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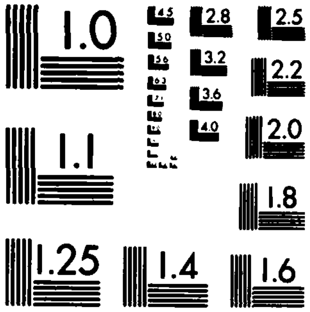

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The interaction of methanol with Pd(111) has been studied using high resolution electron energy loss spectroscopy (HREELS). We find both a chemisorbed and a physisorbed phase on the surface at 140K. Desorption of the physisorbed phase occurs by 160K and approximately 90% of the chemisorbed layer desorbs by 300K. Exposure to methanol at 300K causes dissociation to chemisorbed CO. Decomposition of chemisorbed methanol to a methoxy species occurs near 200K in the presence of a preadsorbed p(2x2) oxygen layer whereas no methoxy is detected on the clean surface. Further dehydrogenation to CO is observed by

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300K on the oxidized surface.

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Technical Report No. 6

# METHANOL ADSORPTION AND DECOMPOSITION ON CLEAN AND OXIDIZED PALLADIUM (111)

by

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25 March 1983

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## Abstract

The interaction of methanol with Pd(111) has been studied using high resolution electron energy loss spectroscopy (HREELS). We find both a chemisorbed and a physisorbed phase on the surface at 140K. Desorption of the physisorbed phase occurs by 160K and approximately 90% of the chemisorbed layer desorbs by 300K. Exposure to methanol at 300K causes dissociation to chemisorbed CO. Decomposition of chemisorbed methanol to a methoxy species occurs near 200K in the presence of a preadsorbed p(2x2) oxygen layer whereas no methoxy is detected on the clean surface. Further dehydrogenation to CO is observed by 300K on the oxidized surface.

## I. Introduction

The interaction of alcohols with single crystal metal surfaces has received much attention in the last ten years (1,2). Alcohol-like intermediates are believed to be involved in Fischer-Tropsch synthesis reactions (3). Decomposition of alcohols on metal surfaces form such products as formaldehyde, carbon dioxide, and methyl formate (1).

Studies on Cu(110) (4) and Ag(110) (5) first identified a methoxide ($CH_3O$-) intermediate in methanol decomposition under the conditions of a single crystal substrate and an ultrahigh vacuum. Since then, methoxy has been identified using high resolution electron energy loss spectroscopy (HREELS), ultraviolet photoemission spectroscopy (UPS), and other methods on Ni(111) (6), Cu(100) (7), Pt(111) (8), and Ni(100) (9). The relatively high stability of this intermediate on copper and silver has been related to the high selectivity for formaldehyde formation on these surfaces (7). Sexton (8) has suggested that methoxy stability is higher on surfaces with low heats of adsorption of CO and $H_2$. One important component in most of the above mentioned studies (4,5,7,8) is that preadsorbed oxygen enhances the stability of the methoxy intermediate presumably by offering a mechanism, $H_2O$ formation, for the removal of the hydroxyl hydrogen atoms (1).

Studies on palladium surfaces are motivated by reports that this metal can catalyze methanol formation from carbon monoxide and hydrogen with high efficiency under certain conditions

(10,11). Fajula, et al. (11) found that while the competing methanation reaction is dependent on the catalytic support, methanol formation is dependent on the adsorption properties of the metal crystallites. Methanol adsorption has been studied with UPS on polycrystalline Pd foils (12) and with UPS, thermal desorption spectroscopy (TDS), low energy electron diffraction (LEED), HREELS, and work function measurements on clean Pd(100) (13). While the latter work contains more detail, results indicate that at low temperatures methanol adsorbs "intact" and then mainly desorbs by 300K.

We have studied the interaction of methanol with clean and oxidized Pd(111) surfaces using HREELS over a wide temperature range. In agreement with the previous investigation on Pd(100) (13), we find that methanol chemisorbs at low temperatures (~140K) and then mostly desorbs from the surface by 300K. Methanol exposure at 300K results in dissociative adsorption in the form of CO and H as reported on Pd foils (12). The presence of preadsorbed oxygen, however, allows the formation of a methoxy species near 200K. This species then decomposes to adsorbed CO by 300K.

## II. Experimental Methods

Experiments were performed in a stainless steel, ion-pumped ultra-high vacuum system (base pressure $10^{-10}$ Torr (1 Torr = 133.3 $Nm^{-2}$)). The chamber is equipped with Varian LEED/Auger electron optics, a UTI quadrupole mass spectrometer, and an ion bombardment gun in addition to the high resolution electron spectrometer. The spectrometer is a cylindrical 127° monochromator and analyzer system described elsewhere (<u>14</u>). A beam energy of 3.3 eV was used to maximize the signal. Resolution varied between 70 and 90 $cm^{-1}$ throughout the experiment. Initially, spectra were obtained after the sample cooled to less than 150K. However, this was found to give misleading results due to the combination of background methanol gas in the vacuum chamber and the long cool-down time (~30 min). As noted below, fast (~10 min.) scans of the spectrum immediately after heating gave more accurate results. All spectra were observed repeatedly and frequency values given here were reproducible within 10 $cm^{-1}$. (The exception is the broad OH stretching band on the oxidized surface which has an uncertainty of 18 $cm^{-1}$.)

