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VIBRATIONAL SPECTRA OF CARBON MONOXIDE CHEMISORBED ON ALUMINA-S--ETC(U)

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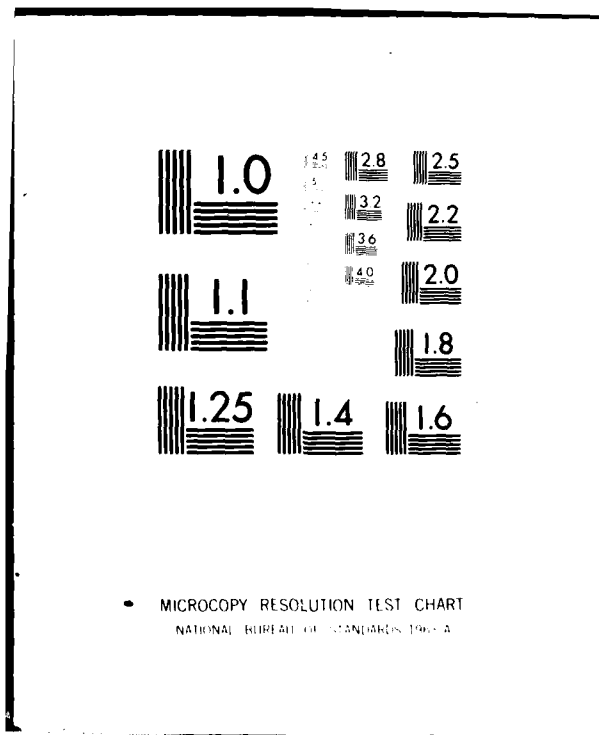
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⁶ Vibrational Spectra of Carbon Monoxide
Chemisorbed on Alumina-Supported Nickel Particles:
A Tunneling Spectroscopy Study

by

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Vibrational Spectra of Carbon Monoxide
Chemisorbed on Alumina-Supported Nickel Particles:
A Tunneling Spectroscopy Study

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ABSTRACT

Tunneling spectroscopy is used to study the chemisorption of CO on small nickel particles. The particles are grown from vapor on a thermally oxidized aluminum substrate. Carbon monoxide is observed to chemisorb in at least four distinct ways, giving CO stretching frequencies of 256.5, 246, 222 and 207 meV. The 256.5 meV species has low frequency modes at 45.5 and 59.5 meV. The low frequency modes of the remaining three species are not resolved sufficiently for identification. The frequencies of all modes were found to have some coverage dependence. The largest shift is seen in a CO stretching vibration that moves from 200 to 207 meV with increasing coverage. The effect of H₂ co-adsorption is examined and evidence for the presence of oxygen on the particles is presented. The reaction of the chemisorbed CO with H₂ on these nickel particles is found to produce very little surface hydrocarbon in contrast to results found previously for rhodium particles under similar conditions.

1. Introduction

Vibrational spectroscopy is a powerful tool for the investigation of the chemisorption of molecules on surfaces.¹ The complete vibrational spectrum of an adsorbate can give information on the adsorption site,² the structure³ and the orientation of the surface species.⁴ Comparisons between species can give further information as to relative bond strengths,⁵ the effects of co-adsorption of various species,⁶ and identify reaction pathways.⁷ For the chemisorption of CO on nickel the CO stretching vibration is evidence for non-dissociative adsorption. The comparison of stretching frequencies between species gives information about the number and types of adsorption sites.⁸ Vibrational spectra for the adsorption of CO on nickel has been obtained with both electrons⁹ and photons.¹⁰ The surfaces studied range from single crystal faces¹¹ to supported particles.¹² In this work inelastic electron tunneling spectroscopy¹³⁻²¹ is used to study the chemisorption of CO on alumina-supported nickel particles. Other recent applications of tunneling spectroscopy to problems in catalysis have included studies of CO adsorption¹⁷ and hydrogenation³ on alumina-supported Rh, CO adsorption on alumina-supported Fe,¹⁸ partial oxidation on alumina,¹⁹ chemisorption on alumina-supported Ag,²⁰ and supported-complex catalysts.²¹ The spectral range,²² sensitivity,²³ resolution²⁴ and selection rules²⁵ of tunneling spectroscopy allow the observation of new vibrational modes in this well-studied system in the low frequency region. Although the CO stretching mode is thought to be broadened and downshifted for modes with large dipole derivatives²⁶ at least four types of adsorption are observed in this region. One species, with vibrations at 256.5, 59.5 and 45.5 meV compares very favorably with the "on-top" species found in ELS experiments.²⁷ The low frequency modes of the remaining three species are found within the frequency range 40 meV to 70 meV, but are not resolved. The identification of linear vs. bridged adsorption is not attempted for these species other than to note that the assignment of an

assymmetric Ni-C stretch of a "ketonic" bridging species below 67 meV requires an unexpectedly small Ni-C force constant.²⁸ We find it interesting to note that the frequencies of two of these species, at 220-222 and 243-246 meV compare favorably with those found for CO on Ni (100) p (2x2) O, without correction for possible downshifts.²⁹ The co-adsorption of H₂ with CO on these particles causes the formation of OH groups, which also suggests that there is oxygen on the particles. The experiments with hydrogen and CO also show new vibrations at 510 and 80 meV. The mode near 80 meV has been reported in the literature;³⁰ the mode at 510 meV is due to H₂ in the junctions. Heating of junctions in H₂ is seen to form very little surface hydrocarbon.

