CO on Pt(335): Vibrational overtones and site dependence of the vibrational Stark effect

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Electron energy loss spectroscopy is used to compare atop CO at two sites on Pt(335): on the flat (111) terrace and on the step edge. The cross section for the C–O stretch overtone of the terrace species is not significantly larger than that of the edge species. Previous experiments have shown that the vibrational frequency of terrace CO responds much less to applied electrostatic field than does edge CO, even though their ir cross sections are about the same. The present experiment shows that CO has similar molecular properties at the two sites: a chemical explanation for the different Stark tuning rates is ruled out. The difference could be due to spatial variation of the electric field. Local screening of almost all the static electric field at terrace sites is one possibility, but a simple jellium model is unable to explain the observed effect. Interaction of the molecular quadrupole moment with the spatially varying field near the surface is also important.

I. INTRODUCTION

We have obtained experimental results that challenge the conventional interpretation of the vibrational Stark effect of CO at metal surfaces. Previous measurements of the Stark tuning rate of CO adsorbed on Pt in various situations[1–11] are summarized in Table I. (The Stark tuning rate is the change of vibrational frequency with electric field.) Simple models have been unable to explain why the Stark tuning rate is so different in these situations. In the present experiment, electron energy loss spectroscopy (EELS) was used to search for a chemical origin for the difference between atop CO at two sites on Pt(335).

The Pt(335) surface is shown in Fig. 1. It consists of (111) terraces four atoms wide separated by monatomic height steps of (100) orientation. CO adsorbs either on the edge or on the terrace, and is either atop or bridge bonded. At any given total CO coverage, the equilibrium coverage of each of the four CO species is known.[12]

We have obtained EELS spectra at a series of CO coverages on Pt(335). The spectra show both the fundamental and overtone transitions of the C–O stretch vibration. The coverage dependence of atop CO's overtone transition intensity is of particular interest. The overtone intensity is an indication of the curvature of CO's dipole moment function. The same quantity affects CO's Stark tuning rate. If the electric fields at edge and terrace sites are assumed to be equal, as suggested by the similar ir cross sections for CO at the two sites, it is possible to relate our EELS data to the previously measured difference in the CO Stark tuning rate at the two sites. The comparison of overtone cross sections between edge and terrace sites is complicated by the fact that EELS is unable to resolve the overtone lines from CO at the two sites. To isolate the cross section of each species we correlate line intensity vs total coverage with the species populations vs total coverage.

There have been previous EELS studies of overtone intensity vs coverage.[13–21] Vibrational overtones of adsorbed species have also been observed with ir spectroscopy.[22–26] In ir studies, the intensity of *observed* overtone lines is usually enhanced by mixing with some other allowed ir transition. Without enhancement, ir overtone lines of adsorbed species are often too weak to be observed in a single reflection experiment. The vibrational overtones of many free molecules have been studied with ir to learn about their dipole moment functions and potential energy functions.

An experimental approach similar to ours helped establish why adsorbed CO and free CO have different vibrational frequencies. The various effects that contribute to adsorbed CO's frequency shift can be classified as either "chemical" or "physical." Chemical effects are explained by a rearrangement of electronic states arising from the overlap of wave functions. Physical effects are explained in terms of classical mechanics and electrodynamics. For example, the C–O stretch frequency of adsorbed CO is different from the gas phase value, in part because of dipole coupling to its own image[27] and dynamical coupling to the adsorbate–substrate vibrations;[28] these are regarded as physical effects. The dominant effect, however, is backdonation of electrons from the metal into the $2\pi^*$ orbital of the molecule,[29] a chemical effect. As CO coverage changes, the C–O stretch vibrational frequency also changes. A physical explanation for the coverage-dependent shift is dipole–dipole coupling. It is also possible for chemical interactions between nearby CO molecules to change the frequency. The dipolar and chemical contributions to fre-

TABLE I. The Stark tuning rate dv/dE of atop CO in four different situations.

Surface	Ambient	Site	dv/dE $[10^{-7}\ \mathrm{cm^{-1}/(V/cm)}]$
Pt(111)	Vacuum	···	7.5 ± 0.9[a]
Pt(111)	Aqueous electrolyte	···	16[b]
Pt(335)	Vacuum	Edge	7.5 ± 2.0[c]
Pt(335)	Vacuum	Terrace	$\leqslant 0.8$[c]

[a]Low coverage limit of the Stark tuning rate from Ref. 1. The Stark tuning rate of CO on Pt(111) at saturation CO coverage was reported in Ref. 2.

[b]Deduced from a measurement reported in Ref. 3. The experiment used 0.12 ML of CO on a Pt(111) electrode in aqueous $0.1M$ $HClO_4$ electrolyte. The models discussed in Ref. 4 were used to interpret electrode potential change as change of the E field in the double layer. Other ir studies of the vibrational Stark effect for CO on Pt(111) electrodes in electrochemical cells are reported in Refs. 5–10.

[c]Local E-field Stark tuning rate obtained by fitting a dipole–dipole coupling model to coverage-dependent data in Ref. 11.

quency shifts have been separated through isotopic dilution experiments.[30–38] Theoretical calculations and the experimental comparison of coadsorbate effects have also provided insight.