The palladium sample was cut to within 1/2° of the (111) surface from a single crystal cylinder ~1 $cm^2$ in diameter and polished down to 0.25μ grit size using standard crystallographic techniques. A tungsten filament mounted behind the sample was used for heating. Cooling was accomplished with liquid nitrogen. A chromel-alumel thermocouple was mounted on the sample holder next to the crystal. During the experiment, thermocouple readings were held constant for five minutes to assure that the crystal surface reached the desired temperature. Initial cleaning of the Pd(111) sample was described elsewhere (<u>14</u>). Routine cleaning consisted of 500 eV argon ion bombardment and annealing to ~600°C.

Vapor pressure reagent grade $CH_3OH$ and $CD_3OD$ were used. The purity was checked with the mass spectrometer through comparison with the known cracking pattern of methanol (15). Sample dosing occured through a leak valve into the main vacuum chamber. Pressure readings during methanol exposure were divided by 1.9 to correct for ion gauge sensitivity (16).

## III. Results

### A. Interaction of $CH_3OH$ and $CD_3OD$ with clean Pd(111)

Vibrational spectra obtained from exposure of Pd(111) to methanol and deuterated methanol are shown in Fig. 1. Saturation coverage could be attained at 140K and resulted in the lower curves (c,f). We typically used a 30L ($1L = 10^{-6}$ Torr-sec) exposure although HREELS spectra did not change after ~5L. Frequency values and assignments are tabulated along with those of liquid phase methanol (17) in Table 1. The close agreement indicates that a condensed layer exists on the palladium surface at this temperature. The vibrational spectrum of vitreous solid methanol (18) is very similar to that of the liquid phase. Both spectra are characterized by broad OH stretching and out-of-plane bending bands resulting from hydrogen bonding. These features are also evident in Fig. 1c and f. The OH stretching frequency on palladium is close to the liquid phase value and 100 $cm^{-1}$ higher than in the solid phase. Observation of the LEED pattern showed that since increased exposure intensifies the background but produces no new features, methanol does not form a long range ordered structure on Pd(111).

Heating the condensed layer to 160K leaves a chemisorbed monolayer (Fig. 1b,e). Similar spectra resulted from a 1L exposure at 140K as seen in Fig. 1a and d. The appearance of OH and $CH_3$ stretching modes, a $CH_3$ deformation mode, and a CO stretching mode indicate that methanol is associatively chemisorbed on Pd(111). Frequency values and assignments are given in Table 2 along with corresponding data on the oxygen-covered surface referred to in the next section.

We also exposed the clean Pd(111) surface to methanol at 300K with results shown in Fig. 2. In this case, methanol dissociates to CO upon adsorption as evidenced by characteristic modes at 1822 $cm^{-1}$ ($\nu_{CO}$) and 329 $cm^{-1}$ ($\nu_{CM}$). This species desorbs at 450-500K in good agreement with TDS studies of CO on palladium (19). Decomposition to adsorbed CO at 300K is also in agreement with UPS results on polycrystalline Pd (12). Surface hydrogen, although expected from TDS data on other surfaces (13,20,21), is not detected in our spectra. Hydrogen adsorption on clean Pd(111) results in a weak mode near 450 $cm^{-1}$ at low temperatures (~150K). At higher temperatures hydrogen occupies subsurface sites (22) and the HREELS spectrum is too weak to observe.

As seen in Fig. 2a, heating low temperature chemisorbed methanol past ~200K causes most of the surface species to desorb. Preliminary data erroneously indicated dissociation of the surface species to CO at higher temperatures. However, by recording fast spectra (~10 min) without waiting for the sample to cool, we found that most, if not all, of the observed CO was derived from background methanol in the chamber. After heating, we continuously observed the vibrational spectra until the sample was below 150K. The peak near 1800 $cm^{-1}$ reached a maximum intensity and then chemisorbed methanol features appeared at lower temperatures.

## B. Interaction of $CH_3OH$ and $CD_3OD$ with Pd(111)-p(2x2) 0

The bottom curves (d and h) in Fig. 3 show the vibrational spectrum of an 8L exposure to $O_2$ at 300K. This corresponds to p(2x2) LEED pattern ($\theta = 0.25$) in agreement with Conrad, et al. (23). Oxygen dissociatively adsorbs at 300K giving an oxygen-metal stretching frequency at 475 $cm^{-1}$. The oxygen atoms are believed to occupy the threefold hollow sites on the (111) surface (23).

