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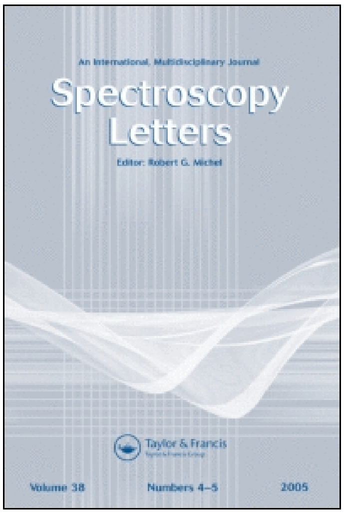

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RAMAN SPECTRA OF CO ADSORBED ON Ni(100)*

Key Words: Raman, Nickel

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ABSTRACT

Experimental results are discussed for laser Raman spectra of CO adsorbed on Ni(100) at -131C. Raman shifts are observed at 2050, 2028, 466 and 419 cm^{-1}. Assignments are made for the modes based upon C_{2v} and C_{4v} point groups. The assignments are compared with earlier experimental and theoretical work.

INTRODUCTION

Until several years ago, laser Raman spectroscopy was not used to study the adsorption of CO on smooth nickel surfaces. However, a usable signal-noise ratio can now be attained in these studies by combinations of careful optical design,[1,2,3] surface enhancement, and the use of a digital computer for

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digital filtering of the Raman signal. Reported here is the observation of four modes of CO adsorbed on Ni(100). These modes have sufficient intensity to be observed without digital filtering of the Raman signal. The enhancement expected for CO adsorbed on nickel (100) is the order of 70-100. This magnitude is not enough to improve the signal-noise ratio to the point that efficient collection optics can be ignored.

EXPERIMENTAL

The design of the ultra-high vacuum system used for this study has been presented elsewhere. A single crystal of nickel was obtained from Materials Research Corporation and a 1/4" cube was cut with a diamond saw and polished mechanically in a water-alumina slurry which had successive alumina particle sizes of 1.0, 0.3 and 0.05 μ. The cube was etched chemically in a solution of $HNO_3:H_3PO_4:HCH_3COO$. An X-ray diffraction of the cube was obtained, and the well-defined Laue spots indicated that the (100) plane was to within ±1° of the sample surface.

This nickel crystal was mounted on a sample holder and placed in the ultra-high vacuum chamber which was evacuated to a pressure of 2×10^{-9} Torr with the Ni crystal at 320°C. To remove sulfur impurities from the crystal, the crystal temperature was raised to 700°C and H_2 (Matheson Research Grade) was leaked into the chamber through a variable leak valve to a pressure of 0.5 Torr which was followed by evacuation. This H_2 exposure and evacuation was repeated several times until no sulfur signature (Auger spectroscopy) was present. A Raman spectrum was run after each exposure to H_2 but no Raman bands were present. Beginning with a chamber pressure of 2×10^{-9} Torr and a sample temperature of -131°C, CO was admitted to a pressure of 5×10^{-7} Torr and the pressure increased gradually while scanning the spectral region 2500-10 cm^{-1}. No Raman bands were observed after several hours exposure to pressures as high as 100 μ. The CO pressure was increased to 500 μ, and after several minutes exposure, the Raman bands shown in Figs. 1 and 2 were recorded. When the spectrum in Fig. 2 was recorded, the sample temperature had risen slightly to -127°C.

DISCUSSION

Evidence from low energy electron diffraction[4] indicates that CO on Ni(100) at 77K and a pressure of $\sim10^{-7}$ Torr produces low coverage, $\theta \leq 0.1$, and a bond of CO to Ni may not result. This result is substantiated by our Raman data at -130C which show that on the Ni(100) surface no Ni-C modes are observed until the CO pressure is increased to ~500 μ. Then one observes two Raman bands in the region of 2050 cm^{-1} and two bands in the 400-500 cm^{-1} region. It is clear that these frequencies are dependent upon the surface, the bonding type (bridged or linear), the temperature and the coverage. The temperature and surface dependence of the C=O stretching vibration of CO adsorbed on Ni(111), Ni(110) and Ni(100) was discussed previously.[5] For adsorbed CO ($\theta \simeq 0.1$ to 0.2) at a