In the present study we want to make a similar distinction. Are the different Stark tuning rates due to different molecular properties (chemical) or to spatial variation of the electric field (physical)? We study the coverage dependence of C–O stretch overtone intensity to answer this question.

II. EXPERIMENT

The EELS apparatus[39] and our procedures for sample preparation[2,12] have been described elsewhere. The sample was held at 100 K for CO dosing, and then annealed at 280 K for 1 min to obtain an equilibrated surface. EEL spectra were measured after the sample cooled again to 100 K. Annealing affected the fundamental peaks at coverages above $\theta = 0.3$ and affected the double loss and overtone peaks at all coverages. A second annealing did not change the spectra further. While EEL spectra were measured both before and after annealing, only the data for the annealed surfaces are considered here. Coverages were determined by temperature programmed desorption, assuming $\theta = 0.625$ at saturation, as determined by Lambert and Tobin.[11]
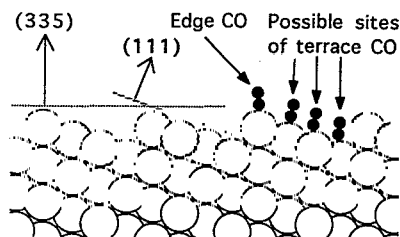

FIG. 1. Side view of the Pt(335) surface, showing atop adsorption sites for edge and terrace CO.

To reduce scanning time and the possibility of contamination by background gases, spectra were only taken from 1800 to 4500 $\mathrm{cm^{-1}}$; however, the elastic peak was always measured. To compensate for possible variations in spectrometer efficiency, all overtone and double loss intensities are normalized to the intensity of the appropriate fundamental peak. Since the width of each peak was limited by the spectrometer resolution, intensities are determined from the peak height above a smooth base line. The error bars are determined from the noise in the spectrum.

III. THEORY

Our object is to link the intensity of the C–O stretch overtone peak—seen with EELS—to the Stark tuning rate of CO on the same surface—seen with ir. We do this with a semiclassical model that describes both processes.

In the model, CO is a semiclassical oscillator that vibrates along the surface normal. The deviation of the C–O distance from its equilibrium value at zero applied E field is x. Associated with the oscillator is a C–O interaction potential $U(x)$ at zero applied E field, and a dipole moment function $p(x)$. Both $U(x)$ and $p(x)$ are expressed as Taylor series about the $E=0$ equilibrium point:

$$U(x) = a_{00} + a_{20}x^2 + a_{30}x^3 + \cdots ,$$
$$-p(x) = a_{01} + a_{11}x + a_{21}x^2 + \cdots . \tag{1}$$

Equation (1) uses the same notation as Ref. 4. The a_{20} term is the curvature of the potential energy curve at $x=0$. It determines the resonant vibrational frequency v with $E=0$, in the limit of small vibrations. The a_{30} term is closely related to the binding energy. The dipole moment derivative or Szigeti charge e^* is $-a_{11}$. It determines the ir cross section. The a_{21} term is of greatest interest in the present experiment. It affects both the Stark tuning rate and the overtone EELS cross section.

The Stark tuning rate is the effect of an applied E field on the resonant frequency of the C–O stretch vibration. In our model, E is constant within the empty adsorption site. With a uniform applied E field the potential energy function is $V(x) = U(x) - \mathbf{E} \cdot \mathbf{p}(x)$. We assume that $\mathbf{E}$ and $\mathbf{p}$ are parallel so $V(x) = U(x) - Ep(x)$. This is plausible. The macroscopic boundary condition at a metal surface is that E is directed normal to the surface. There is also evidence that CO on Pt(335) is oriented along the surface normal at both edge and terrace sites.[40]

To solve for dv/dE, the Stark tuning rate, perturbation theory is used. In the limit of small vibrational amplitude, the resonant vibrational frequency v is determined by the curvature at the minimum of $V(x)$. The Stark tuning rate is[41]

$$\frac{dv}{dE} = \frac{a_{11}}{4\pi(2\mu a_{20})^{1/2}} \left(\frac{2a_{21}}{a_{11}} - \frac{3a_{30}}{a_{20}} \right). \tag{2}$$

Here μ is CO's reduced mass.

In EELS, an electron approaches the surface with a definite energy and direction. Upon reflection, the electron can lose energy by raising the oscillator to one of its excited states. One measures the ratio of intensity at two loss en-

ergies: the fundamental $0 \rightarrow 1$ transition at v and the overtone $0 \rightarrow 2$ transition at $\sim 2v$. For dipole excitation, the ratio of the overtone intensity to the fundamental intensity is[2]

$$\frac{I_2}{I_1} = \frac{f_2}{f_1} \frac{\hbar}{4(2\mu a_{20})^{1/2}} \left(\frac{2a_{21}}{a_{11}} + \frac{a_{30}}{a_{20}} \right)^2. \tag{3}$$

Here f_1 and f_2 are determined by the EELS spectrometer as discussed in Sec. IV.