Saturation coverage of methanol and deuterated methanol on the oxygen-covered surface at 140K exhibits the vibrational spectra shown in Fig. 3c and g. Comparison with Fig. 1 shows that an oxygen layer inhibits condensation, but not chemisorption. We note that the strong loss at 520 $cm^{-1}$ (Fig. 3c) appears to be a composite of the atomic oxygen-metal stretch at 475 $cm^{-1}$ and the methanol bending mode near 578 $cm^{-1}$ (Fig. 1b). There is a significant shift and broadening in the OH stretching region in the presence of oxygen. Frequencies and assignments for chemisorbed $CH_3OH$ and $CD_3OD$ are given in Table 2.

Dissociation to methoxy occurs by 200K (Fig. 3b,f) as indicated by several characteristic spectral changes. The OH stretching mode has disappeared and a metal-oxygen mode has appeared at 302 $\text{cm}^{-1}$. The high intensity CO stretching mode (1041 $\text{cm}^{-1}$) suggests that this bond is close to perpendicular to the surface. Some atomic oxygen remains on the surface giving rise to the loss at 479 $\text{cm}^{-1}$. Frequency data for the methoxy species are enumerated in Table 3.

By 300K, the surface species is CO (Fig. 3a,e). These spectra were obtained, as explained in the last section, immediately after heating. It is clear that atomic surface oxygen provides a mechanism for the formation of CO from adsorbed methanol, via a methoxy intermediate.

## IV. Discussion

Christmann and Demuth (13) conducted a detailed study of methanol adsorption at low temperatures on Pd(100). They were able to distinguish the first physisorbed layer from subsequent layers by slightly different desorption temperatures of ~145K and ~142K. We associate the condensed spectra of Fig. 1c and f with this first physisorbed layer for several reasons. First, we adsorbed near the desorption temperature of condensed methanol on both Pd(100) (142K) (13) and Pt(111) (140K) (8). Second, we observe saturation of the condensed phase. On Cu(100) (7), there is a continuous degradation of the HREELS elastic beam intensity with increased methanol exposure at 100K. We observed no change after ~5L. Substrate LEED features eventually disappear with increased condensation on Pd(100) at 77K (13), but not on Pd(111) at 140K. Finally, we did not obtain a physisorbed phase in the presence of preadsorbed oxygen, an effect which is not expected under conditions favorable to multilayer formation (7,8).

In Table 4, we have compared the vibrational frequencies of chemisorbed methanol on several substrates. UPS work has shown that methanol is weakly chemisorbed via the oxygen lone-pair orbital on Ni(111) (20), Pd(100) (13), polycrystalline Pd (12), and Cu(110) (4). The close agreement in vibrational frequencies indicates the same bonding scheme on Pd(111). While we did not carry out quantitative work function measurements, we did find it necessary to apply a negative potential to the crystal to compensate for the work function decrease due to the chemisorbed layer. This also supports a bonding model placing the negative (oxygen) end of the molecule closest to the surface.

We should point out that Christmann and Demuth (13) reported the formation of methoxy at low temperature for very low $CH_3OH$ exposures (~0.05L) on Pd(100). We found the effects of such low coverages very difficult to reproduce in our system. Peaks in the $CH_3$ and OH stretching regions of the spectrum were not visible above background. However, we did find a loss peak near 300 $cm^{-1}$ which may be the oxygen-metal bond mode in methoxy, but we cannot confidently eliminate the role of surface defects in the formation of this species.

As on Pt(111) (8), Cu(100) (7), Cu(110) (4), and Ag(110) (5), we find that surface oxygen stabilizes methoxy on Pd(111). This species remains on Ag(110) (5), Cu(100) (7), and Cu(110) (4) at temperatures in excess of 400K whereas decomposition to CO and $H_2$ occurs by 300K on platinum (8) and palladium. It has been suggested that the stability of methoxy is related to a low heat of adsorption of CO and $H_2$ (8). The only exception to this has been the observation of methoxy at 300K on Ti(001) (24).

