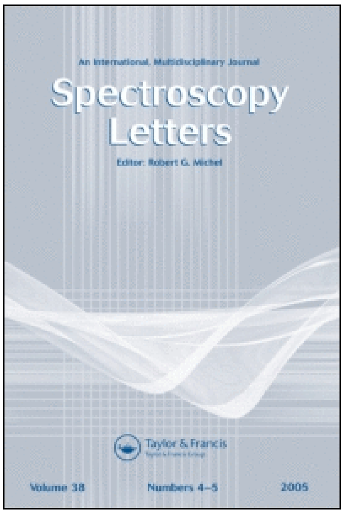

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Normal Unenhanced Raman Spectra of ^{13}CO Adsorbed on Ni(111): A Comparison Study

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NORMAL UNENHANCED RAMAN SPECTRA OF ^{13}CO ADSORBED ON Ni(111): A COMPARISON STUDY

Keywords: Raman, ^{13}CO, Ni(111)

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Abstract

Normal unenhanced Raman spectra (NURS) of low-polarizability CO molecules adsorbed on Ni(111) at liquid nitrogen temperature have been recorded. The ^{13}CO has been used for the first time to confirm previously reported Raman spectra of ^{12}CO adsorbed on Ni(111). The exposure used in one set of experiments was 10^6L ^{13}CO. Residual ^{12}CO gas was present and gave rise to spectra identical to that reported previously. The expected shifted Raman bands due to ^{13}CO were observed. These included the ^{13}C-O stretches and their matching Ni-^{13}C frequencies. Another set of experiments were performed while the Ni(111) sample was exposed to a static 1-atmosphere ^{13}CO pressure. Striking features were observed at such high pressure. Two tentative models are presented to explain the observed spectra.

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1. Introduction

The isotopic substitution of ^{12}CO by ^{13}CO leads to isotopic shifts of the Raman bands of coadsorbed CO species on Ni. This leads, in turn, to independent confirmation of the observed bands using ^{12}CO only providing that the physical conditions of the surface are the same (coverage, temperature, degree of cleanliness of the surface to start with, etc.). The shift in frequency (ν) can be anticipated by using either of the following simple formulae

$$\nu(^{13}CO)/\nu(^{12}CO) \doteq \sqrt{\mu(^{12}CO)/\mu(^{13}CO)} \quad (1)$$

or

$$\nu(^{13}CM)/\nu(^{12}CM) \doteq \sqrt{\mu(^{12}CM)/\mu(^{13}CM)} \quad (2)$$

where

$\nu(^{13}CO)$ = the frequency of ^{13}CO molecule.

$\nu(^{12}CO)$ = the frequency of ^{12}CO molecule.

$\mu(^{13}CO)$ = the reduced mass of ^{13}CO molecule.

$\mu(^{12}CO)$ = the reduced mass of ^{12}CO molecule.

$\mu(^{13}CM)$ = the reduced mass of ^{13}CM specie.

$\mu(^{12}CM)$ = the reduced mass of ^{12}CM specie.

M = surface atom upon which a CO molecule is chemisorbed (Ni, Co, etc.)

Therefore, since the ^{12}C-O stretch in its gaseous state is at 2143 cm^{-1} that of the ^{13}C-O is calculated to be: 2143 x 0.9777759 = 2095 cm^{-1}. Upon adsorption this frequency is subject to drop to lower frequencies exactly as in the case ^{12}CO.

We have reported previously[1] the Raman spectra of 10^6L ^{12}CO adsorbed on Ni(111) at 98 K. Several ^{12}CO and Ni^{12}C bands were observed and assigned. Two tentative models were advanced to explain the observed spectra. In this work we have used the isotopic ^{13}CO to arrive at independent confirmation of the previously observed ^{12}CO Raman bands. It is the high resolution of Raman spectroscopy (also IR spectroscopy) that allows us to observe bands separated by 10-40 cm^{-1}. The lack of this kind of resolution prohibits the use of EELS in such studies. Therefore, Raman spectroscopy manifests its power over the EELS in isotopic studies. (No such study on the Ni(111) surface has been published before in the literature.) Also high pressure studies is one of the unique features Raman spectroscopy posses (also IR spectroscopy) over EELS.

1.1. Experiment

The Ni crystal was purchased from Materials Research Corporation, then oriented and cut to 6 mm cube with a diamond saw. The sample was mechanically polished in water-alumina slurry which had successive particle sizes of 1.0, 0.3 and 0.05 μm. After etching, the x-ray diffraction patterns showed well-defined Laue spots indicating the (111) plane was ±1.5^{o} of the sample surface. Since our set-up does not include AES, the sample was placed in a scanning electron microscope for elemental analysis of the surface. The electron beam was focused on various spots on the (111) face to see if any surface impurities could be detected. Only strong nickel peaks showed in all scans.

The oriented single crystal was then placed in a UHV chamber described elsewhere[2] and Ar^+ bombarded at 2 KV for about an hour. The sample during the bombardment was maintained at 170°C. After the bombardment the sample was annealed to 300°C and a number of reduction cycles using research grade hydrogen were performed for 15 minutes each. The surface was then cooled to 98 K using the cold finger. Mass spectrometer analysis of the residual gas in the UHV cell revealed the presence of ^{12}CO, H_2, H_2O, O_2, and CO_2 with the same levels observed prior to the set experiments involving the ^{12}CO reported previously[1]. The spectra presented in this work have been reproduced more than 90% of the time.

2. Results and Discussion.

2.1. Raman Spectra of ^{13}CO adsorbed on Ni(111) after an exposure of 10^6L of ^{13}CO.

^{13}CO of 99% purity was admitted using the leak value and exposure of 10^6L ^{13}CO was achieved for the first set of experiments reported below. The sample temperature was kept at 98 K.