The ratio of the two terms in Eq. (2) provides a useful dimensionless parameter with which to compare the overtone EELS intensity with the Stark tuning rate. The ratio is

$$\beta = \frac{2a_{21}/a_{11}}{3a_{30}/a_{20}}. \tag{4}$$

Expressed in terms of β, Eqs. (2) and (3) are

$$\frac{dv}{dE} = \frac{a_{11}}{4\pi(2\mu a_{20})^{1/2}} \left(\frac{3a_{30}}{a_{20}} \right) (\beta - 1), \tag{5}$$

$$\frac{I_2}{I_1} = \frac{f_2}{f_1} \frac{\hbar}{4(2\mu a_{20})^{1/2}} \left(\frac{a_{30}}{a_{20}} \right)^2 (1 + 3\beta)^2. \tag{6}$$

The parameter β describes the relative significance of the anharmonicity of the potential and the curvature of the dipole moment. For free CO,[41,42] $\beta = 0.025 \pm 0.009$, and both the Stark tuning rate and the overtone intensity are dominated by the anharmonic term a_{30}. If $\beta \sim 1$, then anharmonicity and dipole nonlinearity would make equal and opposite contributions to the Stark tuning rate, giving zero Stark shift; the overtone intensity would then be dominated by the a_{21} term.

This model is simple, but it is a reasonable first approximation. It is based on the Born–Oppenheimer approximation. The model implicitly assumes that the local electric field varies slowly over the region occupied by an adsorbate, and that the effect of electric field on the molecule's vibrational frequency can be described in terms of the molecule's electronic ground state properties. Alternative models explain the effect of an electric field on adsorbed molecules using excited electronic states.[43–46] A model for the ir overtone has also been proposed that involves excited electronic states.[47] Although the importance of excited states has been a subject of controversy, the Stark tuning rate given in Eq. (2) is the leading term in the exact quantum mechanical expression.[4] For oriented CO in a uniform E field, Eq. (2) is 99.7% accurate. *Ab initio* calculations[48–52] have also confirmed the accuracy of Eq. (2).

In the quantum theory for the vibrational Stark effect of an adsorbed molecule, a_{20}, a_{30}, a_{11}, and a_{21} in Eq. (2) are reinterpreted as coefficients in the double Taylor expansion of total energy with respect to x and the externally applied E field. To apply Eq. (2) at the molecular level, the expansion with respect to total energy must be related to local quantities. This is discussed in Sec. V.

Our model neglects coupling between molecules. At the CO coverages used in our experiment there is strong dipole–dipole coupling between adsorbates so it would be better to treat the fundamental and overtone transitions as surface phonons rather than as localized vibra-
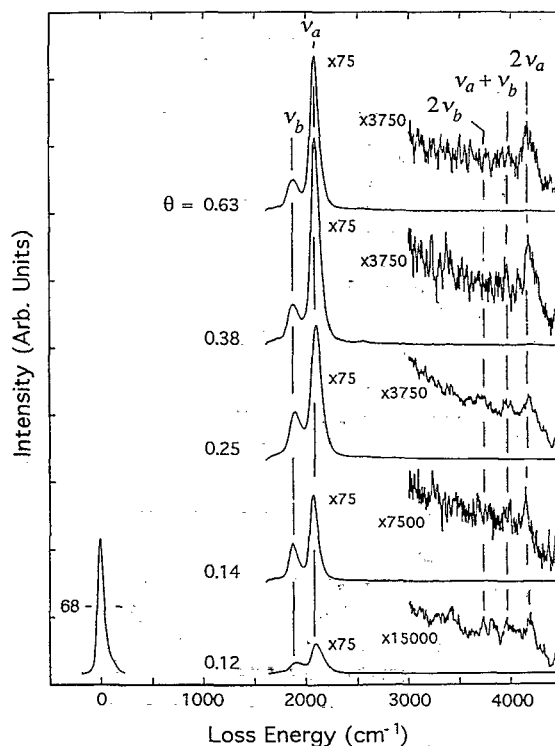

FIG. 2. EEL spectra of CO on Pt(335) vs coverage. The sample was dosed with CO at 100 K, then annealed at 280 K for 1 min to obtain an equilibrated layer. Spectra were measured with the sample at 100 K.

tions.[11,19,31,53–55] However, since we use the model to predict only the *ratio* of EELS intensity at two frequencies, the effect of coupling is expected to cancel out. To first approximation, the effect of dipole coupling on EELS intensity is frequency independent[31] since it arises from CO's electronic polarizability. Dipole–dipole coupling was explicitly included in the determination of the Stark tuning rates in Ref. 11.

IV. RESULTS AND ANALYSIS

As shown in Fig. 2, for EEL spectra taken in the specular direction, five peaks are seen. Let v_a and v_b denote the fundamental $0 \rightarrow 1$ transition frequencies for atop and bridging CO, respectively. In order of increasing frequency the five peaks are at v_b, v_a, $2v_b$, $v_b + v_a$, and $2v_a$. We designate the intensities of these five peaks as I_b, I_a, I_{2b}, I_{ab}, and I_{2a}.

To relate our data to our model we use the fixed parameters given in Table II. All are determined from *independent* experimental data. The curvature of the potential a_{20}, and the linear dynamic dipole moment a_{11}, are taken from the ir measurements[11] of Lambert and Tobin. The cubic anharmonicity a_{30} is estimated by an indirect method described in detail below. The EELS parameters f_1 and f_2 are calculated from the known characteristics of our EELS system; this calculation is also discussed below.

To analyze the data, we determine β_e (for edge CO) from the Stark tuning rate, and treat β_t (for terrace CO) as

TABLE II. Parameters used in the calculation of overtone intensities and Stark tuning rates for atop CO on Pt(335). Unless otherwise indicated, all parameters are assumed to be equal for edge and terrace CO. The estimated values are used for Figs. 4 and 5; the range indicates the uncertainty.

