after heating the sample to 260 K. Upon heating, the CO moves from terrace sites to edge sites, while the O moves to terrace sites. The lines are spline fits to the data after smoothing.

CO coverage. We conclude from the data in Fig. 2 that shifting the CO from terrace to edge sites increases $(d\nu/dE)$ by a factor of 2.0 ± 0.2 .

Figure 3 shows RAIR and EV spectra for 0.19 ML of CO adsorbed on a surface predosed with 0.1 L of O_2 , before and after moving the CO to edge sites. As in the H-coadsorption experiment, the site switch reduces ν from 2004 to 1986 cm^{-1} , and increases S . The intensity increases by a factor of 1.4 ± 0.2 and $(d\nu/dE)$ increases by a factor of 2.0 ± 0.2 . The site-dependent changes in S and $(d\nu/dE)$ are analyzed in Sec. III C.

Figure 4 shows RAIR and EV spectra for 0.26 ML of CO on Pt(335). At this coverage both edge and terrace sites are occupied. The Stark tuning rate of terrace CO seen here, as well as in the electrochemical work of Kim *et al.*^{18,19} is much larger than that reported in Ref. 13. At a comparable coverage the RAIR spectrum in Ref. 13 is similar, with edge and terrace CO peaks of comparable intensity. However, in Ref. 13 the EV spectrum showed a strong EVS signal from edge CO, but no EVS signal from terrace CO. In fact a small peak was observed at terrace CO's ν , where a zero crossing would ordinarily be expected. It was concluded that $(d\nu/dE)$ of terrace CO is at most 13% that of edge CO. Our EV spectrum, however, shows EVS peaks of comparable size for both CO species, and $(d\nu/dE)$ differs by only a factor of 2.

We have no firm explanation for this discrepancy. The same sample was studied in the two experiments, and during each, the spectra were reproducible. We investigated coadsorption with O and H, as well as C contamination, but were unable to reproduce the results in Ref. 13. We offer two observations: the sample was repolished between the two experiments, and the experiment described in Ref. 13 initially saw Sn contamination—although for the final data, the Sn concentration was below the threshold for Auger detection.

B. HREELS

Figure 5 shows EEL spectra of CO on Pt(335) that had been precovered with 0.25 ML of H at 95 K. The spectra in

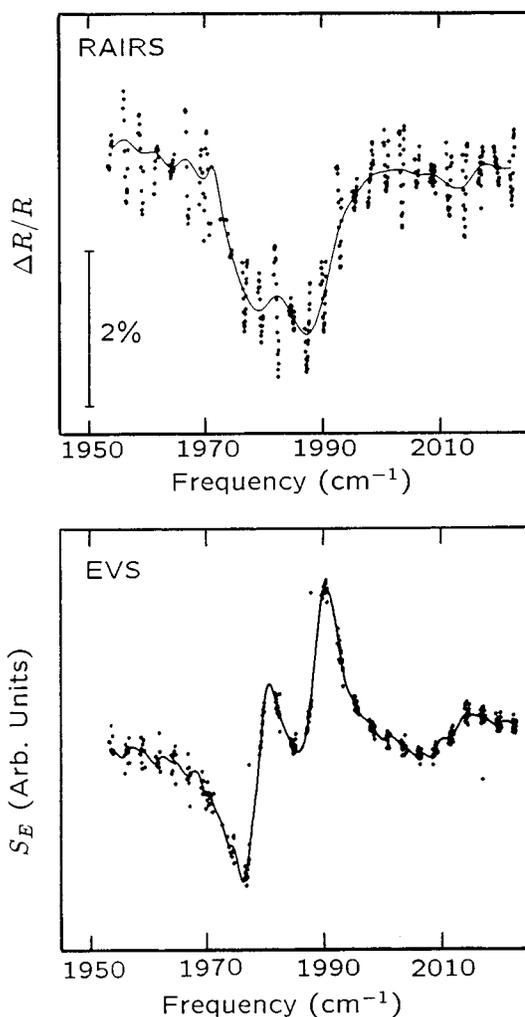


FIG. 4. EV and RAIR spectra of 0.26 ML of CO on clean Pt(335). Strong EV features are seen near both peaks in the RAIR spectrum, indicating that edge and terrace CO have comparable Stark tuning rates. The zero crossings in the EV spectrum occur at the same frequencies as the peaks in the RAIR spectrum. These results are in contrast to those reported in Ref. 13. The lines are spline fits to the data after smoothing.