II. Experimental Methods

The fabrication of tunneling junctions for inelastic electron tunneling spectroscopy involved four steps:

- a) the formation of a bottom electrode, usually aluminum;
- b) the oxidation of the bottom electrode to form an insulating barrier;
- c) the doping of the insulator surface with the substance to be studied;
- d) the completion of the tunneling junction with a top electrode, usually lead.

The details of steps a), b) and d) are well reported in the literature.¹³⁻¹⁶ Step c) will be discussed below. The electronics used for spectrum measurement have been previously discussed.²² The dopant in this work is small nickel particles formed by the evaporation of nickel wire from a tungsten filament. The particles are grown on the oxidized aluminum surface while it is held near 150K. This reduced temperature is necessary to obtain spectra without large background structure believed to be due to the formation of large particles.^{31,32} The size of the particles is also kept small by evaporating only small amounts of nickel as measured by a quartz microbalance. The spectra shown, with one noted exception, are for junctions with nickel loadings that correspond to approximately one monolayer. The size of the particles that form have not been measured directly, but by reference to previous work¹⁷ are expected to have diameters on the order of 10 Å.

The particles can be formed in ultra-high vacuum or in the presence of gases. The spectra shown, with one noted exception, are for nickel particles formed in pressures of CO, typically 10^{-3} Pa (7.5×10^{-6} ton). The spectra obtained are very sensitive to the temperature of the surface during the evaporation of the top lead electrode. After the top electrode is deposited, all junctions are warmed to room temperature prior to measurement at 4.2K.

III. Results

Figure 1 shows four spectra obtained from the chemisorption of CO on nickel particles. The nickel was given a saturation exposure of CO at 150K in each case followed by warming in vacuum to the following temperatures prior to the lead evaporation: a) 296K; b) 284K; c) 273K; and d) 250K. The CO is observed to desorb with increasing temperature. Spectrum d) has four chemisorbed species as evidenced by the four distinct CO stretching frequencies. Spectra c), b) and a) each have three, two and one, respectively. Junctions warmed more than 300K prior to completion have no chemisorbed CO. While it is not possible to resolve and assign each observed mode, some frequencies can be measured from figure 1. Spectrum a) contains peaks at 50.5 meV and 240 meV. The measureable frequencies of spectrum b) are 49.5 meV, a shoulder near 60 meV, 218 meV and 241 meV. The modes in spectrum c) are found at 48.5 meV, 58 meV, 65 meV, 200 meV, 219 meV and 242 meV. Finally, the frequencies of spectrum d) have a maximum at 50 meV in the low frequency region, with shoulders at 53 meV, 59 meV and 65 meV. The high frequency region has a new mode at 256.5 meV in addition to modes at 243 meV, 220 meV and a weak mode near 200 meV.

Figure 2 examines the temperature range from 225K to 273K for junctions formed as in figure 1 with the exception that the CO was not removed from the chamber prior to the lead evaporation. The transition from four chemisorbed species to three is still observed, but the frequencies are slightly shifted from figure 1 and all modes are more intense. The frequencies measured in figure 2 are:

- spectrum a) 50 meV, a shoulder near 60 meV, 205 meV 220 meV and 244 meV;
- spectrum b) a shoulder near 45 meV, 48.2 meV, shoulders at 52.8 meV, 59.2 meV and 65.9 meV CO stretching peaks at 206 meV, 221 meV, 245 meV and 255 meV;
- spectrum c) 45.5 meV, 53 meV, 59.5 meV, 207 meV, 222 meV, 246 meV and 256.5 meV.

Figures 3 and 4 show the spectra of a junction fabricated as in figure 2, trace c) that has been heated in vacuum after junction completion. The presence of the lead electrode is seen to give thermal stability to the chemisorbed species. The traces show the desorption of the adsorbed CO for heatings to 300K, 320K and 340K. Frequency shifts are again observed as the CO desorbs. The magnitudes and directions of the shifts are the same as measured in figures 1 and 2. Over all it is seen that the surfaces that have desorbed CO have frequencies lower than those with saturation exposures.