Parameter	Estimate	Range	Units
a_{11}	$1.0^{a,b}$	0.85–1.3	e
a_{20}	5.4^{a}	5.3–5.5	10^{17} eV/cm^2
a_{30}	1.7^{c}	1.5–1.9	10^{26} eV/cm^3
μ	6.86	$\cdots$	amu
f_2/f_1	0.3^{c}	0.25–0.35	$\cdots$
dv/dE (edge)	7.5^{a}	5.5–9.5	10^{-7} cm^{-1}/(V/cm)
dv/dE (terrace)	$<0.8^{a}$	$\cdots$	10^{-7} cm^{-1}/(V/cm)

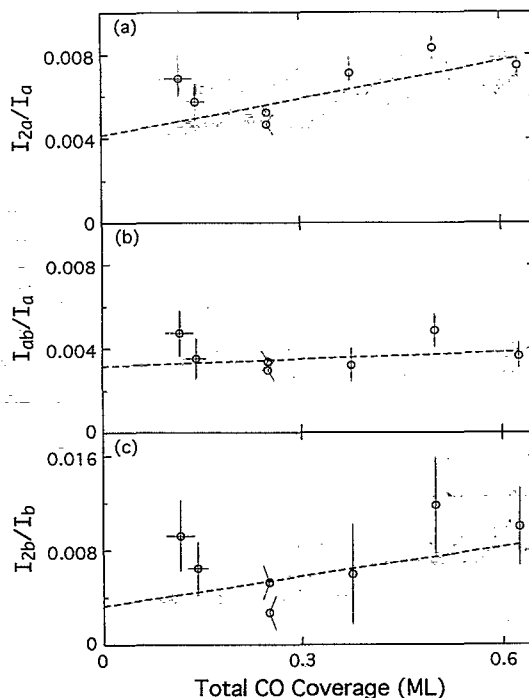[a]Reference 11.
[b]Reference 37.
[c]See text.

FIG. 3. Normalized EELS intensities for the three high frequency peaks, as a function of total CO coverage in monolayers (ML). The lines are linear fits to the data.

a parameter to be determined from the data. We assume (except as indicated) that the parameters listed in Table II are equal for edge and terrace CO.

Our model can explain the small apparent dv/dE of terrace CO by two different molecular property changes: either the anharmonicity of terrace CO is greatly reduced, $(a_{30})_{\text{terrace}} \sim (a_{30})_{\text{edge}}/10$, or the anharmonicity of terrace CO is compensated by a highly nonlinear dipole moment, $\beta_t = 1.0 \pm 0.1$. It is unlikely that the anharmonicity a_{30} is significantly different at the two sites, since it is closely related to the dissociation energy D_e. If $U(x)$ is modeled by a Morse potential, for example, $D_e \propto (a_{30})^{-2}$, so a difference of a factor 10 in a_{30} would imply a difference of a factor 100 in D_e. The measured difference in CO's heat of adsorption $E_a(\text{CO})$ between edge and terrace sites, however, is less than 20 kcal/mol,[12,56–59] which leads to only about a 10% variation in D_e; even if $E_a(C)$, the adsorption energy of a carbon atom, were zero at edge sites D_e would increase by only a factor of 2 [see Eq. (10)].

Accordingly, we wish to test the other possibility, that the dipole nonlinearity a_{21} (or equivalently β) is much larger for terrace CO than for edge CO. If $\beta_e \sim 0$ and $\beta_t \sim 1$, then Eq. (6) implies that the overtone cross section per molecule for terrace CO would be 16 times larger than for edge CO. This difference would appear in the coverage dependence of the overall (edge+terrace) overtone intensity. At low coverage, CO on Pt(335) predominantly occupies edge sites.[11,12,54] Terrace sites begin to be occupied at $\theta \sim 0.15$ and the terrace coverage increases rapidly between $\theta = 0.15$ and $\theta = 0.4$. If $\beta_t \sim 1$ then we would expect a dramatic increase in the total overtone intensity in this coverage range. The spectra in Fig. 2 do not agree with this expectation.

Our quantitative analysis of the data is concerned with the $2v_a$ peak. As shown in Fig. 3(a), the ratio I_{2a}/I_a is nearly constant in the 0.15–0.4 ML coverage range (ML denotes monolayer). However, two processes can give rise to peaks at about $2v_a$: the overtone $0 \rightarrow 2$ transition and double scattering with two $0 \rightarrow 1$ transitions.[60] The overtone and double loss peaks usually overlap and are of comparable intensity.[61–63] Accordingly, we treat I_{2a} as the sum

of two independent components, atop CO's dipole overtone I_{oa} and atop CO's double loss I_{aa}, so

$$I_{2a} = I_{oa} + I_{aa}. \tag{7}$$

Our model predicts the intensity only of dipole losses. Experiments have shown, however, that two other scattering mechanisms also give rise to loss features in EELS: impact and resonance scattering.[64,65] It is well established that for CO spectra measured in the specular direction the $0 \rightarrow 1$ fundamental peak is dominated by dipole scattering,[61,66–68] and there is evidence that overtone losses for chemisorbed CO are also predominantly dipole losses.[61,62] We therefore assume that I_{oa}/I_a is well described by Eq. (6). Multiple loss peaks, however, are generally dominated by nondipole processes,[18,62,64] which are not well enough understood to predict I_{aa}, or even its dependence on atop coverage θ_a. There is experimental evidence, however, that the dependence is stronger than linear.[18,63] We therefore model I_{aa} by the power law:

