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Optical Spectroscopy of Aromatic Hydrocarbons on the Ni(111) Surface.

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The importance of developing new techniques for studying molecular structure and chemical reactions on metal surfaces need hardly be emphasized. To date, however, there has been virtually no UV-visible optical spectroscopy reported for molecules adsorbed on single crystal surfaces. Presumably this has been due in part to the apparent lack of sensitivity of conventional techniques.

In this letter we wish to report on the application of spectroscopic ellipsometry\(^1\) for obtaining the optical spectrum of mono and multilayer molecular overlayers of aromatic hydrocarbons on single crystal nickel surfaces at low temperatures. Although we have studied a variety of hydrocarbons on nickel surfaces, only the results of pyrazine on nickel
will be reported in this preliminary communication. In particular, we have been able to observe most of the salient features of the $1_{\pi\pi}^*$ and $1_{n\pi}^*$ regions of physisorbed pyrazine condensed on nickel(111) at temperatures below 50°K. The analysis of the spectrum gives the electronic excited state energy levels, the vibrational frequencies in the excited states and semiquantitative information about the molecular geometry of the molecules at the surface. To the best of our knowledge, this represents the first optical spectroscopy study of molecules on single crystal metal surfaces.

Nickel single crystals (MRC, typical 99.9%) were oriented to within 2° of the (111) face by Laue back reflection and mechanically polished through 0.05 micron alumina. The crystal was mounted on a variable temperature (10-300°K) cold tip which was modified for UHV use and the crystal was held in a stainless steel UHV chamber with base pressure less than $1 \times 10^{-10}$ torr. The metal surface was cleaned by electron bombardment, heating in oxygen, hydrogen, or by argon ion sputtering and subsequently annealed. Surface cleanliness and order were checked by Auger Spectroscopy and LEED, respectively. The details of the instrumentation and the data reduction procedure will be reported later.²

Pyrazine was deposited on a clean well oriented nickel-(111) surface at 10°K. Fig. 1 shows the near UV spectra (10Å resolution) at 10°K of a monolayer (3Å thick) and multilayer (11Å thick) overlayer of pyrazine adsorbed on Ni(111).
The low temperature deposition of pyrazine on nickel prevents reaction with the nickel surface and allows the multilayer condensation of pyrazine. The monolayer spectrum, while noisy, shows the same principle features as the thicker layers. The absorbance and index of refraction (not shown) of the pyrazine overlayer are calculated from the difference in ellipsometric parameters for the pyrazine-covered and clean nickel substrates. The adlayer thickness is obtained from the ellipsometric parameters assuming overlayer transparency at 3500Å. The pyrazine overlayer can be annealed by raising the temperature to 120°K for a period of time after the deposition. This causes the adlayer to contract slightly (10%) and causes intensity changes in the spectrum and the appearance of resolved vibronic structure around 3200Å as shown in Fig. 2. This structure is not observed in the unannealed layer.

The pyrazine spectrum on Nickel is qualitatively similar to that of pure pyrazine. In the pure molecular phase at 4.2°K, pyrazine has two well resolved transitions in the singlet region. The first is a singlet nπ* transition which occurs at 30,350 cm⁻¹ and the second is a singlet ππ* transition which occurs at 36,850 cm⁻¹. The singlet nπ* is appreciably weaker than the ππ* transition and has its transition dipole moment polarized perpendicular to the ππ* orbitals; consequently it is aligned in a direction normal to the aromatic ring. On nickel, the ¹nπ* state electronic origin
is at 30,057 cm\(^{-1}\) and while the \(1\pi\pi^*\) origin is at 37,400 cm\(^{-1}\); thus, the Nickel(111) surface induces about a 300 and 500 cm\(^{-1}\) shift in the \(1\pi\pi^*\) and \(1\pi\pi^*\) transitions, respectively. On this basis, we identify the absorbing species as physisorbed or condensed pyrazine, rather than chemisorbed or dissociated products.