2.1.1. Linear on-top species.

A scan of the spectral region 1900-2147 cm^{-1} is shown in Fig. 1. This spectrum was taken at 98 K. The bands observed at 2056

cm^{-1}, 2067 cm^{-1} and 2108 cm^{-1} are assigned to the C-O stretches of ^{12}CO species in the linear on-top positions. These bands are compared to those observed previously[1] (2058 cm^{-1}, 2073 cm^{-1} and 2110 cm^{-1}, respectively). The previously observed bands at 2036 cm^{-1} and 2092 cm^{-1} are not observed. However, the band at 2088 cm^{-1} is within the experimental error (± 5 cm^{-1}) from the 2092 cm^{-1} band, but this band could also be assigned to the ^{13}C-O stretch of ^{13}CO physisorbed on the sample (see below). The band at 2138 cm^{-1} is assigned to the ^{12}C-O stretch of ^{12}CO physisorbed on the sample.

Applying the simple formula (1) presented above one can estimate the expected frequency positions of the ^{13}CO species equivalent to the ^{12}CO species observed previously. The expected ^{13}CO frequencies for the 2056 cm^{-1}, 2067 cm^{-1} and 2108 cm^{-1} bands are 2010 cm^{-1}, 2021 cm^{-1} and 2061 cm^{-1}. We observe in Fig. 1 the two bands at 2008 cm^{-1}, 2025 cm^{-1} which are in remarkable agreement with the anticipated ^{13}CO frequencies. Examining the band at 2056 cm^{-1} we see that its FWHM = 18 cm^{-1}, this could very well carry in it the anticipated frequency 2061 cm^{-1}.

The estimated ^{13}CO frequency corresponding to a possible ^{12}CO frequency at 2088 cm^{-1} is 2042 cm^{-1}. No band at 2042 cm^{-1} is observed. This could mean that the ^{13}CO species equivalent to (having the same neighboring species) those ^{12}CO species giving rise to the 2088 cm^{-1} frequency are not available. If we consider the 2088 cm^{-1} band as a one due to the ^{13}CO species, the corresponding ^{12}CO frequency is estimated to be 2136 cm^{-1}. We do

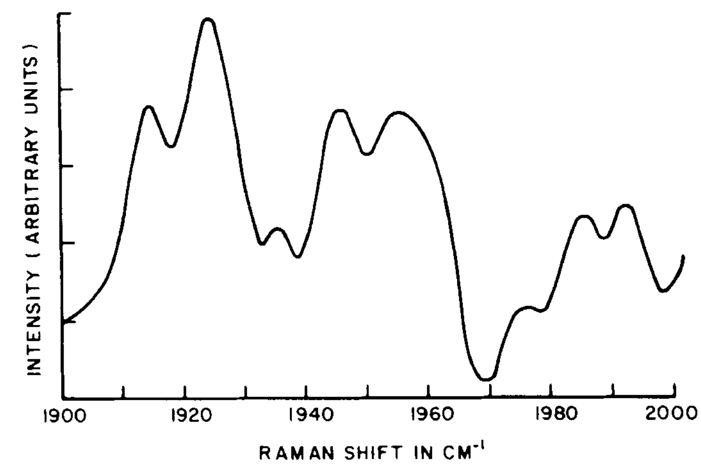

FIG. 1(a) The Raman spectrum in the region 1900-2000 cm^{-1} of CO adsorbed on Ni(111) after an exposure of 10^6L ^{13}CO + ^{12}CO (Residual Gas). T = -160^oC. The laser power is 2 Watts, 4880 $\overset{o}{A}$. The slit widths = 300 μ and the count time is 20 seconds/step.

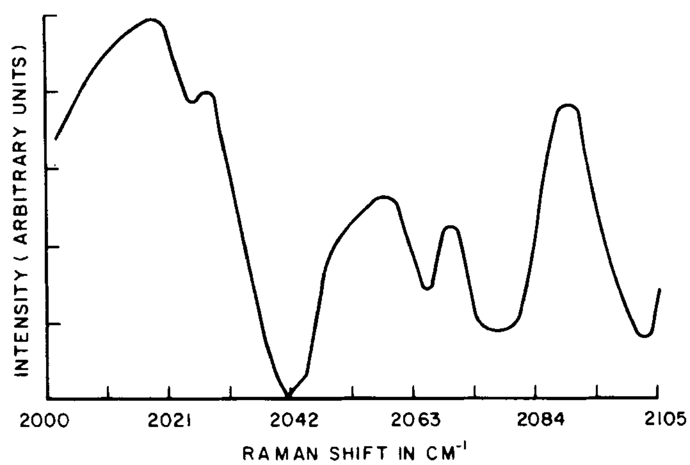

FIG. 1(b) The Raman spectrum in the region 2000-2105 cm^{-1} of CO adsorbed on Ni(111) after an exposure of 10^6L ^{13}CO + ^{12}CO (Residual Gas). T = -160^oC. The laser power is 2 Watts, 4880 $\overset{o}{A}$. The slit widths = 300 μ and the count time is 20 seconds/step.