IV. Discussion

The chemisorption of CO on nickel surfaces has long been known to be complex.^{33,34} The observation of four distinct species in figures 1, 2 and 3 reflects this complex nature once again. The presence of many types of surface species complicates the interpretation of vibrational spectra. Identifications of species based on frequency comparisons between compounds instead of on vibrational analysis of complete vibrational spectra are subject to uncertainties and are often the subject of controversy. An example of this is the discussion of the assignment of CO stretching modes above $2,000\text{ cm}^{-1}$ as due to linear species and those below $2,000\text{ cm}^{-1}$ as due to bridging species.³⁵ Arguments both for³⁶ and against³⁷ this rule can be found in the literature based on frequency comparisons between compounds. As a result, we do not identify the three lowest species as to adsorption site. Assignments found in other works for similar spectra have identified the highest frequency as a linear species, and the lower frequencies as CO bonded on two-fold, three-fold and four-fold sites.³⁸

The species with vibrations at 265.5, 59.5, and 45.5 meV can be identified as a linear species. Confirmation of this identification is possible with isotopes; the two low frequency modes are predicted to shift as stretching and bending vibrations.³⁹ By comparison to ELS studies^{9,11,27} that see vibrations near 59.5 and 256.5 meV, with the assumptions that the dipole selection rule holds and that the species is perpendicular to the surface,⁴⁰ the 59.5 meV vibration should be the Ni-C stretching mode, and the 45.5 meV vibration the Ni-C≡O bending mode. This assignment is supported by tunneling studies with isotopes on the chemisorption of CO on other metals.^{17,18} Linearly adsorbed CO on Rh has bend/stretch vibrations at 51.6/70 meV and 58.1/73 meV for the two species observed.⁴¹ In both cases the bending frequency is found approximately 15 meV below the stretching frequency.

The identification of this linear species with the "on-top" species observed elsewhere leads to the comparison of observed peak positions and peak widths. In general tunneling spectra of CO stretching vibrations have been found to be downshifted from published I.R. frequencies.^{17,18} This downshift has been previously explained as an image dipole effect resulting from the presence of the top lead electrode.²⁶ The magnitude of the shift is predicted to vary with the square of the dipole derivative and inversely with the cube of the oscillator-electrode separation. The observed frequency of the linear CO stretching vibration on Ni is not appreciably downshifted from that reported in other studies. In addition, the width of the observed vibration is less than 4 meV, in contrast to the normally observed widths of 10-12 meV. While at present we cannot distinguish between a smaller than normal dipole derivative and a larger than normal lead-molecule distance, it is interesting to note that W. Erley et al.²⁷ find the dynamical dipole moments for this species to be three times smaller than those of another species Ni. This would imply nine times smaller peak downshifts.

The failure to resolve the low frequency modes of the remaining species prevents reliable assignments as to their linear or bridging nature. This is a disappointment because tunneling spectroscopy is theoretically able to resolve the controversy between linear and bridged adsorption. While it is possible that future work may yet resolve the low frequency modes, at present the most that can be reliably obtained from the spectra is an upper limit on the frequencies involved. Figure 4 shows the low frequency region from 30 to 100 meV. No modes are observed above 67 meV. This restricts the Ni-C force constant possible for a "ketonic" bridging species. Calculations by N.V. Richardson and A.M. Bradshaw²⁸ indicate that an "asymmetric stretching" frequency below 67 meV requires a Ni-C force constant of approximately half that of the linear species.

There is some question in the literature as to the presence of a mode near 81.5^{27,28,30} meV. As discussed above, we do not see a mode in this region for the

chemisorption of CO. We do see a mode near 80 meV for surfaces exposed to hydrogen. Figure 5 shows the spectra resulting from the CO adsorption of H₂ and CO (spectra b, c, d) and D₂ and CO (spectrum a). In these experiments the surface was exposed to approximately 1 L of CO after Ni particle formation in vacuum. Following CO exposure the surface was given a saturation exposure to hydrogen. The surfaces exposed to H₂ have a broad vibrational mode near 80 meV in addition to a mode at 50 meV with shoulders at 43 and 60 meV and at least two CO stretching modes.

These spectra with H₂ have a mode at 510 meV. This mode downshifts to 266 meV with the substitution of D₂ for H₂. We identify this species as molecular hydrogen present in the tunneling junctions. We do not know whether or not it is chemisorbed on the Ni surface; it is possible that it is physically trapped in the junction after desorbing from the Ni particles. We note, however, that junctions without Ni particles in these experiments do not have the H₂ vibrations.

Figure 5 also shows the formation of OH (OD) groups on the surface. Oxygen is present on the alumina surface in OH groups prior to Ni particle formation. During the Ni evaporation the OH groups on the oxide surface are destroyed. The growth of OH groups with exposure to H₂ and OD groups with exposure to D₂ could be due to oxygen present on the particles reacting with the hydrogen. This indication of oxygen on the Ni surface suggests that the tunneling frequencies should be compared to those of surfaces with oxygen. S. Anderson²⁹ has found that CO adsorbed on Ni(100) p (2 x 2) 0 gives CO stretching frequencies of 220 meV and 245 meV, frequencies close to those of this work. The uncertainty in frequency measurement due to possible dipole shifts, however, still needs to be resolved.