The resolved structure obtained by annealing (Cf. Fig. 2) appears to be a vibrational progression in the \(\nu_6\) totally symmetric ring stretching mode. This is also the principle feature of the \(1\pi\pi^*\) transition in the pure pyrazine absorption spectrum.\(^3\) For adlayer thicknesses ranging from 4 to 30\(\AA\), the observed splitting between the maxima of origin and first vibronic peak is 525 ± 25 cm\(^{-1}\). This is significantly outside the range of 600-580 cm\(^{-1}\) measured for pyrazine in a wide variety of molecular environments, including the gas phase,\(^4\) single crystal,\(^3\) solid and liquid solutions. The lower frequency suggests that the local environment for the annealed pyrazine molecules on nickel, through direct or indirect interaction with the surface, is significantly altered from that in the gas phase or solid bulk phases.

Information about molecular geometry and local environment of pyrazine on nickel can be deduced from changes in the optical transition intensity as a function of annealing. This is so because the \(1\pi\pi^*\) transition dipole moment is polarized along the nitrogen-nitrogen (N-N) axis while the \(1\pi\pi^*\) transition dipole moment is polarized out of the automatic
plane and transition dipole moments oriented parallel or perpendicular to the nickel surface induce different phase shifts in the reflected electric field. At 3000 Å the reflectivity of nickel is about ~ 0.3 and thus intensity of a 3000 Å transition polarized parallel to the (111) surface will be attenuated by a factor of 3.3 with respect to a transition normal to the surface. The annealing process increases the absorbance of the $^1\pi\pi^*$ transition as shown in Fig. 3, while the intensity of the $^1\pi\pi^*$ transition remains constant. Assuming an amorphous distribution of molecular orientations in the initially deposited layer at 10 K, a uniform reorientation upon annealing to give the N-N axis normal to the surface, as proposed for chemisorbed pyridine on Pt(111) and polycrystalline nickel would triple the $^1\pi\pi^*$ absorbance and almost eliminate the $^1\pi\pi^*$ transition.

If the plane of the ring were allowed to tip approximately thirty-five degrees from the surface normal (cf. Fig. 4) so that both N-N and out-of-plane polarizations had perpendicular components, the $^1\pi\pi^*$ absorbance would double and the $^1\pi\pi^*$ transition would remain constant, as observed experimentally. Absorbance changes upon overlayer contraction, the imperfect reflectivity of nickel, and difficulty in accurately measuring the total integrated intensity of each transition preclude a more precise determination of molecular geometry.

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References


2. A. R. Gallo and C. B. Harris, unpublished results.


Figure Captions

Figure 1. Absorbance spectra of 3Å (~1 monolayer) and 11Å overlayers of pyrazine on Ni(111) surface at 10K showing \( \pi^* \) and \( n\pi^* \) transitions. Absorbance, \( k \), is related to the molar extinction coefficient, \( \varepsilon \), by \( k = \ln(10) \frac{\varepsilon c \lambda}{4\pi} \) where \( c \) is concentration in moles/liter and \( \lambda \) is in decimeters. The left hand scale refers to the 11Å data; the inset scale to the 3Å data. A heavy line is drawn through the noise in the 3Å data to show the principle feature of these results.

Figure 2. Absorbance spectrum of 9Å overlayer of pyrazine on Ni(111) surface at 10K showing \( n\pi^* \) transition.

Figure 3. Absorbance spectra of \( 1\pi^* \) (top) and \( 1\pi\pi^* \) (bottom) transitions of ~8Å pyrazine overlayers on Ni(111) at 10K. Left hand spectra show unannealed overlayers and right hand spectra show overlayers after annealing at 120K.

Figure 4. Proposed surface geometry of annealed pyrazine molecules on the Ni(111) surface below 160K. Angles shown are between plane of molecule and surface.
Figure 1
Figure 2

Pyrazine - Ni(III)
9 Å

$510 \text{ cm}^{-1}$

$380 \text{ cm}^{-1}$
Figure 3
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