$$I_{aa} = C(\theta_a)^\eta, \tag{8}$$

with parameters C and η. One reasonable scenario is that I_{aa} is caused by two independent losses and that the probability of a single loss is proportional to θ_a. This would imply that $\eta = 2$ as Chen, Crowell, and Yates found[18] for high coverages of Al_2O_3 on Al. Another possibility is that I_{aa} is caused by a single resonance scattering event, with a probability proportional to θ_a, giving $\eta = 1$. Such a weak coverage dependence is unlikely, however, particularly at low coverage, where the vibrational modes are localized and the two excitations must occur on distinct adsorbates.
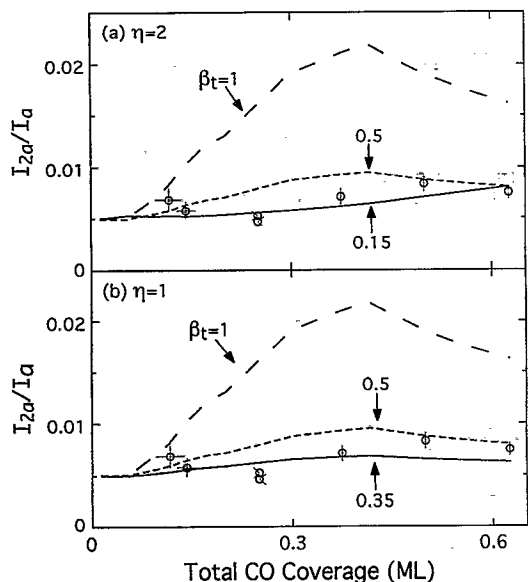
FIG. 4. Comparison of the measured intensity ratio I_{2a}/I_a (from Fig. 3) with the calculated intensities for various values of β_t. A value of β_t close to 1 is required for terrace CO's molecular properties to explain its small Stark tuning rate. (a) Calculation assumes two uncorrelated scattering events ($\eta=2$). To be consistent with the data, $\beta_t<0.4$; the best fit is $\beta_t=0.15$. The dipole contribution I_{oa}/I_{2a} at saturation is 0.53, 0.98, and 1.00 for $\beta_t=0.15$, 0.5, and 1.0, respectively. The off-specular EEL spectra suggest that I_{oa}/I_{2a} is in the range 0.25–0.75. (b) Calculation assumes a single scattering event ($\eta=1$). The best fit is for $\beta_t=0.35$. $I_{oa}/I_{2a}=0.98$, 0.98, and 1.0 for $\beta_t=0.35$, 0.5, and 1.0, respectively.

Once β_t and η are specified, the only free parameter in Eq. (7) is C. We adjust C to obtain the best fit to the data. The best fits with $\eta=1$ and 2, and with various values of β_t, are shown in Fig. 4. It is apparent that values of β_t approaching 1 are excluded by the data. As expected, for $\beta_t>\beta_e$ the model predicts a large increase in I_{2a}/I_a between $\theta=0.15$ and $\theta=0.40$, which is not present in the data. In fact, for the parameter values in Table II, values of β_t exceeding about 0.4 are excluded. This maximum value of β_t corresponds to a minimum (dv/dE) for terrace CO of 5.8×10^{-7} cm^{-1}/(V/cm), more than seven times greater than the upper limit set by Lambert and Tobin.[11] The small (dv/dE) of CO at terrace sites is not explained by a large dipole nonlinearity a_{21} of CO at terrace sites.

We have investigated the sensitivity of this conclusion to all of the parameters and assumptions in the model. The optimum β_t and the quality of the fit are most sensitive to the anharmonicity a_{30} and the EELS sensitivity ratio f_2/f_1. These are discussed in detail.

We estimate a_{30} by the method described by Lambert,[4] using the gas phase value of a_{30} and the dissociation energies D_e of free and adsorbed CO:

$$(a_{30})_{\text{ads}}=(a_{30})_{\text{gas}}\left(\frac{\nu_{\text{ads}}}{\nu_{\text{gas}}}\right)^3\left[\frac{(D_e)_{\text{gas}}}{(D_e)_{\text{ads}}}\right]^{1/2}. \quad (9)$$

The dissociation energy of adsorbed CO is not known directly, but is estimated as