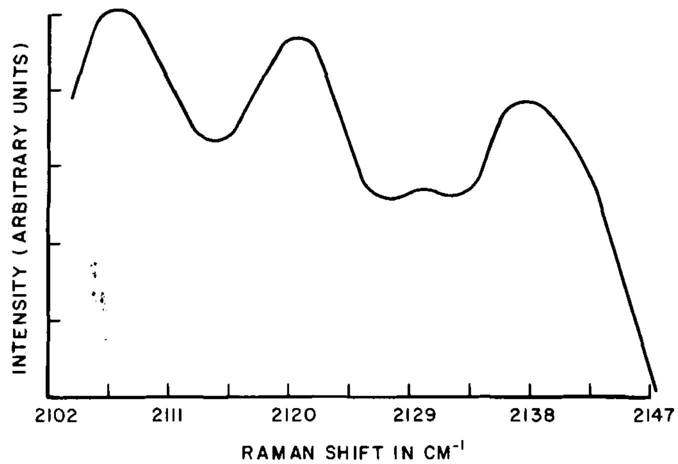

FIG. 1(c) The Raman spectrum in the region 2102-2147 cm^{-1} of CO adsorbed on Ni(111) after an exposure of 10^6L ^{13}CO + ^{12}CO (Residual Gas). T = -160°C. The laser power is 2 Watts, 4880 Å. The slit widths = 300 μ and the count time is 20 seconds/step.

observe a band at 2138 cm^{-1} which we assigned above to the ^{12}C-O stretch ^{12}CO physisorbed on the sample. Therefore, the 2088 cm^{-1} could very possible be assigned to the ^{13}C-O stretch of ^{13}CO physisorbed on the sample. Also this band may be of dual nature, one due to ^{12}CO species chemisorbed as pictured in the tentative model (see section 2.3) and is also due to ^{13}CO physisorbed on the sample. The band at 2120 cm^{-1} may be due to ^{12}CO linear species with neighboring species not considered in our tentative model reported earlier[1].

2.1.2. CO Bridge Species

The bands observed at 1954 cm^{-1}, 1984 cm^{-1}, 1992 cm^{-1} and 2008 cm^{-1} in Fig. 1 are assigned to the ^{12}C-O stretches of ^{12}CO

species in the bridge 2-fold positions. These bands are compared to those observed previously[1] (1958 cm^{-1}, 1980 cm^{-1}, 1991 cm^{-1} and 2009 cm^{-1}, respectively). The estimated ^{13}CO frequencies corresponding to the above mentioned ^{12}CO bridge frequencies are 1911 cm^{-1}, 1940 cm^{-1}, 1948 cm^{-1} and 1964 cm^{-1}, respectively. One observes in Fig. 1 the three frequencies 1913 cm^{-1}, 1935 cm^{-1} and 1944 cm^{-1} which are in remarkable agreement with the anticipated ^{13}CO frequencies. We do not observe a band at 1964 cm^{-1}. This could mean that the ^{13}CO species equivalent to those ^{12}CO species giving rise to the 2008 cm^{-1} frequency are not available. The band at 2008 cm^{-1} has a FWHM = 25 cm^{-1} which gives the possibility that this band is of a double nature: (1) the ^{13}CO frequency corresponding to the 2056 cm^{-1} ^{12}CO frequency, (2) the ^{12}CO bridge frequency pictured in the tentative model (see section 2.3).

2.1.3. Ni-C Stretch of CO On-top Species

A scan of the spectral region 340-535 cm^{-1} is shown in Fig. 2. This spectrum was recorded at 98 K. The observed bands at 504 cm^{-1}, 486 cm^{-1} and 454 cm^{-1} are assigned to the Ni-^{12}C stretches of ^{12}CO species in the linear on-top positions adsorbed on the sample. These bands are compared to those observed previously[1] (509 cm^{-1}, 483 cm^{-1} and 460 cm^{-1}, respectively) for the Ni-^{12}C stretches. These Ni-^{12}C stretches are matched with the ^{12}C-O linear stretches discussed above, namely: 2056 cm^{-1}, 2067 cm^{-1} and 2088 cm^{-1} bands, respectively. The band at 526 cm^{-1} is the Ni-^{12}C stretch corresponding to the ^{12}C-O stretch 2036 cm^{-1}. Even though

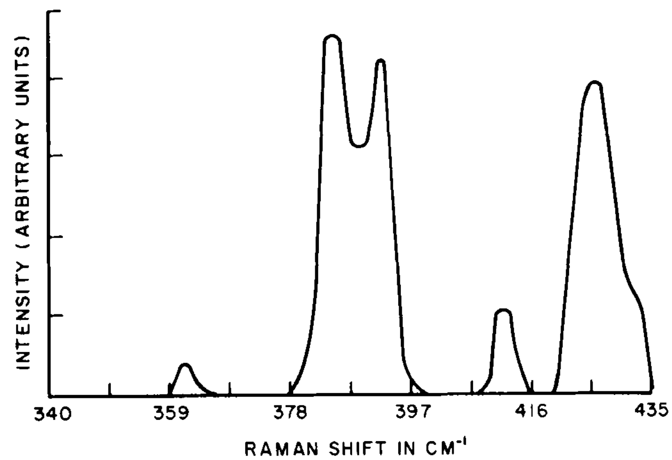

FIG. 2(a) The Raman spectrum in the region 340-435 cm^{-1} of CO adsorbed on Ni(111) after an exposure of 10^6L ^{13}CO + ^{12}CO (Residual Gas). T = -160°. The laser power is 2 Watts, 4880 Å. The slit widths = 300 μ and the count time is 20 seconds/step.