Fig. 5(a) were measured before heating, those in Fig. 5(b) after heating to 420 K to desorb the H. The peaks between 1870 and 1890 cm^{-1} are assigned to bridge bonded CO, those between 2060 and 2110 cm^{-1} to atop CO. As with the ir spectra, H-desorption tends to decrease ν and to increase the intensity of the atop CO band. For $\theta_{CO}=0.05, 0.08, 0.13,$ and 0.16 ML, $\Delta\nu=-8, 0, -32,$ and -27 cm^{-1} , respectively. The apparent absence of a shift at 0.08 ML could be due to uncertainty in identifying the peak position; its spectrum before annealing is noisier than most and the atop peak exhibits an unusual and probably spurious asymmetry. The HREEL spectra also show that H affects the intensity of the band due to bridge-bonded CO. In the next section we take this into account in estimating the change in atop CO's cross section.

C. Analysis of the atop intensity

Table I summarizes our results. The intensity ratio $= (S \text{ after annealing}) / (S \text{ before annealing})$. Of greater interest is the cross-section ratio, the ratio of S per CO for edge CO to

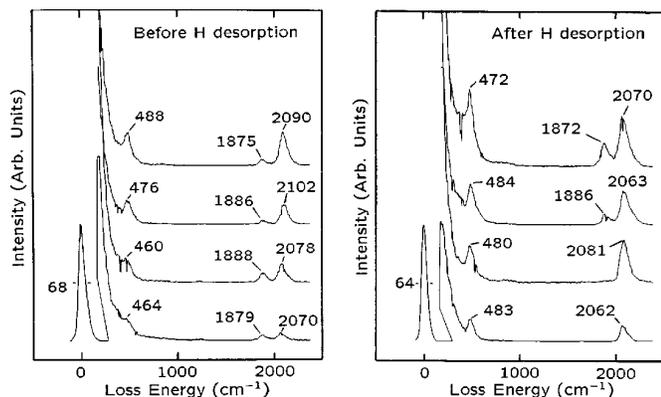


FIG. 5. HREEL spectra for 0.16, 0.13, 0.08, and 0.05 ML of CO (from top to bottom) on a Pt(335) surface precovered with 0.25 ML of H, before and after heating to 420 K to desorb the H.

the same quantity for terrace CO. The two ratios differ because annealing changes the amount of atop CO. Some CO is lost during the anneal; for the IR experiments we estimate this loss at 5% with coadsorbed H and 15% with coadsorbed O; for EELS the loss was <5%. Also, as seen in the EEL spectra of Fig. 5, heating caused some CO to change from atop to bridge bonding, and some CO to migrate from the terrace to the edge.

To determine the relative populations of bridge and atop CO from the EEL spectra, we need the ratio of atop CO's cross section to that of bridge CO, although our results are insensitive to the value assumed. The bridge CO seen before the anneal is presumed to be on the H-saturated step edge—terrace bridge sites are not occupied at these coverages.^{15,50} Previous EELS measurements have shown that the cross sections of edge bridge CO (with H) and edge atop CO (without H) are equal.⁵⁰ Any bridge CO on the terrace would, by analogy with Pt(111),⁵⁷ be expected to have an EELS cross section 1.8 times smaller than that of terrace atop CO. It is clear from TPD that *after* annealing all the CO is on the step edge. The H is gone so the bridge CO cross section is not accurately known, but it is certainly between 1.0 and 1.8 times smaller than the atop CO cross section.⁵⁰ For the IR

TABLE I. Ratios of vibrational intensity, vibrational cross section, and Stark tuning rate of edge atop CO compared to terrace atop CO. The intensity and Stark tuning rate ratios are determined directly from the experimental data. The cross-section ratio takes the change in atop CO coverage into account, as discussed in the text.