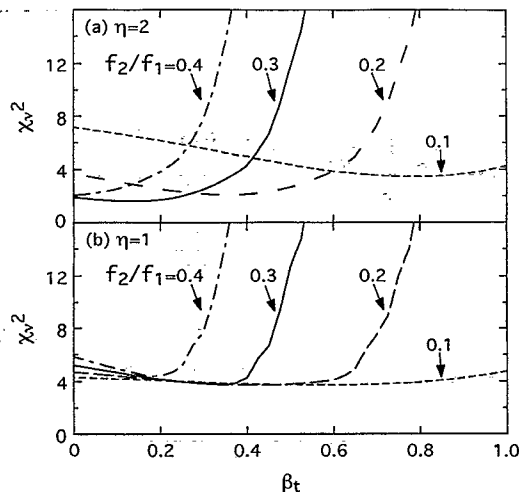$$(D_e)_{\text{ads}}=(D_e)_{\text{gas}}+E_a(\text{CO})-E_a(\text{C}), \quad (10)$$

where $E_a(\text{CO})$ and $E_a(\text{C})$ are the adsorption energies of CO and C. For the Pt(111) surface, Shustarovich and Bell give[69] $(D_e)_{\text{gas}}=257$ kcal/mol, $E_a(\text{CO})=32$ kcal/mol, and $E_a(\text{C})=139$ kcal/mol. The least certain of these is $E_a(\text{C})$, which is an extrapolation[70] from the 171 kcal/mol measured for C on Ni(111). From the values tabulated in Ref. 69 it is apparent that the heats of adsorption of small molecules on Pt(111) and Ni(111) rarely differ by more than 25%, and that E_a on Pt is invariably smaller than on Ni. We estimate that $125 < E_a(\text{C}) < 175$ kcal/mol, which leads to the range of a_{30} given in Table II. [The early theoretical estimate[71] $E_a(\text{C})=63$ kcal/mol conflicts with subsequent experimental data.] Variation of a_{30} over this range does not change the ultimate conclusion; the minimum a_{30} allows β_t to increase to about 0.6 and still be consistent with the data, but $\beta_t\sim1$ is still excluded unless f_2/f_1 is much smaller than we assume.

The ratio f_2/f_1 directly affects I_{oa}/I_a in Eq. (6). If f_2/f_1 were very small then most of I_{2a} would come from I_{aa}, and our measurements would tell us little about β_t. In the dipole scattering theory of specular EELS, the factor $f(\phi,\omega,E_0)$ accounts for the finite angular acceptance of the spectrometer:

$$f=\frac{\sin^2\phi-2\cos^2\phi}{1+\alpha^2}+(1+\cos^2\phi)\ln(1+1/\alpha^2), \quad (11)$$

$$\alpha=\hbar\omega/(2E_0\theta_c), \quad (12)$$

where ϕ is the angle of incidence, E_0 is the primary beam energy, ω is the frequency corresponding to the loss energy, and θ_c is the acceptance angle of the spectrometer.[61,66] For our experimental conditions, $\alpha=1.67$ for the fundamental and 3.34 for the overtone, and $\phi=60°$; the first term in Eq. (11) is negligible, and $f_2/f_1\approx\alpha_1^2/(2\alpha_1^2)^2=0.25$, where α_1 is the value of α at the fundamental frequency. A more accurate calculation gives $f_2/f_1=0.3$. This quantity is insensitive to the exact values of α and ϕ, and is ≥0.25. To the extent that the dipole theory is ade-

FIG. 5. Reduced chi-squared χ_ν^2 as a function of β_t, for various values of the EELS sensitivity ratio f_2/f_1 and for (a) $\eta=2$ and (b) $\eta=1$. Values of β_t near unity are possible only for unrealistically small values of f_2/f_1.

quate, f_2/f_1 is close to 0.3. There is always the possibility, however, of unexpected experimental effects, so we have explored the effect of changes in f_2/f_1 on our conclusions.

Figure 5 summarizes the effect of the exponent η and the ratio f_2/f_1 on our estimate of β_t. We plot the reduced chi-squared[72] χ_ν^2 for the model as a function of β_t for various values of f_1/f_2 and for both $\eta=2$ and $\eta=1$. The minimum χ_ν^2 for $\eta=2$ and $f_2/f_1=0.3$ is 1.64 and occurs at $\beta_t=0.18$. Since $\chi_\nu^2 \simeq 1$ indicates good agreement, and in view of the uncertainties and approximations involved, we regard this as a reasonable fit to the data. For smaller values of β_t the increase in χ_ν^2 is slight, but χ_ν^2 increases rapidly for higher values of β_t. If f_2/f_1 is much smaller than our estimated value, the minimum of χ_ν^2 moves to higher values of β_t, but the fit also becomes significantly inferior. For $\eta=1$ the trends are the same, but the values of χ_ν^2 are consistently higher, suggesting that I_{aa} arises largely from independent or weakly correlated scattering events. The minima are flatter than for $\eta=2$, but values of β_t greater than 0.8 are ruled out provided that $f_2/f_1 > 0.1$; only if the spectrometer sensitivity decreases unexpectedly by a factor 3 between 2000 and 4000 cm^{-1} can f_2/f_1 reach such a low value. We consider that possibility extremely unlikely.

Two observations provide empirical support for our method of analysis and choice of parameters. First, at low coverage only edge sites are occupied, so I_{oa}/I_a is completely determined by Eq. (6) and the parameters in Table II. At the same time, if $\eta > 1$, as indicated by experiment,[18,63] then the nondipole term I_{aa}/I_a is negligible at low coverage, and $I_{2a} \simeq I_{oa}$. Our model therefore predicts I_{2a}/I_a at low coverage *with no adjustable parameters*. The good agreement evident in Fig. 4(a) supports the validity of Eq. (6) and the parameter values in Table II. In particular, a value of f_2/f_1 as low as 0.1 would result in too little intensity at the lowest coverage.

