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The Raman Spectrum of Carbon Monoxide Chemisorbed on Silica-Supported Nickel

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The Raman spectrum of carbon monoxide chemisorbed on silica-supported nickel has been investigated at pressures below 10 Torr. Two ν(C–O) stretching vibrations are found and assigned to linearly and bridge-bonded CO molecules, respectively. With decreasing pressure a frequency shift from 2100 to 2065 cm^{-1} is observed for the linear species and from 1940 to 1770 cm^{-1} for the bridge-bonded species. At lower wavenumbers several bands are found, which are assigned to ν(Ni–C) stretching vibrations of the two chemisorbed species located on different lattice sites. The observed frequency of the δ(Ni–C–O) deformation vibration agrees well with calculations based on the evaluation of electron energy loss spectroscopy data. For the assignment of the vibrational bands, an FG matrix calculation has been carried out.

INTRODUCTION

Carbon monoxide chemisorbed on nickel has been studied extensively by infrared and electron energy loss spectroscopy (*2–5*). With infrared spectroscopy, generally only the ν(C–O) stretching vibration is investigated; with electron energy loss spectroscopy, the low-frequency bands can also be measured. Raman spectroscopy combines the advantages of electron energy loss spectroscopy (possibility of the measurement of the low-frequency bands with relatively low resolution) and infrared spectroscopy (measurement of the high-frequency bands with high resolution). Of special interest are the dynamics of the vibrations of those atoms which are directly bonded to the surface by chemisorption. Generally, these vibrations can be found in the frequency region below 700 cm^{-1}. Only if very light atoms are adsorbed can the frequencies of the vibrations be observed in the high-frequency region.

In a previous paper (*1*) we reported the Raman spectra of carbon monoxide chemisorbed on Raney nickel and on silica-supported nickel at pressures higher than 20 Torr. We now present results obtained at lower pressures in the range of 0.05–10 Torr.

EXPERIMENTAL

The silica-supported nickel was heated in a vacuum of 10^{-6} Torr at 650°C and then reduced in a stream of hydrogen for several hours. At the end of the reduction, the hydrogen was pumped off for about 14 hr at 450°C. The carbon monoxide was added at −50°C in order to avoid the formation of nickel tetracarbonyl. The Raman spectrometer and the Raman cell are described elsewhere (*1, 6*). In order to avoid heating of the black-colored sample and desorption of the chemisorbed molecules, the sample was cooled to 100 K and rotated by an external

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motor. Moreover, the laser beam was slightly defocused by a cylindrical lens and shifted periodically up and down by a vibrating glass plate. The wavelength of the excitation source was $\lambda = 5145$ Å; the power of the laser beam never exceeded 150 mW. The Raman spectra were measured in back scattering geometry. As the Raman intensities were very weak (about 10 photocounts per second in the maximum of the signal), we used a multichannel analyzer (DIDAC 4000, Intertechnique) in order to integrate the spectra.

RESULTS AND DISCUSSION

1. The Raman Spectrum of CO

The Raman data are given in Table 1 and are compared with results of electron energy loss spectroscopy of carbon monoxide chemisorbed on Ni(111). There is evidence for two different adsorption species for CO chemisorbed on nickel (*7*), namely, a linear species with one CO molecule bonded to one nickel atom and a bridge-bonded species with one CO molecule bonded simultaneously to two or more nickel atoms.

For the description of the vibrational modes, the concept of surface molecule is used. The surface molecule consists of the adsorbate and a few atoms of the adsorbent. Photoemission spectroscopy (*8*) suggests that for the system CO–Ni/SiO$_2$, the concept of the surface molecule is a good approximation. For the assignment of the vibrational modes it is then very important to know how many nickel atoms of the surface contribute to the surface molecule. Extended Hückel calculations (*9*) show that in particular the frequency of the ν(C–O) stretching vibrations depend very strongly on the number of nickel atoms bonded to the CO molecule.[2]

