

Observation of the First-Order Stark Effect of Co on Ni(110)

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The first-order Stark effect is observed for CO adsorbed on Ni(110). The Stark tuning rate is $(1.1 \pm 0.4) \times 10^{-6} \text{ cm}^{-1}/(\text{V}/\text{cm})$. The present measurement agrees with a model calculation. By electric field modulation of the resonant vibrational frequency of adsorbed molecules, the derivative vibrational spectrum can be measured. The spectra of CO on Ni(110) obtained are consistent with published electron-energy-loss spectra. The new technique is zero background, surface selective, and can be used in UHV or atmospheric pressure.

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Vibrational spectra of molecules adsorbed on surfaces are an important source of chemical information about the adsorbed species. I have demonstrated a new infrared technique for obtaining such spectra, which I call electroreflectance vibrational spectroscopy (EVS). Spectra are obtained by applying a large ac electric field to the surface and measuring the synchronous modulation of reflectivity, as the optical frequency is tuned through the vibrational absorption of the molecules. The observed spectra are due to the first-order Stark effect of CO adsorbed on Ni(110). This is the first measurement of the change in vibrational frequency of adsorbed molecules caused by an applied electric field. Therefore, in addition to providing a potentially useful new tool for surface studies, EVS also involves new physics.

Many techniques for measuring the vibrational spectra of adsorbed molecules have been reported. These include electron-energy-loss spectroscopy (EELS),¹ a number of infrared techniques,² Raman spectroscopy,³ and several nonlinear optical techniques.⁴ The EVS technique described here is operationally similar to another recently reported electroreflectance technique in which the potential across the dipole layer at a solid to electrolyte interface is modulated.⁵ The physical process giving rise to a signal in that case is believed to be a change in the electrochemical state of the surface.

Some of the characteristics that make EVS attractive are surface selectivity, the ability to study surfaces in UHV conditions or exposed to gas at atmospheric pressure, extremely high resolution, and good sensitivity—especially to fine structure since it is a derivative technique. An important characteristic of EVS is that it is a zero-background measurement.

Adsorbed molecules are oriented relative to

the surface normal. As a consequence of the loss of full rotational symmetry, the vibrational absorption of an infrared-active adsorbed molecule is predicted⁶ to exhibit a first-order Stark effect with applied electric field. Gas-phase molecules, on the other hand, exhibit only a second-order Stark effect except in special cases of degeneracy.⁷ To estimate the first-order Stark tuning rate we consider the classical model of diatomic molecule adsorbed along the normal of a rigid surface. I make the simplifying assumptions that the electric field acting on the molecule is uniform and that the molecule does not interact with the surface. Let $U(x)$ and $M(x)$ be the potential function and dipole moment function, respectively, in terms of the relative coordinate x . The Hamiltonian of the vibrating molecule is

$$H = p^2/2\mu + U - \vec{M} \cdot \vec{E}. \quad (1)$$

Here μ is the reduced mass of the molecule. We expand $U(x)$ and $M(x)$ as power series in x :

$$\begin{aligned} U(x) &= U_0 + a_1 x^2 + a_2 x^3 + \dots, \\ M(x) &= M_0 + M_1 x + M_2 x^2 + \dots \end{aligned} \quad (2)$$

Solving for the change in vibration frequency ω as a function of E one finds

$$d\omega/dE = \omega(\frac{3}{2}M_1a_2 - a_1M_2)/a_1^2. \quad (3)$$

The quantities a_1 , a_2 , M_1 , and M_2 are available from the literature for a number of gas-phase molecules.⁶ In particular, for CO a Stark tuning rate of $8.6 \times 10^{-7} \text{ cm}^{-1}/(\text{V}/\text{cm})$ is found.