Finally, completed junctions with CO chemisorbed on Ni particles were heated in H₂. Similar experiments with Fe, Co and Rh have formed hydrocarbons from the CO. Figure 6 shows the spectra of a junction prepared with three times the previous Ni loading both before and after heating. Junctions with less Ni

form no detectable hydrocarbons upon heating. Junctions with this increased amount of Ni have more CO adsorbed as the lower CO stretching frequency species. The low frequency band maximum is at 58 meV. After heating to 425K very little surface hydrocarbon is formed. This is in contrast to similar work with Rh particles,³ in which a C₂ species readily forms upon heating. This is consistent with the greater selectivity of Ni catalysts for methanation.³¹⁻⁴²

V. Conclusions

- 1) CO chemisorbs on alumina-supported Ni particles in at least four distinct ways.
- 2) One of these species has low frequency modes at 45.5, 59.5 meV and a CO stretching frequency of 256.5 meV. It is identified as a linear species.
- 3) The identification of any of the other three species as a "ketonic" bridging CO species requires a Ni-C stretching force constant no more than one-half the strength of the Ni-C force constant of the identified linear species.
- 4) All frequencies vary with the amount of CO coverage of the surface. Higher frequencies are observed for surfaces with saturation coverages.

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Figure Captions

Figure 1. Tunneling spectra of CO chemisorbed on alumina-supported nickel particles. The four spectra show the order of desorption of the four chemisorbed species as the temperature of junction fabrication is raised. The junctions were completed at the following temperatures:

a) 300K; b) 285K; c) 273K; d) 250K.

Figure 2. Spectra showing the correlation of the peaks at 44.5 meV and 59.5 meV with the high frequency CO stretch at 256.5 meV. The loss of this species with increasing temperature of junction fabrication is accompanied by the growth of a species seen at 50 meV and 244 meV. The junctions were completed at the following temperatures:

a) 273K; b) 250K; c) 225K.

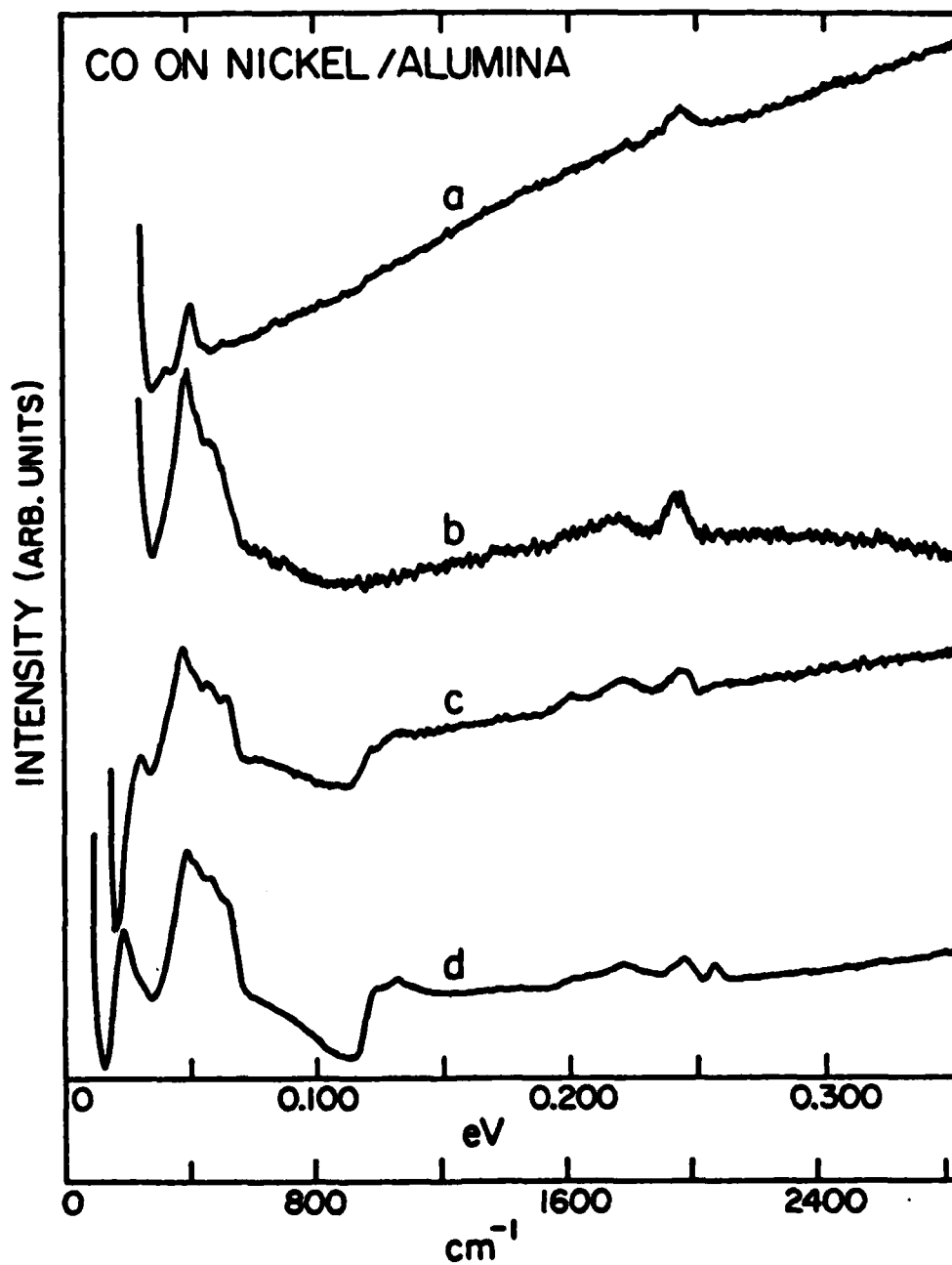
Figure 3. Spectra showing the desorption of the chemisorbed CO with increasing temperature for a completed junction. The thermal stability of all four species is greatly increased by the presence of the top Pb electrode. This junction was fabricated at 225K, and subsequently warmed to 300K, 320K, and 340K. Note the downshifts in the frequency of the CO stretch modes after warming (and the resultant desorption of some CO). All spectra were taken at 4.2K with a modulation voltage of 2 meV. The indicated instrumental resolution is 3.9 meV.