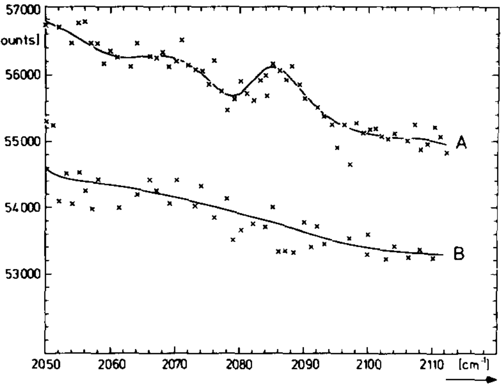

FIG. 1. CO stretching vibration, presumably of linear bonded species. $p_{ads} = 1$ Torr; $T_{ads} = -50$°C. A, Spectrum of fused quartz + CO–Ni/SiO$_2$; B, background, fused quartz + Ni/SiO$_2$.

TABLE 1

Raman and Electron Energy Loss Data of Chemisorbed CO[a]

Raman cm^{-1}	Electron energy loss cm^{-1}	Assignment	Irreducible representation
2086		$\omega(CO)_{linear}$	A_1
2070	$\omega(CO)_{linear}$	A_1 (different lattice site)	
	2022	$\omega(CO)_{linear}$	A_1
1804	1848	$\omega(CO)_{bridged}$	A_1
640	632	$\omega(CO)_{bridged}$	E
535		$\delta(NiCO/NiCNi)_{bridged}$	A_1
		$\delta(OCNi)_{linear}$	E
362	377	$\nu(Ni–C)_{bridged}$	A_1
355		$\nu(Ni–C)_{linear}$	A_1
345		$\nu(Ni–C)_{bridged}$	B_1
330		R_x; R_y (?)	E
307		$\delta(NiCO)_{bridged}$	E
226		$\delta(NiCNi)_{bridged}$	B_2
173		$\delta(OCNi)_{bridged}$	B_1
164		$\delta(NiCNi)_{bridged}$	E

[a] The CO pressure in the Raman cell was 1 Torr.

For both the linear and the bridge-bonded species, the calculations predict a decrease in the ν(C–O) stretching frequency as the number of the bonded nickel atoms increases. The frequencies of the bridge-bonded structure may be shifted below 1800 cm^{-1}, and the frequencies of the linear species below 1900 cm^{-1}. With Raman spectroscopy (*1*), two vibrational bands have been found at 2100 and 1940 cm^{-1} for 30 Torr pressure. These bands are shifted to 2060 and 1770 cm^{-1} when lowering the pressure to 0.05 Torr. Figures 1 and 2 show the Raman spectra of the two ν(C–

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[2] Other effects, such as dipole–dipole coupling between CO molecules and chemisorption on different lattices sites, are presumed to influence the behavior of the ν(CO) stretching vibration not so strongly.

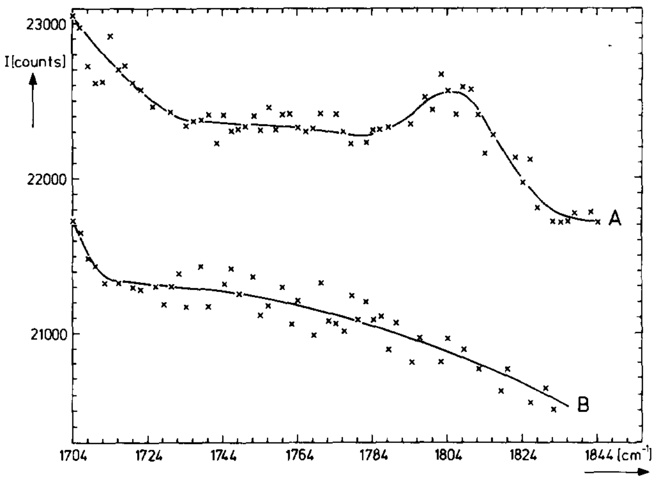
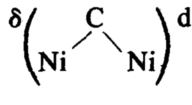


FIG. 2. CO stretching vibration, presumably of a bridge-bonded species. p_{ads} = 1 Torr; T_{ads} = −50°C. A, Spectrum of fused quartz + CO–Ni/SiO$_2$; B, background, fused quartz + Ni/SiO$_2$.

