Orientation of Chemisorbed Molecules from Surface-Absorption Fine-Structure Measurements: CO and NO on Ni(100)

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(Received 19 March 1981)

Surface-absorption fine-structure studies for CO and NO on Ni(100) exhibit two pronounced resonances above the C, N, and O K edges. A strong polarization dependence of these resonances, which correspond to a $\sigma \rightarrow \pi$ discrete absorption and a $\sigma \rightarrow \sigma$ shape resonance, allows the precise determination of molecular orientation. Both molecules are found to be aligned along the surface normal within 10°.

PACS numbers: 78.70.Dm, 68.20. +t

Following the theoretical work of Dehmer and Dill[1] and Davenport,[2] molecular orientation on surfaces has been widely studied by polarization-dependent angle-resolved photoemission.[3-5] Other experiments involved electron energy loss,[6] low-energy electron diffraction[7] (LEED), and photoelectron diffraction.[8] Here we present a new experimental approach which allows accurate determination of molecular orientation by simply measuring the *polarization-dependent photoabsorption* near a core level threshold. Such surface-absorption fine-structure (SAFS) measurements offer significant simplifications in data acquisition and interpretation since they depend solely on the orientation of the x-ray polarization vector with respect to the sample. The purpose of the present paper is to establish SAFS as a new powerful technique for the study of molecular orientation on surfaces and to determine the previously unknown orientation of molecular NO on Ni(100).

Previous photoemission studies have established the existence of a σ shape resonance for CO on Ni (Refs. 4 and 5) and Cu.[9] Our data show for the first time the existence of a second pronounced resonance close to threshold for both CO and NO on Ni(100). This resonance is identified as originating from a discrete $\sigma \rightarrow \pi$ bound-state transition. In fact it is the narrow width and intensity of this resonance which provides an enhanced sensitivity for the molecular orientation on the surface. Since bound-state resonances generally exist for molecules, SAFS measurements should allow structural studies of many molecular chemisorption systems.

Experiments were performed with use of the grasshopper monochromator (1200 l/mm holographic grating) on beam line I-1 at the Stanford Synchrotron Radiation Laboratory. The Ni(100) single crystal was cleaned by Ar^+ bombardment to remove S and by oxygen treatment to remove C and checked by LEED and Auger measurements. Experiments were performed in the temperature range 80–300 K for CO and at 80 K for NO at saturation ($\sim \frac{1}{2}$ monolayer) coverage, respectively (the base pressure was 2×10^{-10} Torr). The sample was rotatable about a vertical axis. The x rays were incident at an angle θ from the crystal surface (Fig. 1) with the $\vec{E}$ vector in the horizontal plane, parallel to the axis of the cylindrical mirror analyzer (CMA). The flux-normalized[10] absorption spectra were recorded by angle-integrated Auger partial-yield spectroscopy[11] with the energy window of the CMA set on the C (264 eV), N (379 eV), or O (509 eV) Auger lines. This allowed measurement of the fine structures up to ~ 40 eV above the K edges without interference of substrate and adsorbate photoemission peaks.[11]

Figure 1 shows the polarization-dependent absorption fine structure near the C K edge for CO on Ni(100). The spectra were temperature independent in the range 80–300 K. At normal incidence ($\theta = 90°$) a large absorption peak A around 287.5 eV is observed which dominates over the absorption at higher energies. As the sample is rotated to grazing incidence angles (i.e., as the $\vec{E}$ vector approaches the sample normal) peak A decreases in intensity and another peak B emerges around $h\nu = 303.5$ eV. At $\theta = 10°$ the SAFS spectrum is dominated by this peak and peak A has almost vanished. The SAFS spectra for NO above the N K edge in Fig. 2 show very similar behavior. The spectra were recorded at 80 K to avoid molecular dissociation. Here peak A falls at 401.5 eV and peak B at 414.5 eV. Spectra recorded above the O K edge for both molecules exhibited the same resonances and polarization dependence as for the respective C and N K edges.