Experiment	Intensity ratio	Cross-section ratio	Stark tuning rate ratio
IR—H coadsorption			
$\theta_{\text{CO}}=0.16$	1.6 ± 0.2	2.1 ± 0.3	2.0 ± 0.2
IR—O coadsorption			
$\theta_{\text{CO}}=0.19$	1.4 ± 0.2	2.0 ± 0.4	2.0 ± 0.2
HREELS—H coadsorption			
$\theta_{\text{CO}}=0.05$	2.3	1.4 ± 0.4	
$\theta_{\text{CO}}=0.08$	2.6	1.8 ± 0.4	
$\theta_{\text{CO}}=0.13$	2.2	2.3 ± 0.3	
$\theta_{\text{CO}}=0.16$	1.7	2.1 ± 0.2	
Average:		2.0 ± 0.2	2.0 ± 0.2

experiments we estimate the bridge CO correction from the EELS data at $\theta_{\text{CO}}=0.16$ ML. The uncertainties in Table I include both experimental errors and systematic uncertainties in determining the atop and bridge populations.

In the data in Table I, edge CO's vibrational cross section is consistently larger than that of terrace CO. Their ratio is 2.0 ± 0.2 .

The Stark tuning rate data in Table I are less affected by changes in the amount of atop CO. The measured ($d\nu/dE$), both before and after the site switch, is the ratio of a peak in the integrated EV spectrum to a peak in the RAIR spectrum. Since ($d\nu/dE$) varies slowly as a function of the atop CO coverage, coverage changes have little effect. We find that the Stark tuning rate of edge atop CO is also 2.0 ± 0.2 times that of terrace atop CO.

IV. DISCUSSION

To analyze the variation of CO's cross section and Stark tuning rate between edge and terrace sites, we consider three possible explanations: First, that the coadsorbed H or O affects the CO; second, that the chemical structure or geometrical configuration (e.g., the tilt angle) of CO at the two sites is different; and finally that local E is screened differently at the two sites.

All the evidence suggests that the effect of H desorption on CO's vibrational intensity and Stark tuning rate is primarily due to CO's site change—any direct interaction with H is insignificant by comparison. Coadsorbed H and CO on Pt(335) have been studied with HREELS and TPD.^{17,50} Edge CO is strongly affected by coadsorbed H. In the present work, however, the H is all gone when the CO is at edge sites. The vibrational properties of terrace CO are *completely insensitive*⁵⁰ to the presence of terrace H. The effect of edge H on terrace CO is also negligible; EEL spectra of terrace CO with the edge saturated by H are virtually identical to those with the edge occupied by CO.^{15,50}

We have less information about the effects of coadsorbed O, but the strong similarity we see between the effects of H and O is consistent with the shift of CO from terrace to edge sites being the most important effect. As seen in Fig. 3(a), terrace CO's ν with coadsorbed O is unusually high, but this is easily explained. It is well established^{17,58} that a change in work function ϕ induces a proportional $\Delta\nu$ for CO, with ($d\nu/d\phi$) = 34 ± 4 cm^{-1}/eV . On Pt(S)[6(111)×(100)] Collins and Spicer⁵⁹ found that filling the edge sites with O increases ϕ by 0.4 eV, that saturating the terrace sites with O increases ϕ by about 0.1 eV, and that filling the edge sites with CO increases ϕ by only 0.03 eV. With the step edge saturated with O, we would expect an O-induced $\Delta\nu$ of $+13$ cm^{-1} for the terrace CO. The observed $\Delta\nu$ is 10 ± 2 cm^{-1} (the estimate of ν without O takes into account the variation of ν with θ_{CO}). After annealing, with O on terrace sites, the expected $\Delta\nu$ for the edge CO is only 3 cm^{-1} , and the observed $\Delta\nu$ = 3 ± 2 cm^{-1} .