Given the Stark tuning rate, the excess absorption $A(\nu)$ of the surface caused by the presence of adsorbed molecules, and the applied electric field ΔE , then the EVS signal $S(\nu)$ is

$$S(\nu) = \frac{dA}{d\omega} \frac{d\omega}{dE} \Delta E. \quad (4)$$

Hence, in this simplified model, the EVS signal

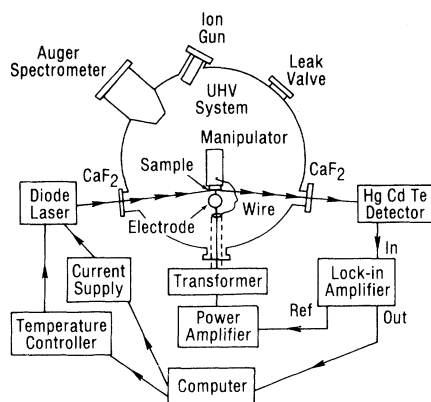


FIG. 1. Block diagram of measurement system.

should be proportional to the derivative of the infrared absorption spectra. In the real case, $d\omega/dE$ is expected to vary with adsorption site, as does ω , and so $S(\nu)$ and $A(\nu)$ are no longer exactly related by Eq. (4).

The measurements were carried out using the system shown in Fig. 1. The optical source was a stripe-geometry double-heterostructure diode laser grown by molecular-beam epitaxy on a PbTe substrate with $\text{Pb}_{0.9985}\text{Eu}_{0.0015}\text{Te}_{0.0019}\text{Se}_{0.9981}$ active region, tuned by laser current and heat-sink temperature. The laser was stepped through a set of predetermined operating conditions, temperature between 70 and 100 K, that resulted in single-mode output. The power at the detector ranged between 19 and 81 μW . The rms intensity noise at 100 kHz, normalized by intensity, ranged between 4.0×10^{-8} and $1.5 \times 10^{-7} \text{ Hz}^{-1/2}$. Light from the laser was focused at an 84.5° angle of incidence on the sample and was polarized with electric field in the plane of incidence. The reflected light was focused onto a photoconductive HgCdTe infrared detector having sufficient area to avoid saturation for the laser intensities used.

The Ni(110) crystal was mounted on a manipulator in a UHV system with 4×10^{-10} Torr base pressure. Cycles of ion bombardment, oxygen dosing, and heating to 800 $^\circ\text{C}$ were used to prepare a clean surface as measured *in situ* by an Auger spectrometer. During EVS measurements the $7.2 \times 11\text{-mm}^2$ sample was positioned 0.4 mm away from a 9.5-mm-diam spherical electrode to which $2.4 \times 10^3 \text{ V}_{\text{rms}}$ at 100 kHz was applied.

Spectra were taken by integrating the electroreflectance signal for 4.5 sec at each point. The lasing frequency and intensity were also measured. The measurement system will be described in greater detail in a later publication.

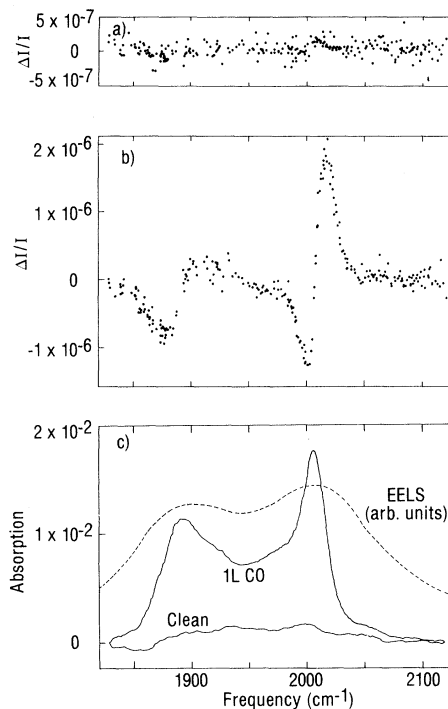


FIG. 2. EVS spectra of (a) clean Ni(110) surface at 300 K and (b) same surface dosed with 1 L of CO. Also, (c) comparison of the CO infrared absorption obtained by integrating the EVS spectra with a portion of an EELS spectra of Ni(110) dosed with 0.9 L of CO at 300 K from Ref. 12. A linear baseline of $-1.53 \times 10^{-5} \text{ cm}$ for the clean surface and $1.91 \times 10^{-5} \text{ cm}$ for the CO-dosed surface have been subtracted from the integrated EVS spectrum.