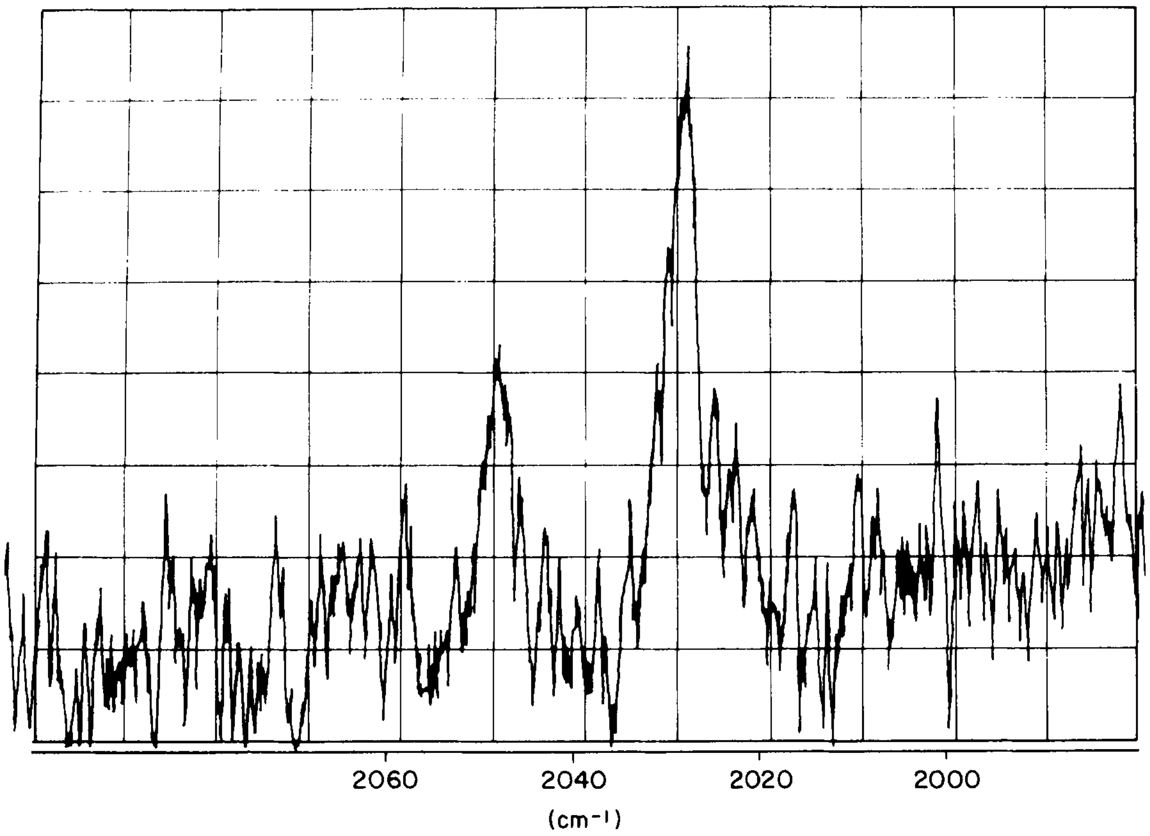

FIG. 1 Raman spectrum of CO adsorbed on Ni(100) at -131C. The CO pressure is 500μ; exciting line is 5145 Å @ 100 mW; slit width = 300μ; full scale counts = 200 counts sec^{-1}.