Additional support for our model comes from loss spectra measured off the specular direction at saturation coverage, shown in Fig. 6. These data confirm that the fundamental intensities I_a and I_b are from dipole scattering (since they decrease rapidly with off-specular angle), while I_{ab} is largely nondipole (as expected for a double loss), in agreement with other groups.[18,62,63] Figure 7(a) shows (on a log scale) the intensities of the elastic peak, the two fundamental peaks, and two of the high frequency peaks as a function of off-axis angle. The peak at I_{2b} was too weak to measure off the specular direction. In Fig. 7(b), the intensities I_a, I_{2a}, and I_{ab} are replotted on a linear scale, normalized to their intensities in the specular direction. The behavior of I_{2a} is intermediate between that of the dipole loss I_a and of the nondipole double loss I_{ab}, indicating that both dipole and nondipole processes contribute significantly to the total intensity.

The off-specular data give an independent check of our separation of I_{2a} into dipole and nondipole components. We assume that the nondipole component I_{aa} has the same dependence on off-specular angle as the atop-bridge double loss I_{ab}. We also assume that the dipole overtone I_{oa} has the same dependence as the fundamental I_a. Then between
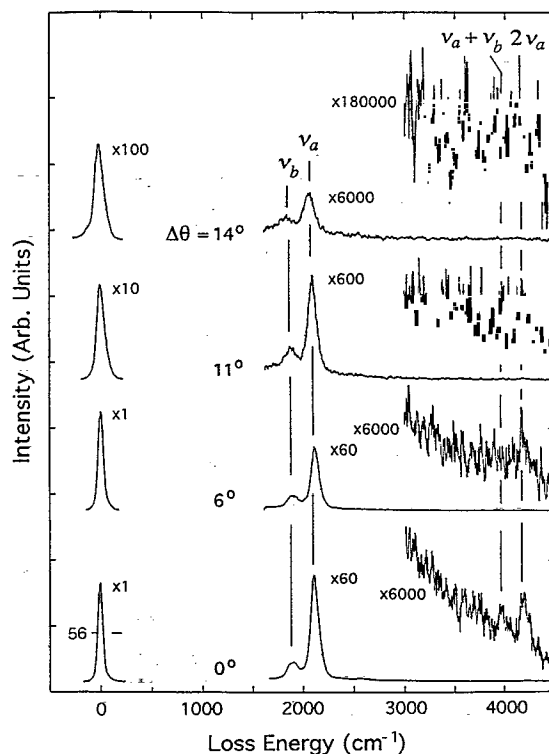

FIG. 6. EEL spectra at saturation coverage (0.63 ML) in the specular direction and at three off-specular angles.
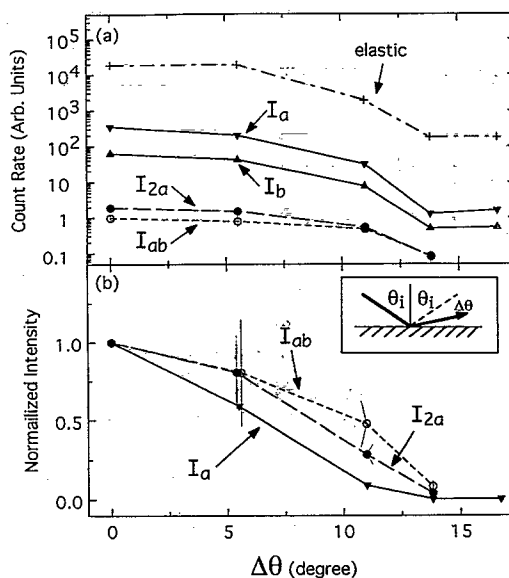

FIG. 7. EELS intensities of the elastic peak and four loss peaks as a function of off-specular angle, from Fig. 6. (a) Uncorrected intensities, on a logarithmic scale. (b) Intensities I_a, I_{ab}, and I_{2a}, normalized to their respective values in the specular direction, on a linear scale. The angular dependence of I_{2a} is intermediate between the dipole loss I_a and the double loss I_{ab}.

25% and 75% of I_{2a} at saturation comes from the dipole term. This is similar to the results of other groups: Andersson and Davenport[61] found $I_{oa}/I_{2a} \sim 0.3$ for CO on Ni(100); dePaola and Hoffmann,[62,73] found $I_{oa}/I_{2a} \sim 0.2$ for CO on clean and potassium-predosed Ru(001). For our system the ratio I_{oa}/I_{2a} at saturation for each model calculation is given in the caption to Fig. 4. For the parameter values that best fit the data ($\eta = 2$, $\beta_t \sim 0.15$), the calculation gives $I_{oa}/I_{2a} \sim 0.5$, in the middle of the range estimated from off-specular measurements.

V. DISCUSSION

Within the context of our model, the data are inconsistent with a simple chemical explanation for the different Stark tuning rates of CO at edge and terrace sites. The Stark tuning rates could be explained if the local static electric field is a factor 10 smaller at the terrace sites than at the edge sites. Some enhancement of the field at the step edge is expected, but not enough to account for the difference. The "lightning rod" concentration of the field near a corner is estimated[74] to give only a factor 1.5 difference in field strength between the edge and the terrace on Pt(335). Screening by conduction electrons also reduces the local E field at the terrace site relative to the edge site. As first discussed by Smoluchowski,[75] the negative charge density from conduction electrons that spill out from the metal is smoothed relative to the positive charge density of the atomic cores. Consequently, there is a deficit of electron density near the edge and a surplus on the terrace. Experimentally, for stepped Pt surfaces, the local work function measured with adsorbed Xe is 1 eV smaller at the Pt step edge than it is on the (111) terrace,[76,77] consistent with reduced electron density at the step edge. This is the largest work function difference measured between the step and terrace of any metal surface.