An example of the spectra obtained for a clean Ni(110) surface at 300 K and the same surface dosed with 1 L [1 L (langmuir) = 10^{-6} Torr sec] of CO are shown in Fig. 2. The normalized EVS signal plotted, $\Delta I/I$, is the rms signal voltage divided by the detector voltage corresponding to the laser intensity. The rms electric field at the sample surface for these spectra was $6.0^{+2.0}_{-1.2} \times 10^4 \text{ V/cm}$. The EVS signal was verified to be linear in the applied voltage to better than 2%.

An Auger spectrum of the Ni surface taken shortly before the EVS spectra showed only S impurity above the noise. With use of a 2-keV primary electron beam at normal incidence the ratio of the derivative 152-eV S peak to the derivative 848-eV Ni peak was 0.23. On the basis of the relative cross section⁸ of S and Ni at 3 keV, the fraction of S in the sampling volume is estimated to be 8%. Subsequent studies showed that increasing the ratio of the S to Ni Auger peaks from 0.70 to 1.21 was correlated with a 6-cm^{-1}

increase in the upper-frequency peak in the integrated EVS spectra.

The Ni(110)-CO system has been studied with use of many different techniques. These include infrared spectroscopy,^{9,10} low-energy electron diffraction,¹¹ EELS,¹²⁻¹⁵ and photoemission.¹⁴ In Fig. 2(c), I have plotted the infrared absorption calculated by integrating the EVS spectra, as indicated by Eq. (4), using the calculated Stark tuning rate. I also plot a portion of an EELS spectra from Ref. 12 in which Ni(110) at 300 K was dosed with 0.9 L of CO. The integrated EVS spectrum of the Ni(110) surface dosed with 1 L of CO at 300 K shows two peaks, at 1894.4 and 2006.4 cm^{-1} . In comparison, EELS spectra taken under the same conditions with much lower resolution also show two peaks—one variously estimated at 1904 to 1910 cm^{-1} , the other at 2010 to 2016 cm^{-1} . An infrared spectrum taken under the same conditions is shown in Ref. 9. Two peaks are also seen in that case, at 1925 cm^{-1} and 2111 cm^{-1} . The infrared spectra were taken in a diffusion-pumped vacuum system that did not include an Auger spectrometer.¹⁰ It is quite possible that sufficient C and S impurities would be present on the surface under these conditions to cause the observed difference in vibrational frequency from the EVS and EELS measurements. Infrared spectra reported subsequently by the same group under similar conditions,¹⁰ when presumably more effort was taken to clean the surface, did show lower vibrational frequencies for the peaks.

The Stark tuning rate is obtained by comparing the integrated infrared absorption from Fig. 2(c), $1.50 \pm 0.38 \text{ cm}^{-1}$ at 84.5° , with that from Fig. 14 of Ref. 9, 0.77 cm^{-1} at 80° . The infrared absorption of CO on Ni at 80° is a factor¹⁶ 0.66 times that at 84.5° . The resulting Stark tuning rate for CO on Ni(110) is $1.1 \times 10^{-6} \text{ cm}^{-1}/(\text{V}/\text{cm})$. The errors are mainly systematic resulting from uncertainty in the electrode-to-sample spacing and differences between the present surface and that studied in Ref. 9. Estimating the integrated infrared absorption obtained from Ref. 9 to be accurate to 30%, the uncertainty in the Stark tuning rate is $\pm 4.0 \times 10^{-7} \text{ cm}^{-1}/(\text{V}/\text{cm})$.

The agreement observed between the present measurement and the model calculation comes in spite of oversimplifications in the model. The assumption that the gas-phase curves of $M(x)$ and $U(x)$ are unchanged for the adsorbed molecule is known to be inaccurate. For CO adsorbed on metals it is generally observed¹⁷ that M_1 increases with respect to the gas phase by about a factor 2.

The integrated infrared absorption from Ref. 9 implies an increase by a factor 2.2 in our case. Significant changes in a_2 and M_2 can be expected as well. The model also ignores surface-state electrostatic screening. With use of the screening charge distribution¹⁸ of Lang and Kohn, together with the bond lengths of CO on metals discussed¹⁹ by Efrima and Metiu, the electric field reduction is estimated to be in the 9% to 18% range. A full quantum-mechanical calculation is needed to elucidate these effects further.