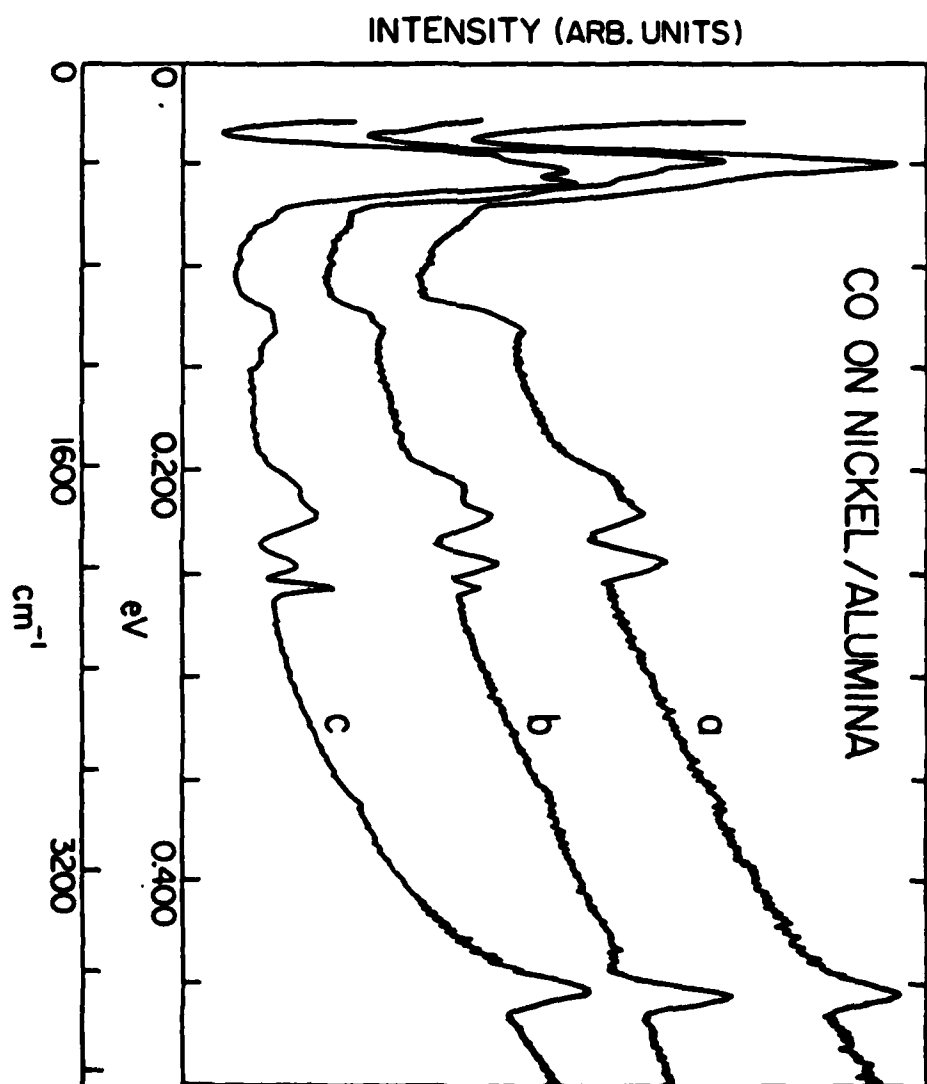
Figure 4. The low-frequency region is shown to contain many overlapping vibrations from approximately 43 meV to 67 meV. No vibrations due to CO have been observed in the frequency range 67 meV - 110 meV, in which a ketonic-like bridging species is expected to have a Ni-C (mostly anti-symmetric) stretching vibration.²⁸ Spectra were taken from the junction used in figure 3, but with a reduced modulation voltage of 1 meV. The indicated instrumental resolution is 2.6 meV.