However, a one-dimensional jellium estimate[11] for the difference in screening between CO at the Pt(335) terrace and edge sites was only able to account for the observed difference if the terrace CO were all concentrated in the deepest part of the trough. A jellium calculation by Thompson and Huntington[78] also indicated that the surplus electron density extends less than one lattice spacing across the terrace. But unless the surplus electron density on the terrace extends for several lattice spacings, electronic screening cannot account for the difference between CO and Pt(111) and terrace CO on Pt(335). It is implausible that all of the terrace CO would be concentrated in the trough at saturation coverage.[12]

Moreover, a difference in static screening between edge and terrace sites is difficult to reconcile with CO's ir cross section at the two sites. Both Lambert and Tobin[11] and Reutt-Robey et al.[59] found that on stepped Pt, atop CO at either edge or terrace sites has about the same ir cross section. In the experiments, with p-polarized light incident near grazing incidence, the ir E field near the surface (but outside the screening charge) is approximately along the surface normal. Inside the screening charge, the normal component of the ir E field decays rapidly, on the length scale of a few Å like the static field, but with a frequency-dependent screening length.[79] Adsorbed molecules are believed to respond mainly to the normal component.[80,81] Jellium models predict that the screening length for the normal component increases with increasing optical frequency, but the change is large only at frequencies comparable to the metal's plasma frequency. Since Pt's plasma frequency[82] $\sim$40 000 cm^{-1}, static and ir E fields are expected to be screened about the same. However, recent Stark tuning rate and ir intensity measurements[1] for CO on Pt(111) provide additional evidence for a difference in the response to static and ir local fields.

The disagreement between observation and the estimated static screening could be due to an oversimplified model of the Pt surface. Jellium does not accurately represent[83] a d-band metal-like Pt. The presence of steps further complicates the situation. Self-consistent calculations[84-86] of the screened E field at the Al(001), Ag(001), and Ag(110) surfaces have found a strong dependence of screening on lateral position—an effect not calculable in jellium models. However, there is no known theoretical basis for a radical difference between the static and ir fields at the CO adsorption site on Pt.

The models we have discussed assume that the adsorbate-field interaction is purely dipolar. This assumption is standard in the analysis of ir reflection absorption spectra, but it omits other interactions that can also be important. At a metal surface the electric field varies strongly over atomic dimensions. In this situation the field gradient can be so large that its interaction with the molecular quadrupole moment is comparable to the dipole interaction.[87-90] The quadrupole interaction has been discussed in connection with surface-enhanced Raman scattering[91-93] and second harmonic generation.[89,94-96]

At a Pt surface the screened E field and its derivatives vary strongly within a CO adsorption site. For example, in a jellium model[1,97] for atop CO on Pt(111) the C atom is 0.15 Å $inside$ the image plane, while the O atom is 0.98 Å $outside$ the image plane. The applied E field is screened by a factor of approximately 0.5 at the C site, but 0.8 at the O site. With such strong spatial variation, the $\mathbf{p} \cdot \mathbf{E}$ interaction energy depends strongly upon where the E field is evaluated. The vibrational Stark effect is likewise proportional to local E field so the predicted (but not the actual) Stark tuning rate depends upon where E is evaluated. In the same level of approximation, the predicted ir absorption also depends upon where E is evaluated.

The large difference observed between the Stark shift of CO at edge and terrace sites on Pt(335)—even though the local E field at the center of the C–O bond is expected to vary less—could be a consequence of the strong positional dependence of the E field near the Pt surface. It is conceivable that CO's ir absorption is affected differently by the E field's positional dependence, and this might explain why the same ir cross section is observed for CO at edge and terrace sites. It is unclear, however, how such an explanation could account for the observed difference between the Stark shift in vacuum of terrace CO on Pt(335) and that of CO on Pt(111) (see Table I).

VI. SUMMARY

The results presented here form part of a growing body of evidence that there is a significant difference in an adsorbate's response to electrostatic and ir fields at metal surfaces. The Stark effect measurements[11] of Lambert and Tobin clearly showed a large difference between the tuning rates of edge atop and terrace atop CO on Pt(335). By themselves, however, those measurements could not determine whether the difference arose from different molecular properties (a chemical effect) or from different electrostatic screening (a physical effect). The present work shows that a difference in molecular properties is at most a small part of the effect. We suggest that *strong spatial variation of the electric field* is responsible. One possibility is strong screening of the static (but not ir) field at terrace sites; another is that the quadrupole interaction is important.

The present work also demonstrates that measurements of overtone intensity vs coverage can be used to learn about chemical changes in adsorbed molecules. The combination of Stark effect and overtone intensity measurements is particularly powerful, since the overtone intensity strongly constrains the intrinsic Stark tuning rate. The quantitative interpretation of EELS overtone intensities faces considerable obstacles, however, most importantly that of determining the double loss contribution.

ACKNOWLEDGMENTS

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