In summary, I have observed the first-order Stark effect of CO on Ni(110) at 300 K. The measured Stark tuning rate, $(1.1 \pm 0.4) \times 10^{-6} \text{ cm}^{-1}/(\text{V}/\text{cm})$, agrees with a model calculation. The Stark effect can be used to obtain derivative vibrational spectra of adsorbed molecules with use of a tunable laser. This new technique, EVS, is surface selective, zero background, offers resolution limited only by the sampling interval, and can be used either in UHV or atmospheric pressure.

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¹H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982).

²M. L. Hair, *Infrared Spectroscopy in Surface Chemistry* (Dekker, New York, 1967); N. J. Harrick, *Internal Reflection Spectroscopy* (Interscience, New York, 1967); R. B. Bailey, T. Iri, and P. L. Richards, *Surf. Sci.* **100**, 626 (1980); J. Pritchard, T. Catterick, and R. K. Gupta, *Surf. Sci.* **53**, 1 (1975); M. J. Dignam and J. D. Fedyk, *Appl. Spectrosc. Rev.* **14**, 249 (1978); Y. J. Chabal and A. J. Sievers, *Phys. Rev. Lett.* **44**, 944 (1980); F. Trager, H. Coufal, and T. J. Chuang, *Phys. Rev. Lett.* **49**, 1720 (1982); S. Chiang, R. G. Tobin, and P. L. Richards, *J. Electron. Spectrosc.* **29**, 113 (1983).

³*Surface Enhanced Raman Scattering*, edited by R. K. Chang and T. E. Furtak (Plenum, New York, 1981).

⁴B. F. Levin, C. V. Shank, and J. P. Heritage, *IEEE J. Quantum Electron.* **15**, 1418 (1979); C. K. Chen, A. R. DeCastro, Y. R. Shen, and F. DeMartin, *Phys. Rev. Lett.* **43**, 946 (1979); C. K. Chen, T. F. Heinz, D. Ricard, and Y. R. Shen, *Phys. Rev. Lett.* **46**, 1010 (1981); G. L. Eesley, *IEEE J. Quantum Electron.* **17**, 1285 (1981).

⁵A. Bewick, K. Kunimatsu, J. Robinson, and J. W. Russell, *J. Electroanal. Chem.* **119**, 175 (1981).

⁶D. K. Lambert, *J. Electron. Spectrosc.* **30**, 59 (1983).

- ⁷C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (Dover, New York, 1975), pp. 248-255.
- ⁸L. E. Davis, N. C. MacDonald, P. W. Palmberg, G. E. Riach, and R. E. Weber, *Handbook of Auger Electron Spectroscopy* (Physical Electronics, Eden Prairie, 1978).
- ⁹J. D. Fedyk, P. Mahaffy, and M. J. Dignam, *Surf. Sci.* 89, 404 (1979).
- ¹⁰P. R. Mahaffy and M. J. Dignam, *Surf. Sci.* 97, 377 (1980).
- ¹¹H. H. Madden, J. Kuppers, and G. Ertl, *J. Chem. Phys.* 58, 3401 (1973); T. N. Taylor and P. J. Estrup, *J. Vac. Sci. Technol.* 10, 26 (1973).
- ¹²J. C. Bertolini and B. Tardy, *Surf. Sci.* 102, 131 (1981).
- ¹³N. Nishijima, S. Masuda, Y. Sakisaka, and M. Onchi, *Surf. Sci.* 107, 31 (1981).
- ¹⁴K. Horn, J. DiNardo, W. Eberhardt, H.-H. Freund, and E. W. Plummer, *Surf. Sci.* 118, 465 (1982).
- ¹⁵B. J. Bandy, M. A. Chesters, P. Hollins, J. Pritchard, and N. Sheppard, *J. Mol. Spectrosc.* 80, 203 (1982).
- ¹⁶R. B. Bailey, Ph.D. thesis, University of California, Lawrence Berkeley Laboratory Report No. LBL-8482, 1978 (unpublished), p. 24.
- ¹⁷B. N. J. Persson and R. Ryberg, *Phys. Rev. B* 24, 6954 (1981).
- ¹⁸N. D. Lang and W. Kohn, *Phys. Rev. B* 7, 3541 (1973).
- ¹⁹S. Efrima and H. Metiu, *Surf. Sci.* 92, 433 (1980).