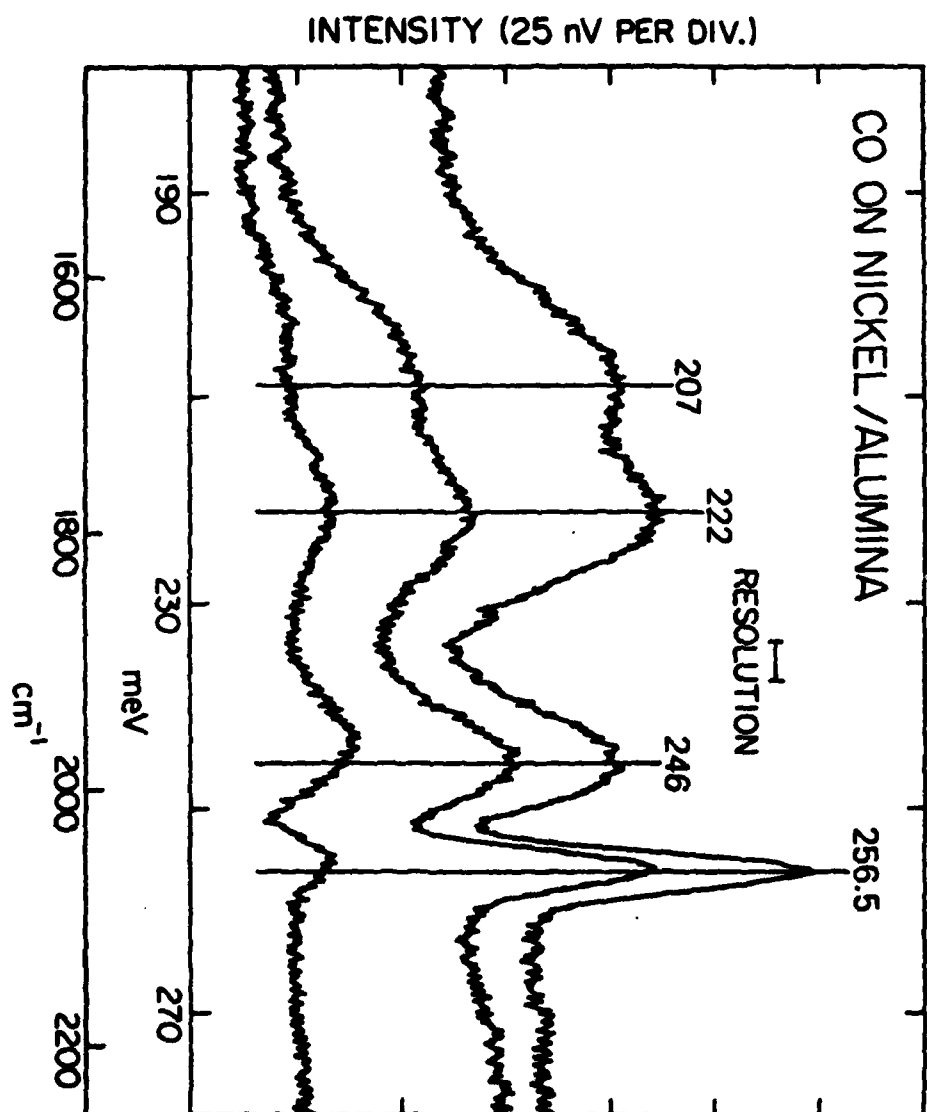
Figure 5. The addition of hydrogen to a nickel surface preexposed to 1 L of CO yields vibrations at 510 meV for H₂ and 266 meV for D₂. The presence of H₂ also produces a peak of 450 meV due to OH groups and a peak near 80 meV possibly due to hydrogen. The temperatures of junction completion are:

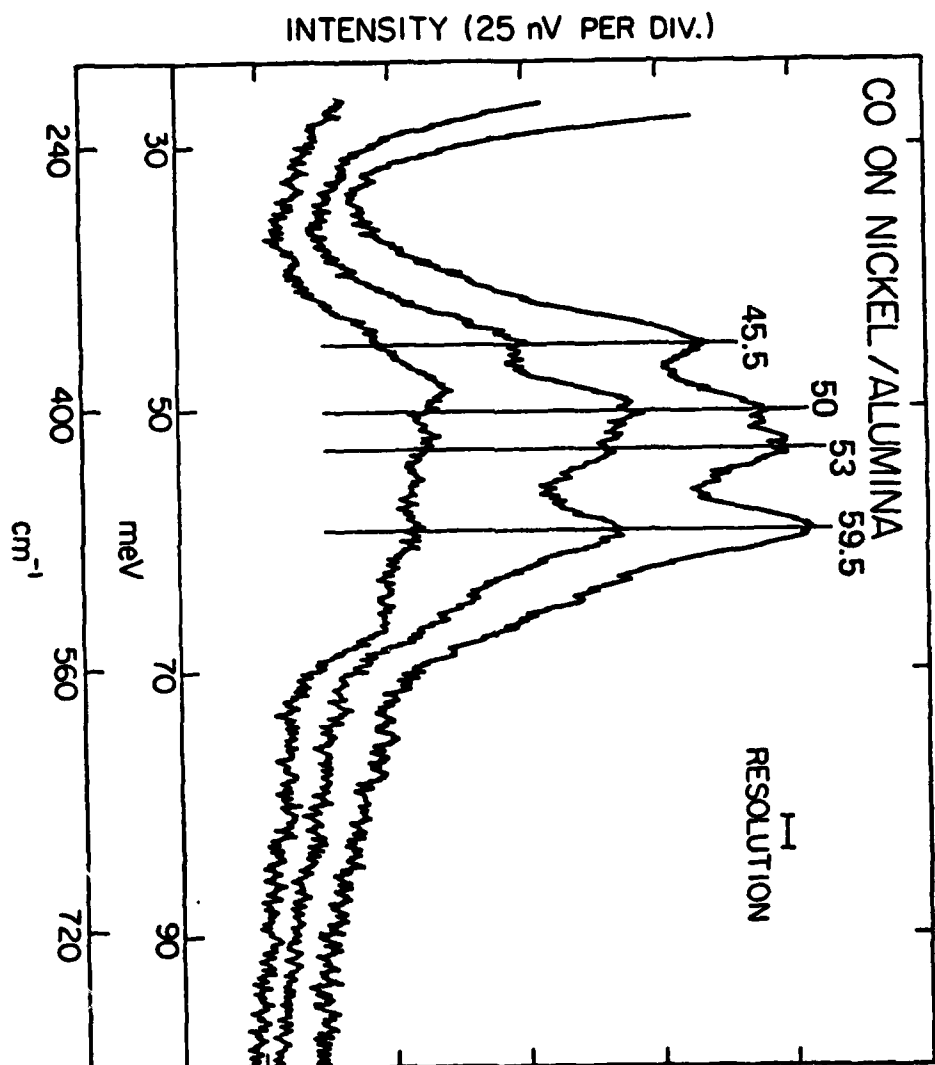
a) 273K; b) 273K; c) 280K; and d) 290K.

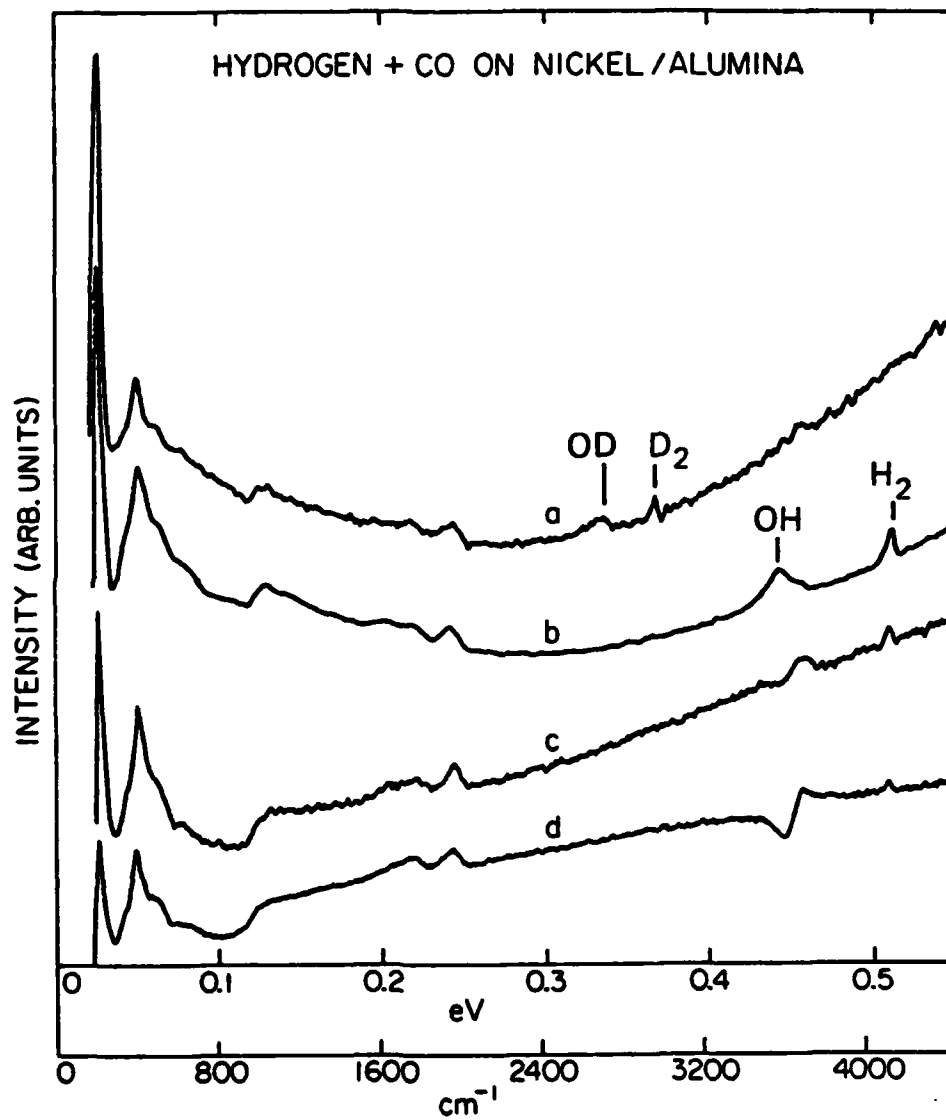
Figure 6. It is possible to form hydrocarbons from chemisorbed CO by heating completed junctions in H₂. Here a junction prepared with CO mostly chemisorbed as the lower CO stretching-frequency species is shown before and after heating. We note that the low frequency modes in the unheated spectrum are not resolved, but give a broad band with a maximum at 58 meV. Upon heating the CO forms very little surface hydrocarbon as evidenced by the very weak CH stretching modes seen at 365 meV. This is in contrast to similar work done with rhodium, in which a C₂ surface species easily forms upon heating.³