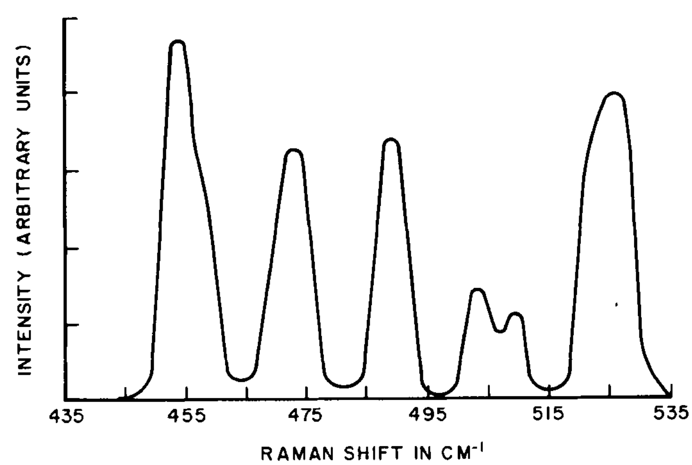

FIG. 2(b) The Raman spectrum in the region 435-535 cm^{-1} of CO adsorbed on Ni(111) after an exposure of 10^6L ^{13}CO + ^{12}CO (Residual Gas). T = -160°. The laser power is 2 Watts, 4880 Å. The slit widths = 300 μ and the count time is 20 seconds/step.

we have not observed a band at 2036 cm^{-1} (± 5 cm^{-1}) we are observing its Ni-^{12}C stretch, this may be due to the effect of the neighboring species have on the C-O bond giving rise to 2036 cm^{-1} band. This may lead to its weakening to the degree that we are not able to observe it. The estimated Ni-^{13}C frequency corresponding to 526 cm^{-1} is 509 cm^{-1}. We observe a band at 508 cm^{-1}; this we assign to the Ni-^{13}C stretch of the ^{13}CO species giving rise to the 1992 cm^{-1} frequency which, in turn, corresponds to the 2036 cm^{-1} ^{12}CO frequency. So even though we do not observe the ^{12}CO 2036 cm^{-1} frequency we do observe its corresponding ^{13}C-O and Ni-^{13}C frequencies. The estimated Ni-^{13}C frequencies corresponding to the Ni-^{12}C frequencies 504 cm^{-1}, 486 cm^{-1} and 454 cm^{-1} are 486 cm^{-1}, 472 cm^{-1} and 440 cm^{-1}, respectively. We observe two bands at 486 cm^{-1} and 476 cm^{-1} in remarkable agreement with the anticipated frequencies. Here the 486 cm^{-1} band may have a dual nature, one due to a Ni-^{12}C stretch and the other due to a Ni-^{13}C stretch. We do not observe a band at 440 cm^{-1} (± 5 cm^{-1}) which would have been matched to a 2042 cm^{-1} band corresponding to Ni-^{13}C and ^{13}C-O stretches, respectively. As mentioned above, we have not observed a band at 2042 cm^{-1} either. The observed band at 454 cm^{-1} is assigned to Ni-^{12}C stretch corresponding to the ^{12}C-O 2088 cm^{-1}. The lack of a corresponding Ni-^{13}C frequency (440 cm^{-1}) leads us to conclude that either there are no ^{13}CO species equivalent to those ^{12}CO species giving rise to the 2088 cm^{-1} band (considering this band to be of dual nature as explained above), or the 440 cm^{-1} (±5 cm^{-1}) band is so weak and screened that we cannot observe it.

2.1.4. Ni-C Stretch of the Bridge Species

The observed bands at 425 cm^{-1}, 392 cm^{-1}, 385 cm^{-1} and 361 cm^{-1} in Fig. 2 are assigned to the Ni-^{12}C stretches of ^{12}CO species in the 2-fold positions adsorbed on the sample. These bands are compared to those observed previously[1] (420 cm^{-1}, 380 cm^{-1}, and 362 cm^{-1}, respectively) for the Ni-^{12}C stretches. The 380 cm^{-1} band was a broad one (FWHM = 30 cm^{-1}) so we believe that the 385 and 392 cm^{-1} bands are the resolved bands contained previously under the 380 cm^{-1} band. These Ni-^{12}C stretches are matched with the ^{12}C-O bridge stretches discussed above, namely; 1954 cm^{-1}, 1984 cm^{-1}, 1992 cm^{-1} and 2008 cm^{-1} bands, respectively (see section 2.3 for tentative model).

The estimated Ni-^{13}C frequencies corresponding to the Ni-^{12}C frequencies 425 cm^{-1}, 392 cm^{-1}, 385 cm^{-1}, and 361 cm^{-1} are 411 cm^{-1}, 380 cm^{-1}, 372 cm^{-1} and 350 cm^{-1}, respectively. We observe a band at 411 cm^{-1} with perfect agreement with the anticipated frequency. This band represents the Ni-^{13}C stretch corresponding to the ^{13}CO bridge species giving rise to the observed 1913 cm^{-1} band. We also observe a band at 385 cm^{-1} with good agreement with the anticipated 380 cm^{-1} band. This band is the Ni-^{13}C stretch corresponding to the ^{13}CO bridge species giving rise to the observed 1935 cm^{-1} band. Here the 385 cm^{-1} band could be of dual nature one represents the Ni-^{12}C stretch corresponding to the 1992 cm^{-1} ^{12}CO stretch and the other is the Ni-^{13}C stretch mentioned above. Since we do not observe a band at 372 cm^{-1} representing the Ni-^{13}C frequency corresponding to the 385 cm^{-1} Ni-^{12}C frequency we may conclude the following:

(a) The 1992 cm^{-1} band represents the ^{13}C-O stretch corresponding to the 2036 cm^{-1} ^{12}CO frequency (we have observed the corresponding Ni-^{13}C as reported above).

(b) The 1992 cm^{-1} band as described in part (a) plus it represents the ^{12}C-O stretch corresponding to the 2-fold ^{12}CO species as pictured in the tentative model (see section 2.3). In this case the 385 cm^{-1} is of dual nature as described above. Also the 1944 cm^{-1} band does not represent the corresponding ^{13}CO frequency stretch.

(c) The 1992 cm^{-1} band is of dual nature as described in (a) and (b) but for some reason we were not able to detect a band at 372 cm^{-1} ($\pm$ 5 cm^{-1}) to represent the Ni-^{13}C stretch of the observed 1944 cm^{-1} ^{13}CO stretch..