Peak B is readily assigned to be the previously found[4,5,12,13] σ shape resonance. The opposite polarization dependence identifies peak A as

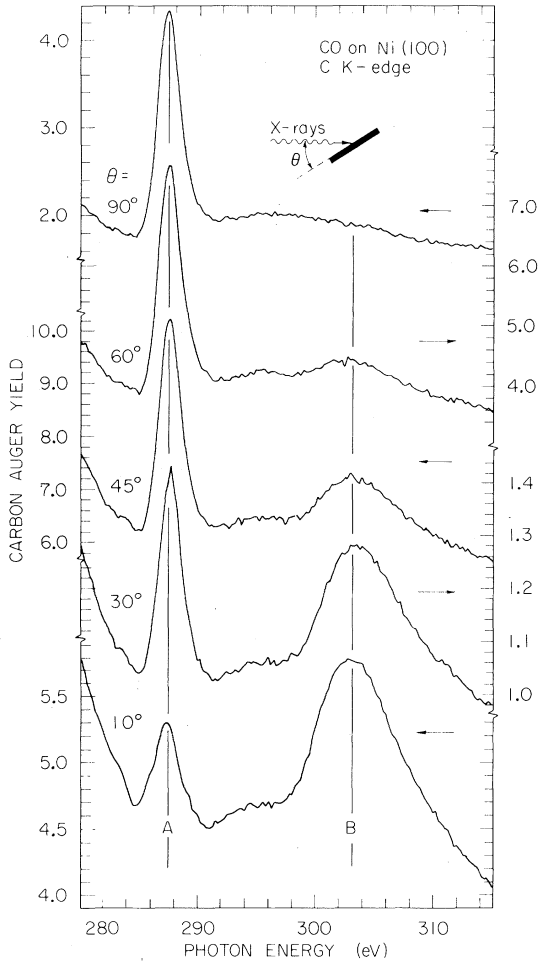

FIG. 1. SAFS spectra above the C K edge for CO on Ni(100) at $T = 180$ K as a function of incidence angle θ.

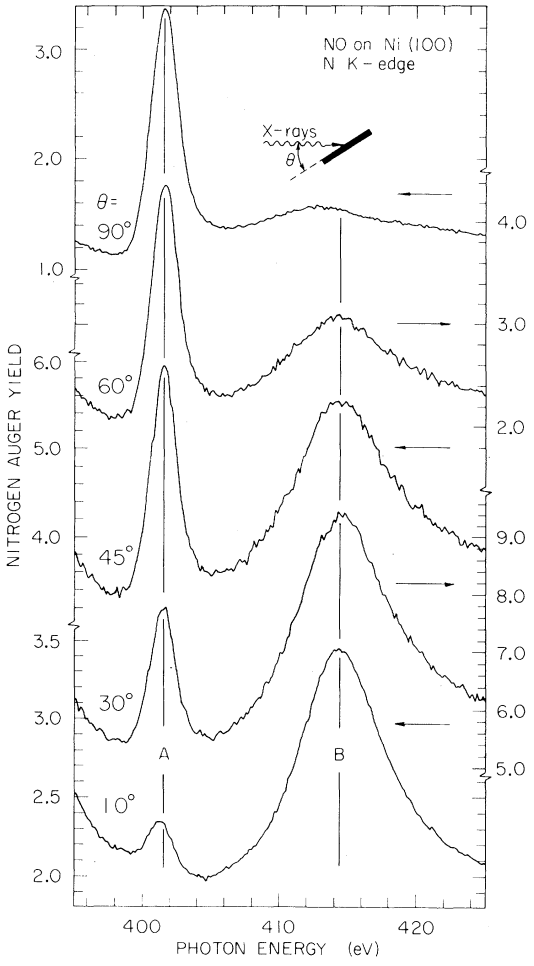

FIG. 2. SAFS spectra above the N K edge for NO on Ni(100) at $T = 80$ K as a function of θ.

originating from transitions to π-type final states. This assigment is in good accord with gas-phase measurements[12] and calculations.[13] As seen from Fig. 1, peak A lies below the continuum K-shell ionization threshold which for CO falls at ~292 eV. This fact and its narrow linewidth indicate that in both cases peak A corresponds to a bound-state transition. This is why it cannot be observed by photoemission.