The second proposed explanation—that a difference in CO's chemical bonding or orientation between the two sites causes the difference in vibrational cross section and Stark tuning rate between edge and terrace sites—is also unlikely. An EELS experiment⁶⁰ that looked at the coverage depen-

dence of CO's overtone intensity (before the sample was repolished) was unable to find any chemical difference between edge and terrace CO. A study⁶¹ of the near edge x-ray absorption fine structure for CO on Pt(335) found that if all of the CO (both edge and terrace) is assumed to be oriented in the same direction then it is rotated by only $10^\circ \pm 7^\circ$ from [335]—the (335) plane's normal—toward [111], the terrace normal. The data were fit equally well by assuming that all the terrace CO is oriented along [111] and that the CO at edge sites is rotated 5° from [335] toward [111]. With CO on a similar stepped surface, Pt(S)[3(111)×(100)], a measurement⁶² of the electron stimulated desorption-ion angular distribution found that terrace CO is only tilted 6.5° from the [111] direction. However, to explain the lower vibrational cross section of terrace CO as a tilting effect, it would have to be tilted by 45° relative to the local ir field. This is clearly ruled out.

Within the context of a local field model, the remaining alternative is that applied E is screened differently at edge and terrace sites. As discussed in Sec. I, Greenler *et al.*²⁵ used an electrostatic model to estimate that the screened E that acts on CO at the edge site is larger than at the terrace site by a factor 1.48 ± 0.07 . Consequently the vibrational cross section of CO at the edge site should be larger by a factor 2.2 ± 0.2 . The observed vibrational cross sections differ by a factor 2.0 ± 0.2 , in agreement with their prediction. However, their prediction also implies that $(d\nu/dE)$ for edge CO should be larger than that of terrace CO by a factor 1.48 ± 0.07 , while the measured factor is 2.0 ± 0.2 . Their prediction does, however, agree with the measured ratio of $(d\nu/dE)$ between low-coverage CO at edge sites on Pt(335) and on Pt(111): 1.30 ± 0.20 .

The failure of their model to account for both the cross-section enhancement and the Stark tuning rate enhancement is a fundamental problem. Let $\gamma = (\text{local } E)/(\text{externally applied } E)$ be the screening factor. Then $(d\nu/dE)$ is proportional to γ while the vibrational cross section is proportional to γ^2 . No matter what approximations are used to calculate γ , it is impossible for *any* local field model to explain how $(d\nu/dE)$ and the vibrational cross section could both double.

A similar failure of local-field models has been noted previously. As CO coverage increases on Pt(111)¹⁶ and on Pt(335),¹⁷ both the vibrational cross section and $(d\nu/dE)$ of the CO decrease—presumably because the local E is screened by the electronic polarizability of nearby CO. Both the static and ir data have been analyzed to determine the dependence of γ on θ_{CO} . The static and ir data give significantly different results.

The electrochemical experiments of Kim *et al.*^{18,19} also suggest that $(d\nu/dE)$ doubles on going from the terrace to the edge. For CO on Pt(335) in aqueous electrolyte they measured the change of ν with electrode potential Φ . They found that $(d\nu/d\Phi) = 75 - 80 \text{ cm}^{-1}/\text{V}$ at low θ_{CO} (for edge CO) and $33 \text{ cm}^{-1}/\text{V}$ at high θ_{CO} (for both edge and terrace CO). In a similar experiment with CO on Pt(111), Leung *et al.*⁶³ found that $(d\nu/d\Phi) = 40 - 44 \text{ cm}^{-1}/\text{V}$ for atop CO at low coverage.

A local field model could explain these results if the screening factor γ is different for static as opposed to ir

fields. However, as discussed in Ref. 16, this explanation is implausible. Simple theoretical considerations suggest that since the ir frequency is small relative to the metal's plasma frequency, both the static E and E from p -polarized ir incident at our angle of incidence should be screened by about the same factor.^{16,34,42}

The explanation for the discrepancy that we find most plausible is that the vibrational Stark effect and ir absorption both involve *nonlocal* interactions with E . For CO on an alkali-halide surface, a nonlocal theory⁶⁴ has been given for $(d\nu/dE)$ and the effect of E on the vibrational intensity S . The theory makes use of E in a situation where all of the substrate charge has been frozen in place and then the CO molecule has been removed. The calculated effects agree with experiment for CO on NaCl(100), despite the fact that at the empty site the local E changes by a factor of 6 between the C and O positions.⁶⁴ The spatial variation of the local E changes $(d\nu/dE)$ and the ir cross section by different factors. Even though the theory in Ref. 64 does not apply to CO chemisorbed on a metal surface (it uses a multipole expansion that converges slowly if at all for CO on a metal surface) it does confirm that *the local field is averaged differently for ir absorption and for the Stark effect.*