Since the width of both the 1992 cm^{-1} band and 385 cm^{-1} band is not wide enough to accommodate two bands in each we are inclined to conclude that conclusion (a) is the most reasonable. This conclusion does not mean that the 1991 cm^{-1} band reported previously[1] could not have been assigned to bridge species as was done...it simply means that the observed and anticipated numbers are too close regarding these potential assignments. A conclusion that the 1992 cm^{-1} band reported previously could have been due to ^{13}CO species (corresponding to the 2036 cm^{-1}) cannot be made since we used ^{12}CO with purity 99.999% and the natural abundance of ^{13}CO (from the residual gas) is about 1%.

As expected no band at 350 cm^{-1} (± 5 cm^{-1}) was observed since no band at 1964 cm^{-1} (±5 cm^{-1}) was observed either. Therefore, the ^{12}CO species giving rise to the 2008 cm^{-1} band does not have equivalent ^{13}CO species. Again as we discussed the case of the 1992 cm^{-1} band, the 2008 cm^{-1} (FWHM = 25 cm^{-1}) may support two bands, one represents the ^{13}C-O linear stretch corresponding to the 2056 cm^{-1} ^{12}CO frequency and the other to the ^{12}C-O bridge stretch as pictured in the tentative model (see section 2.3). The band at 361 cm^{-1} represents the Ni-^{12}C stretch corresponding to the 2008 cm^{-1} ^{12}CO frequency in perfect agreement with our previous work[1].

2.2. Raman Spectra of ^{13}CO adsorbed on Ni(111) after a static exposure of 1-Atmosphere pressure of ^{13}CO.

Under static conditions the pressure in the UHV cell was taken from below 10^{-8} Torr to 1 atmosphere by leaking in ^{13}CO gas of 99% purity at temperature of 151 K. The Raman spectra reported below were taken under this static pressure and temperature. The temperature of the sample under UHV conditions was 98 K. As the pressure went up the temperature went up until it reached 151 K and this temperature was maintained throughout, the experiments.

2.2.1. CO On-Top Species

A scan of the spectral region 1912-2162 cm^{-1} is shown in Fig. 3. This spectrum was taken at 151 K. The first striking feature

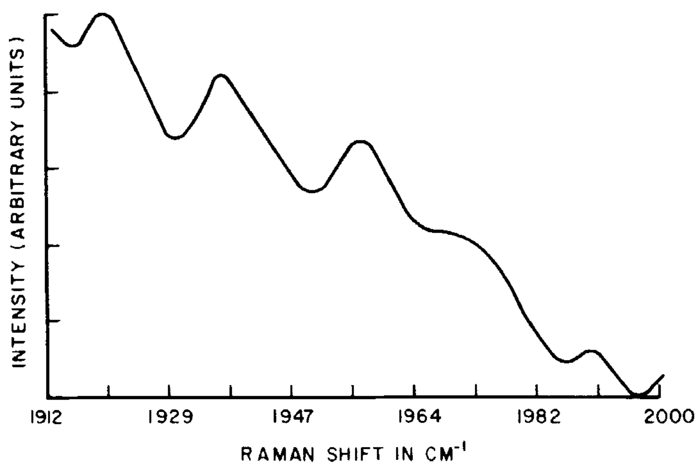

FIG. 3(a) The Raman spectrum in the region 1912-2000 cm^{-1} of CO adsorbed on Ni(111) after an exposure of a static 1-atmosphere ^{13}CO pressure + ^{12}CO (Residual Gas). T = $-122^{o}C$. The laser power is 2 Watts, 4880 Å. The slit widths = 300 μ and the count time is 20 seconds/step.

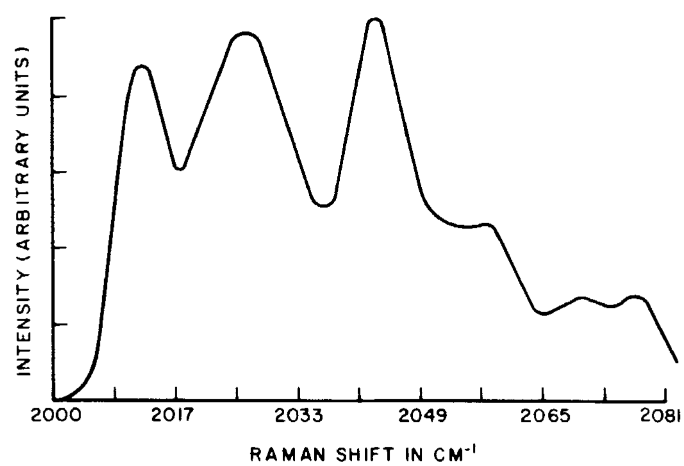

FIG. 3(b) The Raman spectrum in the region 2000-2081 cm^{-1} of CO adsorbed on Ni(111) after an exposure of a static 1-atmosphere ^{13}CO pressure of ^{12}CO (Residual Gas). T = $-122^{o}C$. The laser power is 2 Watts, 4880 Å. The slit widths = 300 μ and the count time is 20 seconds/step.