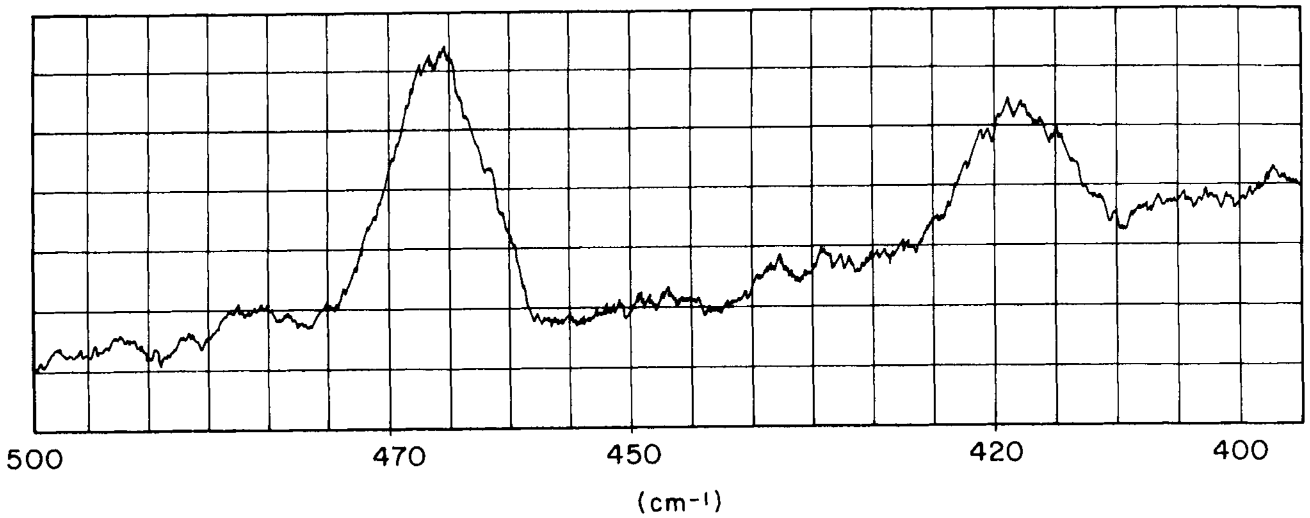

FIG. 2 Raman spectrum of CO adsorbed on Ni(100) at -127C. The CO pressure is 500μ; exciting line is 4880 Å @ 100 mW; slit width = 300μ; full scale counts = 100 counts sec^{-1}.

temperature of 200K, the C-O stretch frequency decreases in going from Ni(111) to Ni(100). Also, for CO adsorbed on Ni(100), the C-O stretch decreases about 5 cm^{-1} as the temperature rises from 125K to 210K.[5] We have concentrated efforts on understanding relationships among these CO and NiC modes, viz., correct assignments of the modes to species of vibration and the effects of surface structure on the frequencies. It is very important to understand the type of bonding of CO to Ni because this bonding determines the precise C-O stretching frequency and may also determine the dissociation temperature of oxygen atoms.

Earlier frequency assignments from i.r. and EELS[6] data are questioned because one possible interpretation of our Raman data does not agree with the earlier assignments of the C-O stretch and the Ni-C stretch for bridged and/or linear bonding. The consensus of the earlier work is that (1) the C-O stretch of the bridge-bonded species occurs at a lower frequency than the C-O stretch of the linear species, and (2) the Ni-C stretch of the bridge-bonded species occurs at a lower frequency than the Ni-C stretch of the linear species. One Raman study[7] of C-O on silica-supported Ni reversed (2) above, i.e., change the word "lower" to "higher". However, the authors concede that for Si-supported Ni there is opportunity for more types of bonding and so the bonding could be more complicated than for well-defined single crystal surfaces.

Richardson and Bradshaw[8] have calculated by the FG matrix method the frequencies, force constants and mean vibration amplitudes for the linear and bridged species of CO on Ni using force constants transferred from $Ni(CO)_4$ and also from fittings of force constants from the EELS data. Summarized in Table 1 is a comparison of our assignments with the others just discussed above. Andersson observed two ν-CO modes; however, Bertolini et al.[9] observe only one mode but state that two modes are possible (but unresolved) in their EELS data. There are indeed two modes of ν-CO as seen in Fig. 1.

Earlier assignments of these modes have been by analogy with the transition metal carbonyls. The bands above 2000 cm^{-1} have often been assigned to the linear structure and bands below 2000 cm^{-1} to the bridged structure. These assignments have been questioned by several workers[10,11] because some metal carbonyls do have CO ligands with frequencies below 1900 cm^{-1}.[12] Since one of the goals of this work is to elucidate the structures of the surface complexes, several complementary types of data are needed to eliminate the uncertainty of the assignments. Such data include molecular orbital wave functions,[13] force constants,[14] and Raman and infrared spectra including measurements of the polarizations of the Raman modes. Some of these data are now available.

Molecular orbital calculations[15] in which overlap populations have been used to provide force constants for harmonic oscillator calculations have produced CO vibration frequencies in the correct spectral region and, as expected, the bridged structures tend to have lower values than the linear ones. However, there was also predicted the existence of a bridged form with a C-O stretch frequency as high as 2065 cm^{-1} (including corrections for an anharmonic oscillator). The predicted frequency is also a sensitive function of the Ni-C distance, dropping to ~1890 cm^{-1} for a Ni-C distance of 2.22 Å. It was also shown that the number of nickel atoms involved in the interaction can be as much of a factor in determining the C-O frequency as whether the complex is bridged or linear.[16] Thus structural differences (bridged or linear) may not lead to a large frequency difference nor may each mode (one for bridged, one for linear) be restricted to just one spectral region.