O) stretching vibrations. Figure 3 shows the behavior of the ν(C–O) stretching vibration for different pressures.

The extended Hückel calculations show that a realistic number of nickel atoms, which influence the ν(CO) stretching vibration, is four. Under the assumption that the site symmetry of the bonded CO molecule is C_{4v}, the linear species consists of five neighboring nickel atoms of the surface and one CO group, which is situated over one nickel atom in the middle of a square formed by four nickel atoms. If one separates the low-frequency modes of the ν(Ni–Ni) stretching vibrations, the δ(Ni$_3$) deformation vibrations and the δ(Ni–Ni–C) deformation vibrations, the linear species shows three vibrational modes: (i) a totally symmetric ν(CO) stretching vibration A_1, (ii) a totally symmetric ν(Ni–C) stretching vibration A_1, and (iii) a degenerte deformation vibration δ(Ni–C–O) with symmetry E.

If one adsorbs a molecule on a surface, the three free translations and rotations become restricted, and can be excited with electromagnetic radiation. The only realistic mode, which should be found in the Raman spectrum at finite frequencies, is the restricted degenerate rotation about the *x* and *y* axis, which are parallel to the surface. The three restricted translations are expected to be found at very low frequencies.

The bridge-bonded structure with one CO molecule bonded to four neighboring nickel atoms simultaneously and with the local symmetry C_{4v} has the following vibrational degrees of freedom: a totally symmetric A_1, an antisymmetric B_1, and a degenerate E ν(Ni–C) stretching vibration, a totally symmetric δ(OCNi/NiCNi) deformation vibration A_1 which represents a coupled system of two dependent deformation coordinate sets, an antisymmetric B_2 and a degenerate E δ  $\left(\begin{smallmatrix} & C & \\ Ni & & Ni \end{smallmatrix}\right)$ deforma-

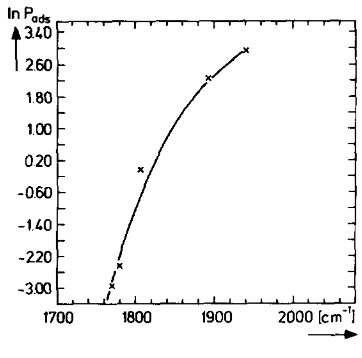


FIG. 3. Pressure dependence of the bridge-bonded ν(C–O) stretching vibration.

tion vibration, and an antisymmetric B_1 and a degenerate E δ(Ni–C–O) deformation vibration (*10*). The vibrations of the Ni–Ni bonds in the surface can be neglected, as their frequencies should be very small and should be found in the phonon continuum of the adsorbent.

In addition, the restricted translation in the *z* direction perpendicular to the surface should give a totally symmetric mode and the translations in the (*xy*) direction parallel to the surface should give a degenerate mode. The same is valid for the rotations. One expects three restricted rotations in the bridge-bonded case, in contrast to the linear case where the rotation about the *z* axis is suppressed.

Considering the ν(Ni–C) stretching vibrations, the linear and bridge-bonded species together should give four stretching modes. Additional modes may result from adsorption on different lattice sites, on edges, and dislocations, etc. Thus one expects a rather complicated spectrum. The low-frequency Raman spectrum in the range of 300–400 cm^{-1} at higher pressures is given in Fig. 4. We find a broad band system at 350–390 cm^{-1}, a band system with several single peaks centered at 330 cm^{-1} and one peak at 307 cm^{-1}. At lower pressures the broad band system with maximum at 370 cm^{-1} is shifted to lower frequencies and split into several lines. The band system with a maximum at 330 cm^{-1} becomes a single line. This behavior is shown in Fig. 5.