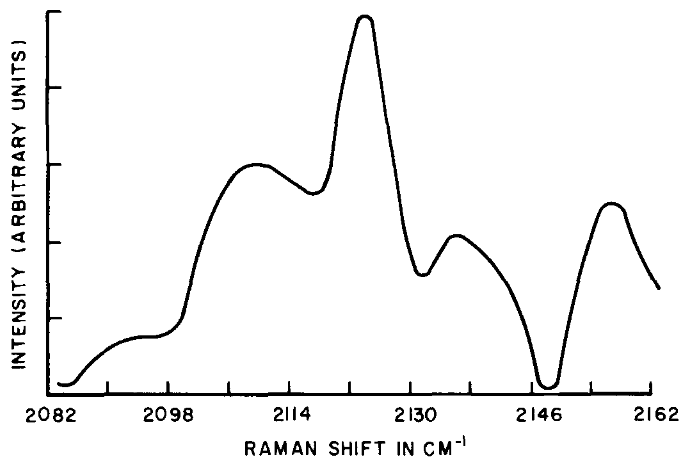

FIG. 3(c) The Raman spectrum in the region 2082-2162 cm^{-1} of CO adsorbed on Ni(111) after an exposure of a static 1-atmosphere ^{13}CO pressure + ^{12}CO (Residual Gas). T = -122^{o}C. The laser power is 2 Watts, 4880 Å. The slit widths = 300 μ and the count time is 20 seconds/step.

in this spectrum is that all ^{12}CO linear bands (2036 cm^{-1}, 2058 cm^{-1}, 2073 cm^{-1} and 2092 cm^{-1}) observed previously[1] and some of which were observed at 10^6L ^{13}CO exposure, as discussed in the previous section, have disappeared. On the other hand one observes bands at 1990 cm^{-1}, 2012 cm^{-1}, 2024 cm^{-1} and 2042 cm^{-1}. The estimated linear frequencies of the ^{13}CO species corresponding to the ^{12}CO linear species 2036 cm^{-1}, 2058 cm^{-1}, 2073 cm^{-1} and 2092 cm^{-1} are 1990 cm^{-1}, 2012 cm^{-1}, 2026 cm^{-1} and 2045 cm^{-1} in perfect agreement with the observed frequencies. Therefore, we readily conclude that at such high static pressure of ^{13}CO, the ^{13}CO species have displaced the linear ^{12}CO species.

The broad band at 2108 cm^{-1} (FWHM = 20 cm^{-1}) seen in Fig. 3 corresponds to the ^{12}CO band observed previously at 2110 cm^{-1}. In-the meantime this band may very well support another band namely, the ^{13}C-O stretch of ^{13}CO physisorbed on the sample. The physisorbed frequency of ^{12}CO on surfaces is expected to be little more or less than the 2143 cm^{-1} gaseous frequency. We observe a band at 2156 cm^{-1} if we assign this band to the physisorbed stretch of ^{12}CO its corresponding ^{13}CO would appear at 2109 cm^{-1}. Since we observe a band at 2108 cm^{-1} it is very possible to assign it to ^{13}CO species physisorbed on the sample as we mentioned above. The band at 2123 cm^{-1} could be that of ^{12}CO linear species with neighboring species not considered in our tentative model reported previously[1]. The band at 2135 cm^{-1} may be due to some sort of physisorbed ^{12}CO or very weakly chemisorbed.

2.2.2. CO Bridge Species

No band at 1967 cm^{-1} (±5 cm^{-1}) is observed in Fig. 3 therefore, the 2012 cm^{-1} band does not have an equivalent ^{13}CO band. No band at 1991 cm^{-1} (±5 cm^{-1}) is observed nor at 1947 cm^{-1} which would constitute its equivalent ^{13}CO counterpart. A band at 1957 cm^{-1} is observed which we assign to the ^{12}C-O stretch of bridge species pictured in a tentative model seen in section 2.3. This band was observed previously[1] at 1957 cm^{-1}. Its estimated ^{13}CO equivalent is 1914 cm^{-1} we observe a and at 1920 cm^{-1} in a good agreement. No band at 1980 cm^{-1} (±5 cm^{-1}) is observed, but its equivalent ^{13}CO band is estimated to be at 1935 cm^{-1}. A band at 1935 cm^{-1} is observed in a perfect agreement. This is assigned to the ^{13}C-O stretch of ^{13}CO species pictured in the tentative model seen in section 2.3.

2.2.3. Ni-C Stretch of CO On-top

A scan of the spectral region 340-525 cm^{-1} is shown in Fig. 4. This spectrum was taken at 153 K. We assign the band at 522 cm^{-1} to the Ni-^{12}C stretch of ^{12}CO species giving rise to a band at 2036 cm^{-1}. We do not observe this band here. This may be due to the weakness of that particular ^{12}C-O stretch as discussed above. The ^{13}C-O stretch equivalent to the 2036 cm^{-1} has been observed as a very weak band at 1990 cm^{-1} as expected and to this stretch we assign the Ni-^{13}C stretch observed at 507 cm^{-1}.

The band observed at 496 cm^{-1} we assign to the Ni-^{13}C stretch as it has fallen from the previously reported Ni-^{12}C stretch at 509 cm^{-1}. These correspond to the 2012 cm^{-1} and 2058 cm^{-1} bands of ^{13}CO and ^{12}CO species, respectively. The band observed at 476 cm^{-1} we assign to the Ni-^{13}C stretch as it has fallen from the previously reported Ni-^{12}C stretch at 483 cm^{-1}. These correspond to the 2024 cm^{-1} and 2073 cm^{-1} bands of ^{13}CO and ^{12}CO species, respectively.

We observe a band at 457 cm^{-1}. We believe that this may be the same band we observed before at 460 cm^{-1}. The corresponding ^{12}C-O stretch is the 2092 cm^{-1}. Even though we do not observe this stretch we observe its Ni-^{12}C stretch. The band observed at 448 cm^{-1} we assign to the Ni-^{13}C stretch as it has fallen from the previously reported Ni-^{12}C stretch at 460 cm^{-1}. These correspond to the 2042 cm^{-1} and 2092 cm^{-1} bands of ^{13}CO and ^{12}CO species, respectively.