For oriented molecules with cylindrical symmetry and for linearly polarized light the absorption cross section μ assumes the simple form[14]

$$\mu(\gamma) \sim 1 + \tfrac{1}{2}\beta(3\cos^2\gamma - 1). \quad (1)$$

Here γ is the angle between the $\vec{E}$ vector and the symmetry axis $\vec{M}$ of the molecule. For $s(\sigma)$ initial and pure σ and π final states the molecular asymmetry parameter[14] is $\beta = 2$ and $\beta = -1$, respectively, and Eq. (1) assumes the simple forms $\mu_\sigma \sim \cos^2\gamma$ and $\mu_\pi \sim \sin^2\gamma$. Thus for a molecule oriented along the surface normal the σ (π) resonance should have a maximum for $\gamma = 0°$ (90°) as observed for both CO and NO on Ni(100).

In order to obtain quantitative information we have analyzed the angular dependence of the π resonance intensities in detail. In both cases the areas of peaks A were determined for several experimental runs and normalized to the incident photon flux and to the CMA acceptance as measured by the count rate just before the K edges. Because of a small residual elliptical component of the polarization[15] the intensity of peak A does not vanish completely for $\theta \to 0°$ but remains finite below $\theta \approx 10°$, in both cases. Since for our experimental geometry the small vertical $\vec{E}$ vector component was constant for all incidence angles θ the CO and NO peak intensities were corrected in an identical fashion by subtracting a

small correction from all measured peak-A intensities. This was done after the CO and NO intensities had been normalized with respect to each other at the "magic angle" $\theta = 54.7°$ (see below).

Figure 3 compares the so-obtained experimental peak-A intensities to theoretical calculations which were carried out as a function of a molecular tilt angle α from the surface normal. We assumed a cylindrically symmetric tilt with limits $\alpha_1 = \alpha - 2°$ and $\alpha_2 = \alpha + 2°$. For the magic angle $\theta = 54.7°$ ($\alpha = 54.7°$) the peak intensity is independent of α (θ). This, in retrospect, justifies normalization of the CO and NO data at this angle. In both cases best agreement is obtained for molecular orientation along the sample normal ($\alpha = 0°$). A tilt angle of $\alpha = 15°$ already leads to a significantly worse fit. For both CO and NO on Ni(100) our data imply that the molecular axis $\vec{M}$ is oriented along the sample normal with an experimental uncertainty of 10°.

The orientation of CO on Ni(100) deduced from our SAFS data is in excellent agreement with previous experimental results.[3-8] The sensitivity of our data to the molecular orientation of CO is as good as that of the most precise published measurements.[4,5] The results for CO also provide the basis for the determination of the orientation of NO on Ni(100). Previous studies on this system were inconclusive or supportive of tilted molecular orientation.[16] Our results of an upright NO orientation on Ni(100) are also in contrast to studies of NO on Pt(100),[17] Pt(111),[18] and Ir(111),[19] which gave evidence for a bent NO configuration. Finally we mention that besides yielding quantitative information on molecular orientation SAFS can also be used to distinguish *molecular* from *atomic* (dissociative) chemisorption since the absorption-edge fine structure is distinctively different.[10,11,20]