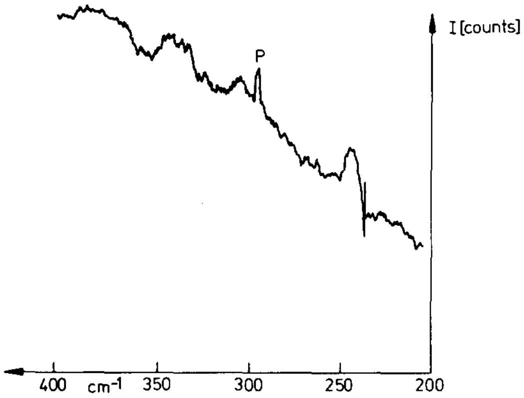


FIG. 4. Raman spectrum in the range of 200–400 cm^{-1}. P_{ads} = 100 Torr; T_{ads} = 20°C. P, Laser plasma.

2. *Vibrational Assignment and Force Constants*

For an assignment of the vibrational bands, a calculation of the force constants has been carried out using the FG matrix method. The assignment of the vibrational bands is made with the data of electron loss spectroscopy (*4, 15, 16*), Raman spectroscopy, and the minimalization conditions for force constants. The force constants are calculated for both cases, the linear species and the bridge-bonded species. We use for the calculation of the G matrix (*12*) r_{CO} = 1.15 Å, r_{NiC} = 1.84 Å, and r_{Ni-Ni} = 2.60 Å. The assignment of the measured vibrational bands resulting from the force constant calculation is given in Table 1. We have made several possible assignments of the vibrational bands to the internal vibrational

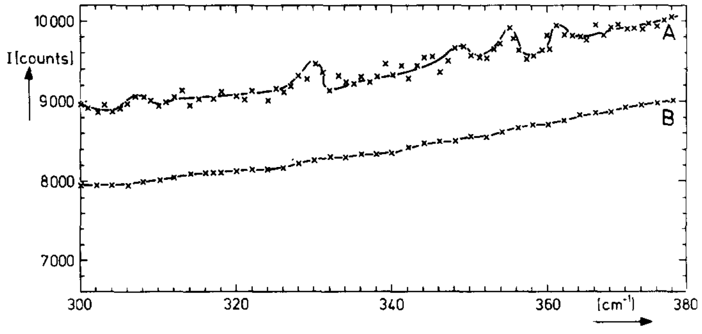


FIG. 5. Raman spectrum in the range of 300–400 cm^{-1}. A, Spectrum of fused quartz + CO–Ni/SiO_2; B, background, fused quartz + Ni/SiO_2. P_{ads} = 1 Torr; T_{ads} = −50°C.

TABLE 2

Force Constants of the Linear and Bridge-Bonded Species with Symmetry C_{4V}

Force constant	Linear species (mdyn/Å)	Bridged species (mdyn/Å)	$Ni(CO)_4$ (*13*) (mdyn/Å)
f_{C-O}	17.41	12.93	16.42
f_{Ni-C}	1.43	2.91	2.78
$f_{Ni-C/C-O}$	0.26	—	
$f_{Ni-C/Ni-C/90^\circ}$		0.10	
$f_{Ni-C/Ni-C/180^\circ}$		1.41	
f_{OCNi}	0.77	~1.26	0.15
$f_{OCNi/OCNi}$		~0.16	
f_{NiCNi}		~0.46	0.08
$f_{NiCNi/NiCNi}$		~0.12	

modes and to the different irreducible representations. The selected assignment results from calculations with minimal interaction force constants, with interactions between the same and different types of internal vibrations. For the linear species we find two ν(CO) stretching vibrations resulting from adsorption on different lattice sites. The remaining line at 330 cm^{-1}, which is not used for the force constant calculations, is possibly the restricted degenerate rotation of the linear species with the rotational axis parallel to the surface. The calculated force constants are given in Table 2. The force constants are described with a generalized valence force field. The calculations were made using the minimalization methods (*14*).

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