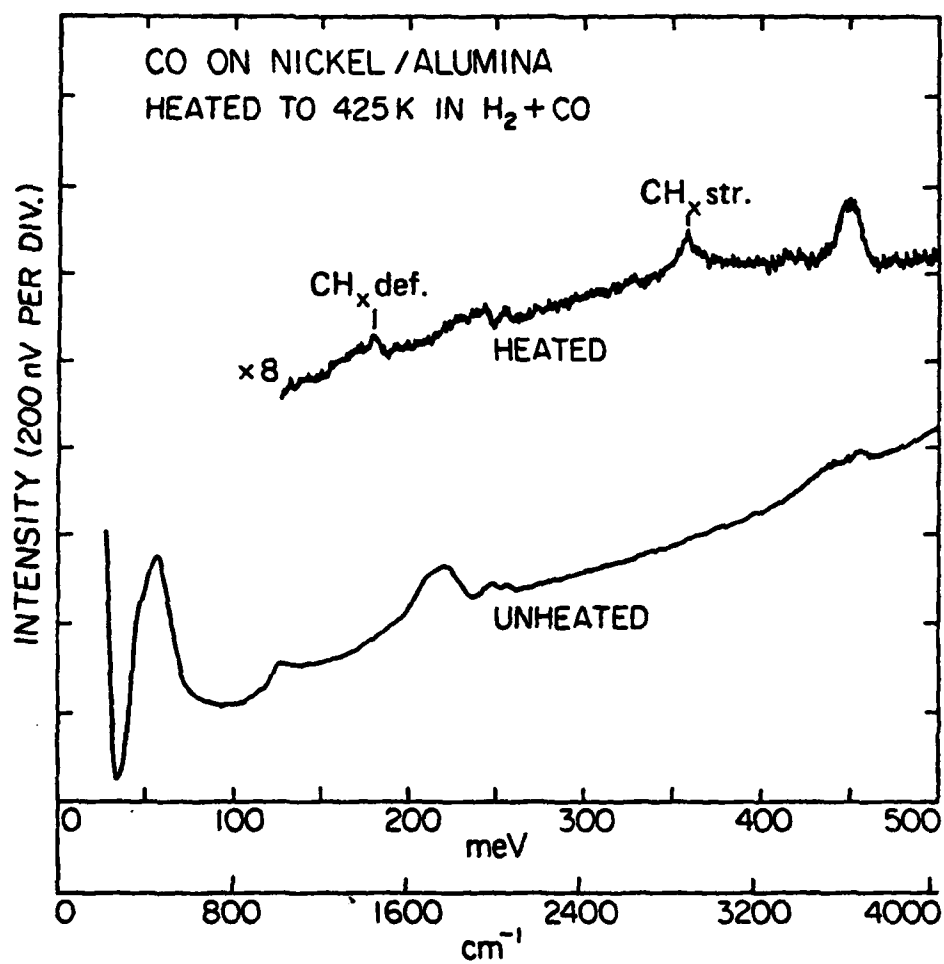












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