

A Fundamental Study of Catalysts Using Laser Raman, Infrared,
Auger Electron Spectroscopy and Low Energy Electron Diffraction

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Research Scope and Objectives

The fundamental goal of this project is to further understanding of catalytic activity and selectivity with the long-range goal of producing better catalysts. Surface laser Raman spectroscopy (non-enhanced) is used along with thermal desorption to study surface structure and bonding of CO and O₂ on Ni(111) and Ni(100) single crystals, beginning at low coverage. Surface structure and bonding are studied as functions of pressure and temperature. The surface coverage is controlled by varying the gas pressure and exposure time.

Description of Research Effort

Surface Raman spectroscopy is used to study CO and O₂ adsorbed on Ni(111) at or near room temperature. Without signal recovery techniques, we have observed Raman-active modes of CO (low polarizability) on a non-enhancing surface (Ni) at exposures less than 100L. This is a significant development in the use of Raman to study adsorbed molecular species on transition metal surfaces. With a dark count of 1-2 cps from a cooled photomultiplier, at 100L exposure CO on Ni(111) Raman signals are 5-50 cps at an exciting wavelength of 5145Å @ 150 mW. At higher exposures of CO(1000L) it is possible to make polarization measurements of the Raman bands. Raman spectra of CO adsorbed on Ni(111) have been recorded from -174° C to 26° C. Exposures varied from 100L to 10⁶L. Raman spectra are also recorded for CO + H₂ on Ni(111) (CO -1 torr; H₂ -3 torr) at temperatures from 200 - 530° C. At 350° C a low-frequency band appears at 74 cm⁻¹ and is assigned as an active carbon mode. The intensity of this mode is sensitive to H₂ and O₂ exposure. Splitting of the mode occurs at ~530° C along with the appearance of additional low-frequency bands that appear to be libration type modes. The Raman band corresponding to physisorbed O₂ on Ni(111) occurs at 1555 cm⁻¹ when O₂ is adsorbed below 290° K, and no Ni-O mode is observed. Raman modes recorded at 26° C are listed in Table 1 along with assignments. Most of these Raman bands have not been observed previously on Ni(111).

Table 1
Vibrational Frequencies of CO on Ni(111) at 26° C.
Exposure 10⁶ L.

Raman (cm ⁻¹)	Assignment
84	CNiNi bend, on-top species
186	OCNi bend, bridge species
223	δ(NiCNi) bridge species
247	bulk phonon mode (?)
448	Ni-C stretch, on-top species (p)
480	Ni-C stretch, bridge species (p)
556	OC(Ni) ₂ bend, bridge species
1114	first overtone of 556 cm ⁻¹ band
1491	CO stretch of trigonally bonded species (?)
1922	
1939	three CO groups, bridge bonded, stretching
1975	
1997	(C ¹³ O)?; CO stretch, bridge species (p)
2099	CO stretch, on-top (p)
2141	(physadsorbed) CO stretch
2161	CO stretch, on-top, bonded to NiO (p)

The bending mode at 84 cm^{-1} is type E, doubly degenerate, on-top site (Ni_5CO). The 186 cm^{-1} band is the OCNi bend of the bridged species, a B_1 mode (Ni_6CO). The deformation (NiCNi), type B_2 , of the bridge species occurs at 223 cm^{-1} . A possible source of the band at 247 cm^{-1} is a short-wavelength bulk phonon mode moving perpendicular to the (111) surface. Such modes are discussed by Erley *et al.*¹ for a $(\sqrt{7} \times \sqrt{7}) R 19.1^\circ$ LEED pattern. Krasser reports a Raman band at 246 cm^{-1} but does not assign it.² The band at 556 cm^{-1} may be attributed to the $\text{OC}(\text{Ni})_2$ bending mode at a bridge site. What we believe to be the first overtone of this band occurs at 1114 cm^{-1} ($\sim 2 \times 556\text{ cm}^{-1}$).³ A tentative assignment of the band at 1491 cm^{-1} is the C-O stretching mode of the trigonally bonded molecule. Workers in infrared and EELS have assigned frequencies below 1850 to such bonds and one expects to find a Ni-C stretching mode belonging to a triple bond at a frequency greater than 460 cm^{-1} but less than 600 cm^{-1} . Therefore, it is possible that the band at 556 cm^{-1} is the NiC stretch of the trigonal bond of C and 1114 cm^{-1} band is its overtone.

The three bands at 1922, 1939 and 1975 cm^{-1} are CO stretches of a complicated bridge structure of three CO groups. Similar Raman band structure was reported by Krasser for CO adsorbed at high pressures on Raney nickel.⁴ The band at 1997 cm^{-1} could be the C^{13}O mode reported by Jones.⁵ Whether the bonding is on-top or bridged is unresolved, but the gas phase C^{13}O stretch occurs at 2018 cm^{-1} . However, because of the small relative abundance of C^{13} ($\sim 2\%$), it is likely that the band at 1997 cm^{-1} is another bridge bonded species.

In the 2000 cm^{-1} region, the band at 2099 cm^{-1} is assigned to the CO stretching mode of the on-top species, an A_1 mode. The band at 2141 cm^{-1} is assigned to physisorbed CO. (As the temperature of the crystal is raised a few more degrees, this band disappears.) Finally, the band at 2161 cm^{-1} is assigned to the CO stretch of the on-top species, bonded to NiO. Some oxygen is present because of a band at 608 cm^{-1} that is attributable to the Ni-O stretching vibration. That the CO stretching frequency on a metal surface may be higher than the gas phase stretching frequency (2143 cm^{-1}) is explained by Politzer and Kasten⁶ who calculate the relative electron shift in the C bond to the metal. Raman studies of CO and O_2 , adsorbed on Ni(100) are in progress.

Future Research

A major advantage of Raman spectroscopy is its application to studies of molecular surface structure and bonding at high pressures. Few techniques exist that can be used in situ for such studies. We will continue studies to 2 atms pressure CO to learn how adsorbate structure changes from that observed at lower pressures of CO.

References

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