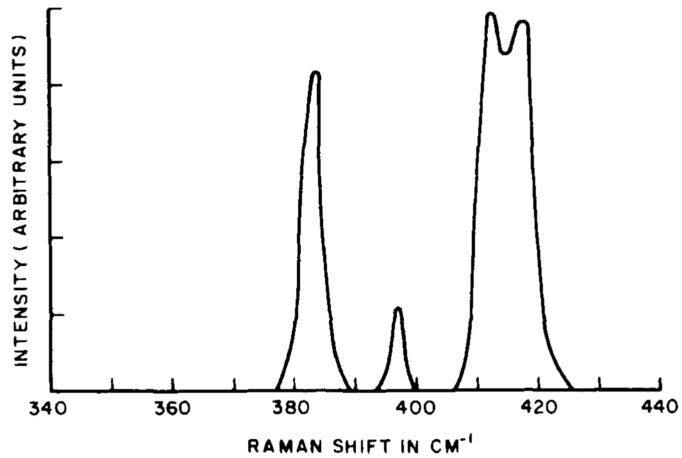

FIG. 4(a) The Raman spectrum in the region 340-440 cm^{-1} of CO adsorbed on Ni(111) after an exposure of a static 1-atmosphere ^{13}CO pressure + ^{12}CO (Residual Gas). T = $-122^{o}C$. The laser power is 2 Watts, 4880 Å. The slit widths = 300 μ and the count time is 20 seconds/step.

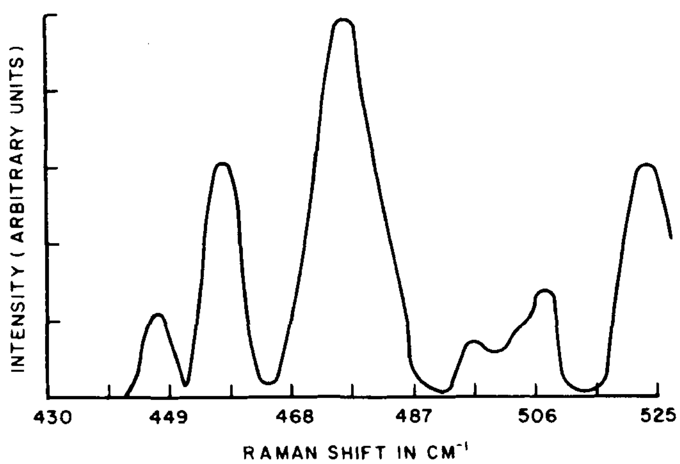

FIG. 4(b) The Raman spectrum in the region 430-525 cm^{-1} of CO adsorbed on Ni(111) after an exposure of a static 1-atmosphere ^{13}CO pressure + ^{12}CO (Residal Gas). T = $-122^{o}C$. The laser power is 2 Watts, 4880 Å. The slit widths = 300 μ and the count time is 20 seconds/step.

2.2.4. Ni-C Stretch of CO Bridge Species

The two bands at 2012 cm^{-1} and 1991 cm^{-1} which we discussed before briefly are now examined more closely in the light of their corresponding Ni-C stretch frequencies as follows:

(a) Had the 2012 cm^{-1} been due to ^{12}C-O stretch of ^{12}CO bridge species, its equivalent ^{13}C-O stretch should have been observed at 1967 cm^{-1} (±5 cm^{-1}). We observe a shoulder at 1970 cm^{-1}. Also its Ni-^{12}C stretch reported earlier at 362 cm^{-1} should have appeared, and its equivalent Ni-^{13}C stretch should have appeared at 350 cm^{-1}. We do not observe any bands at 350 cm^{-1} (±5 cm^{-1}) nor at 362 cm^{-1} (±5 cm^{-1}). This leads us to the following conclusions:

(1) the 2012 cm^{-1} band is a purely ^{13}C-O stretch equivalent to the 2058 cm^{-1} ^{12}C-O stretch.

(2) The 2012 cm^{-1} band is as in (1) plus it also represents ^{12}C-O stretch of ^{12}CO bridge species where the matching Ni-^{12}C stretch is unresolved for some reason.

(3) The 2012 cm^{-1} band is as in (2) plus it has equivalent ^{13}C-O stretch represented by the shoulder at 1970 cm^{-1}. The matching Ni-^{13}C is for some reason screened and unresolved. Since the 2012 cm^{-1} band is not a wide band we are inclined to assign it as in (1).

(b) Since we observe a band at 384 cm^{-1}, this is assigned as reported previously to the Ni-^{12}C stretch of ^{12}CO bridge species giving rise to the ^{12}C-O stretch at 1990 cm^{-1}. The equivalent Ni-^{13}C and ^{13}C-O stretches of this band should have been observed at 369 cm^{-1} and 1947 cm^{-1}, respectively. No bands were observed at these frequencies. Therefore, we conclude that the 1990 cm^{-1}, though weak, may have a dual nature

(1) Due to ^{13}C-O linear stretch corresponding to the 2036 cm^{-1} ^{12}C-O stretch

(2) Due to ^{12}C-O bridge stretch with no equivalent ^{13}CO bridge species.

The observed band at 418 cm^{-1} is assigned to the Ni-^{12}C stretch corresponding to the ^{12}C-O stretch 1957 cm^{-1}. Its corresponding Ni-^{13}C stretch is observed at 412 cm^{-1}.

2.3. Tentative Models

Two tentative models one for the linear on-top species and the other for the bridge two-fold species are shown in Fig. 5 and Fig. 6, respectively. Three sets of data are depicted on each model. These are as follows:

(1) The set of data showing the values of ^{12}C-O and the corresponding Ni-^{12}C stretches observed at 10^6L ^{12}CO exposure, at 98 K, on Ni(111) surface. This set is what we have reported previously[1], which is shown for comparison.