Nonlocal optical effects at metal surfaces have been demonstrated previously. The excitation of bulk plasmons by light with frequency above a metal's plasma frequency is a nonlocal effect³⁴ that has been seen in various ways.⁶⁵⁻⁶⁷ A nonlocal theory of Feibelman⁶⁸ predicts that the surface photoemission spectrum of simple metals should have a peak below the metal's plasma frequency. The predicted feature has been observed in spectra of Al(100)^{69,70} and Na-covered Cu(100).⁷¹ A nonlocal theory of second-harmonic generation^{36-38,40} explains many experimental observations.⁷²⁻⁷⁶ (As mentioned in Sec. I, the effect of step density⁴¹ has not yet been explained.⁴²) Our results suggest that the application of similar ideas will be necessary for a full understanding of the vibrational spectra of adsorbates on metals.

Finally, we discuss a simple nonlocal model that explains how $(d\nu/dE)$ and the vibrational cross section both double as CO goes from terrace sites to edge sites. On a stepped metal surface, as first noted by Smoluchowski,⁷⁷ electron density tends to fill in the troughs and round off the corners of steps so the electrical surface is smoother than the profile of topmost nuclei. This is seen, for example, in the calculated electron density vs position for stepped jellium.^{23,28,29} Suppose that instead of interacting with the local E at the center of the C–O bond, the molecule interacts with the local E at two points: at the C and O nuclei, for example. (Here, E is evaluated with the CO molecule removed.⁷⁸) We assume that

$$S \propto E_{\text{ir}}^2(C) + E_{\text{ir}}^2(O),$$

$$\frac{d\nu}{dE} \propto E_0(C) + E_0(O),$$
(1)

where S is the ir cross section, E_{ir} and E_0 are the ir and induced static fields, and C and O denote the positions of the C and O nuclei. (A quantum mechanical formalism that partitions a molecule's response to an external field among the

molecule's atoms has been developed by Bader.⁷⁹⁾ Suppose further that the fields at the O nuclei are unscreened, owing to their distance from the surface, and that the fields at the C nucleus on the edge are also unscreened, owing to Smoluchowski smoothing. On the terrace, however, we assume that the C nucleus lies within the smoothed electron density, so E there is completely screened. Then on the edge both atoms contribute to the response of the molecule, while on the terrace only the O atom contributes; this implies that S and (dv/dE) are both twice as large for CO on the edge as they are for CO on the terrace.

This model is certainly oversimplified but it does suggest that the strong variation of the local field with position could be important. An *ab initio* calculation of CO's S and (dv/dE) at edge and terrace sites on Pt(335) would be interesting.

V. CONCLUSION

We have compared the vibrational cross section and the Stark tuning rate for terrace and edge atop CO on Pt(335) using RAIRS, EVS, and HREELS. The CO adsorption site was controlled by coadsorption of H and O. The cross-section of edge atop CO is 2.0 ± 0.2 times greater than that of terrace atop CO and the ratio of the Stark tuning rates is also 2.0 ± 0.2 . It is impossible to explain both the difference in ir cross section and in the Stark tuning rate with a model that only uses the local field at a single point.

The discrepancy between our experiment and single-point screening models is consistent with a discrepancy seen in previous studies of screening by coadsorbates.^{16,17} One explanation is that screening is unexpectedly different for static and ir fields, but this is unlikely for theoretical reasons. Another explanation is that the vibrational Stark effect and the ir cross section are both nonlocal. At a metal surface where the local field varies rapidly with position they are no longer directly related. A simplified model based on this idea can account for a factor of 2 difference between the edge and terrace sites for both the Stark tuning rate and the ir cross section.

Our determination that the Stark tuning rate for terrace atop CO on Pt(335) is half that of edge atop CO agrees with an electrochemical study,^{18,19} but contradicts Ref. 13. This difference remains unexplained, but suggests that the Stark tuning rate of terrace CO can be sensitive to surface preparation.

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