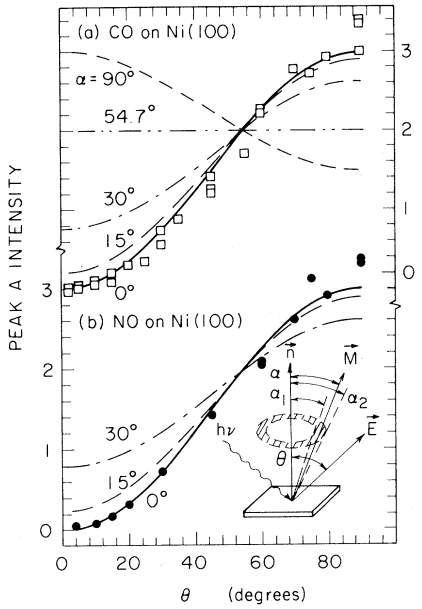

FIG. 3. (a) Experimental peak-A intensity for CO on Ni(100) as a function of θ (squares). Lines are calculated intensity variations with θ as a function of a molecular tilt angle α as shown in (b). (b) Same as in (a) for NO on Ni(100) (circles). Note that θ is the angle of incidence from the surface as well as the angle between the sample normal and $\vec{E}$.

All of the materials incorporated in this work were developed at the Stanford Synchrotron Radiation Laboratory, which is supported by the National Science Foundation (under Contract No. DMR-77-27489), in cooperation with Stanford Linear Accelerator Center and the U. S. Department of Energy. One of us (R.J.) acknowledges the Eastman Kodak Company and the Deutsche Forschungsgemeinschaft for supporting his work at SSRL and one of us (R.T.) would like to thank D. Menzel for enabling his stay at SSRL. This work was also supported in part by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 161) and Bundesministerium für Forschung und Technologie.

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Energy Barrier against Self-Trapping of the Hole in Silver Chloride

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We report the first observation of an energy barrier in the transition of a metastable free hole to the self-trapped state. The lifetime of the free hole was monitored by using electron paramagnetic resonance to measure the competition between self-trapping and trapping at such substitutional ions as Cu^+. Over the range 4.5 to 30 K, the lifetime against self-trapping decreases with increasing temperature, with an activation energy of 1.7 meV.

PACS numbers: 71.38.+i, 71.50.+t, 76.30.-v

In silver chloride (but, interestingly, not silver bromide), the stable state of the valence-band hole below liquid-nitrogen temperature is not that of a free, Bloch-type wave; rather, the hole becomes self-trapped.[1] In contrast to the case of the alkali halides, in which the self-trapped hole is shared between a neighboring pair of anions, here the top of the valence band contains a substantial admixture of silver *d* states, and the localized hole is centered on the cation. Jahn-Teller distortion about the resulting Ag^{2+} ion gives an elongated center with ⟨100⟩ tetragonal symmetry.

Toyozawa[2] has pointed out that, if the coupling of the hole to the lattice deformation potential is not too strong, then there should be a significant energy barrier in the transition from the metastable free state to the stable self-trapped state. Essentially, in order to prepare the site of the trap, one must first spend energy of local elastic deformation before reaping the profit of electrostatic potential energy, when the hole becomes localized. This short-range elastic deformation derives primarily from short-wavelength acoustical lattice modes, so that an energy barrier of the order of meV would not be unreasonable. Moreover, this model makes the interesting prediction that the self-trapping transition should become more difficult as the temperature is decreased, in contrast to the usual situation in which trapping occurs more readily the lower the temperature.

This Letter reports the first observation of such an energy barrier against trapping. We have not attempted to measure directly the lifetime against self-trapping of the free hole; instead, we provide the hole with an alternative trapping channel, in the form of several tens of parts per million (ppm) of a solute ion that acts as a deep trap. The fraction of the originally free holes that reach these fixed impurity traps is then a measure of the lifetime against self-trapping. From a study of the effect of temperature, over the range 4.5 to 30 K, on the competition between these two trapping processes, the existence and the magnitude of the energy barrier have been deduced.

Most of the experiments were performed on a single crystal of AgCl, from a boule grown in our department, prepared in the form of a rec-