(2) The set of data showing the values of ^{13}C-O and the corresponding Ni-^{13}C stretches observed at 10^6L ^{13}CO expo-

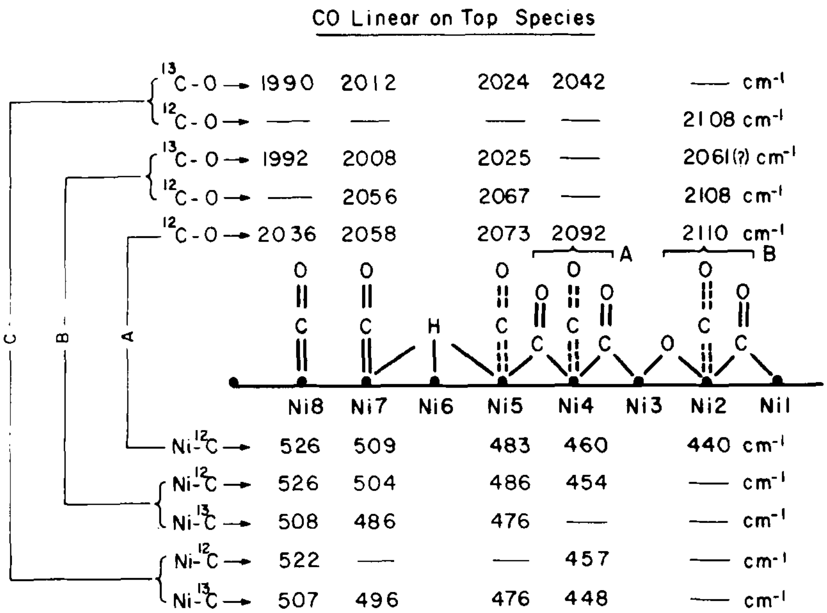

FIG. 5 A schematic showing a tentative model for the linear on-top ^{12}CO and ^{13}CO species coadsorbed on the Ni(111) surface with other CO species, oxygen and hydrogen atoms. Three different pressure conditions (A,B and C) are reported as shown on the schematic. Condition A represents what has been reported in a previous work [ref. 1] and is shown for comparison. Condition B represents adsorption due to 10^6L exposure of ^{13}CO (plus the ^{12}CO residual gas) on the Ni(111) surface at -170^{o}C. Condition C represents adsorption due to a static 1-atmosphere ^{13}CO exposure on the Ni(111) surface at -122^{o}C.

sure, at 98 K, on Ni(111) surface. Also showing these stretches due to ^{12}CO (Residual Gas).

(3) The set of data showing the values of ^{13}C-O and the corresponding Ni-^{13}C stretches observed at 1-atmosphere static pressure ^{13}CO exposure, at 151 K, on Ni(111) surface. Also showing these stretches due to ^{12}CO (Residual Gas).

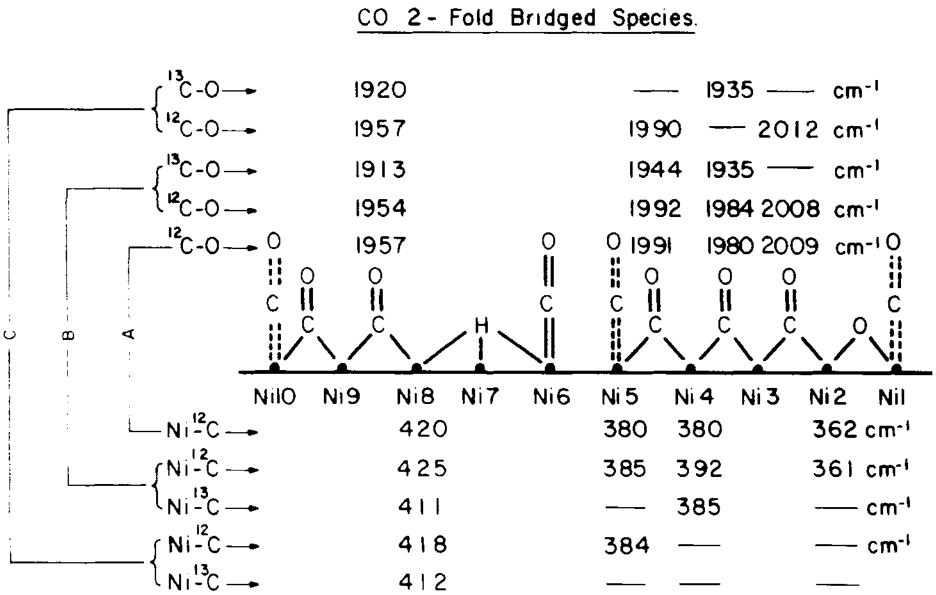

FIG. 6 A schematic showing a tentative model for the 2-fold bridged ^{12}CO and ^{13}CO species coadsorbed on the Ni(111) surface with other CO species, oxygen and hydrogen atoms. Three different pressure conditions (A,B and C) are reported as shown on the schematic. These three conditions are as explained in Figure's 5 caption.

Preliminary theoretical studies[3], using the EHMO method[4], suggest that when the CO molecule in the linear on-top configuration is attached a to 2-fold CO bridged molecule via a surface atom, the linear CO molecule must be inclined with some angle, θ, for the resultant configuration be stable. Therefore, broken lines are used to indicate that some angle of inclination is in order. A complete description of how these models were arrived at is given elsewhere[1].

3. Conclusion

It is shown that normal unenhanced Raman Spectroscopy can be used in observing Raman spectra from low-polarizability CO molecules adsorbed on Ni(111). The high resolution of Raman Spectroscopy has been utilized to advance independent confirmation of the observed Raman bands by the use of isotopic substitution. Also advantage has been taken of the ability of Raman spectroscopy to operate under high pressures to record CO Raman bands at 1-atmosphere pressure.

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