The additional questions which arise are the following: Where should the frequencies of the Ni-C stretch (bridged and linear) occur in the spectrum? Do the same factors affect where these modes occur? One may gain some insight into these questions from the frequency and amplitude calculations of Richardson and Bradshaw.[8] These workers use a model of the Ni surface having 5 Ni atoms for the CO linear structure (C_{4v} point group) and 6 Ni atoms for the CO bridged structure (C_{2v} point group). This use is consistent with the MO calculations of Politzer and Kasten[13] who find that the decrease in π overlap populations levels off after 5 Ni atoms for the linear structure and after 4 Ni atoms for the bridged structure.

The total number of vibrational modes of an adsorbate is equal to the degrees of freedom in the free molecule, but the number of Raman and infrared bands actually observed depends on the adsorption site (which determines the point group). The Raman selection rules allow the modes to be Raman active. Furthermore, the symmetric modes ν_1 and ν_2 should be polarized in the Raman spectrum. We believe that our assignments shown in Table 1 are the correct ones because of selection rules, polarizations and comparisons with the calculations of Richardson and Bradshaw. There are two C-O stretching frequencies seen in Fig. 1. They may be reconciled in the following way. The LEED data indicate that a predominately bridged structure occurs on Ni(100) at low temperatures. A simple intensity argument (see Fig. 1) leads to the conclusion that the most intense line at 2028 cm^{-1} is due to the bridged structure because the scattering is proportional to the number of scatterers having that structure (surface-enhanced effects can be ignored here because the frequencies are very close together). The polarization measurements are not certain because of the high noise background, but both modes appear to be polarized. (However, one must be cautious when trying to determine the relative number of surface bonds of different types by comparing infrared intensities of different C-O bands).[17]

The proximity of the frequencies shown in Fig. 2 to the calculated frequencies $\nu_3 = 411\ cm^{-1}$ and $\nu_2 = 457\ cm^{-1}$ in Table 1

TABLE 1

Comparisons of Assignments of CO Vibrations for CO on Ni

	Richardson and Bradshaw[a]	Andersson EELS[b] @ 293°K, Ni(100)	Krasser et al.[c] (Si-Supported Ni)	This Work Ni(100)
A. On-top (linear) site (C_{4v} point group)				
Species	Assignment			
A_1	ν_1 C-O stretch = 2088 cm^{-1}	ν_1 = 2069	ν_1 = 2086	(p?)ν_1 = 2050(-131°C)
	ν_2 Ni-C stretch = 437	ν_2 = 480	ν_2 = 355	
E	ν_3 OC Ni bend = 411			(dp)ν_3 = 419(-127°C)
	ν_4 C Ni Ni bend = 82			
B. Bridge site (C_{2v} point group)				
A_1	ν_1 C-O stretch = 2099 cm^{-1}	ν_1 = 1932	ν_1 = 1804	(p?)ν_1 = 2028(-131°C)
	ν_2 Ni-C sym. stretch = 457	ν_2 = 359	ν_2 = 362	(p)ν_2 = 466(-127°C)
B_1	ν_3 Ni-C antisym. stretch = 649	ν_3 = 657		
	ν_4 OC Ni bend = 184			
B_2	ν_5 $OC(Ni)_2$ bend = 572			
	ν_6 CNi Ni bend = 76			

[a] See ref. 8; [b] see ref. 6; [c] see ref. 7.

is encouraging and the relative intensity argument can be applied to the assignment of the Raman band at 466 cm^{-1} to the bridged structure. If one believes the calculations, the other Ni-C stretch (linear) at 437 cm^{-1} (Table 1) could be contained in the band shown at 466 cm^{-1} in Fig. 2. The band is not very broad, however, and attempts to resolve it gave negative results. More likely, the weak band shown at 435 cm^{-1} is the other Ni-C stretch but it is too weak for definitive polarization measurements. Thus the remaining band at 419 cm^{-1} in Fig. 2 is chosen as ν_3 of the linear model. Note that the intensity of this band is less than that at 466 cm^{-1}, lending support to the assignment of the 466 cm^{-1} band to a bridged species (in analogy with 2028 cm^{-1}, bridged species).

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15. See Ref. 13(b).

16. See Ref. 13(b).

17. See Ref. 13(a).