Wachs and Madix have confirmed that surface oxygen removes the hydroxyl hydrogen from methanol to form water on Cu(110) (4) and Ag(110) (5). Likewise, water is observed to desorb from Pt(111) after methoxy formation (8). We find that methanol reactions with Pd(111) are similar to Pt(111) in that methoxy can only be identified on the oxygen-covered surface after heating chemisorbed methanol to 170-200K. Higher temperature behavior with and without adsorbed oxygen is also analogous on the two substrates. Therefore, it is likely that water formation accompanies methanol dehydrogenation on Pd(111). Our inability to observe chemisorbed $H_2O$ in our vibrational spectra could be for two reasons. First, desorption of water may occur before 200K since it desorbs from Pt(111) ~190K (8). However, our spectra seem to change continuously from 140-200K with no indication of a different species. Second, vibrational modes of water may be much weaker than methoxy modes on Pd(111). This is indeed the case with platinum (111) on which water adsorption has been studied using HREELS (25). A similar study on Pd(111) would be instructive on this point since it is conceivable that although we do not see an OH stretching vibration in Fig. 3b, the peak at 770 $cm^{-1}$ is in close agreement with the stronger water libration mode on Pt(111) (25).

It is interesting to note that the only significant difference between the vibrational spectra of chemisorbed methanol on clean and oxygen-covered Pd(111) surfaces (Figs. 1a, 3c) is in the OH stretching region. The shift and broadening of this mode in the presence of oxygen shows that there is hydrogen bonding between oxygen and hydroxyl hydrogen atoms prior to complete cleavage of the OH bond. Similar behavior of CH stretching modes has been associated with higher temperature CH bond breaking in other systems (8,26).

Heating chemisorbed methanol on the clean surface resulted primarily in desorption on Pd(100) (13), Pt(111) (8), and Cu(100) (7). About 5% of the methoxy observed on the oxygen-covered surface is formed on clean Cu(100) after heating physisorbed methanol ice (7). Near 200K, desorption claims an estimated 80% and >90% of the monolayer coverage on Pd(100) (13) and Pt(111) (27), respectively. From published spectra, it appears that similar results were found on Ni(111) (6,20). Except for Cu(100), where methoxy is stable at high temperatures (7), the primary decomposition product of the remaining surface species is CO (6,8,13). We also find that most, if not all, of the chemisorbed monolayer on Pd(111) desorbs by 300K. We do not detect any species other than CO on the surface at this temperature (Fig. 2). As mentioned earlier, a problem with $CH_3OH$ and CO background pressure (even at chamber pressures below $10^{-9}$T) prevented us from quantifying small changes in the intensity of the CO stretching mode. By assuming an efficient decomposition of methoxy to CO on the oxygen-covered surface, we estimate that no more than 10% of the original chemisorbed monolayer decomposes to CO by 300K on the clean surface. A similar problem with background methanol pressure was reported by Hanson, et al (24).

In conclusion, we find that at 140K methanol forms both chemisorbed and physisorbed layers on Pd(111). The weak chemisorption bond is through the oxygen lone-pair orbital. This bond is not specific to the substrate as seen in the agreement between vibrational frequencies on different substrates (Table 4). A methoxy intermediate can be formed at 200K in the presence of surface oxygen probably via the mechanism first proposed by Wachs and Madix (4):

$$2(CH_3OH)_{ads} + (O)_{ads} \rightarrow 2(CH_3O)_{ads} + (H_2O)_{ads}$$

Complete dehydrogenation of methoxy to CO occurs by 300K as observed on other group VIII elements (6,8). On the clean Pd(111) surface, methanol desorbs at a lower temperature than required for decomposition. At higher temperatures, gaseous methanol does dehydrogenate to adsorbed CO on Pd(111) as on Pd(100) (13). Therefore, surface oxygen makes decomposition of the adsorbed species possible.

## V. Acknowledgment

This work was supported by the Office of Naval Research.

Table 1. Vibrational frequencies (±10 $cm^{-1}$) of condensed methanol on Pd(111) at 140K. Liquid phase values are from ref. 17.

| Assignment | Liquid | Condensed $CH_3OH$ | Condensed $CD_3OD$ | ratio |
|---|---|---|---|---|
| OH stretch | 3328 | 3320 | 2494 | 1.33 |
| $CH_3$ deg. stretch | 2980<br>2946 | 2950 | 2224 | 1.33 |
| $CH_3$ sym. stretch | 2834 | 2836 | 2107 | 1.35 |
| $CH_3$ deg. deform. | 1480 | 1446 | 1080 | 1.34 |
| $CH_3$ sym. deform. | 1450 | | | |
| OH in plane bend | 1418 | | | |
| CO stretch | 1030 | 1012 | 973 | 1.04 |
| $CH_3$ asym. rock | 1165 | ~1120[b] | 828 | 1.35 |
| $CH_3$ sym. rock | 1115 | | | |
| OH out of plane bend [a] | 655 | 694 | 511 | 1.36 |
| CO torsion | | | | |

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[a] mixed mode (28).

[b] weak shoulder.

Table 2. Vibrational frequencies (±10 $cm^{-1}$) and approximate mode assignments of chemisorbed methanol on Pd(111) with and without preadsorbed oxygen. Values correspond to 1L exposure to methanol. Oxygen exposure is 8L.

| Assignment | $CH_3OH$<br>($CD_3OD$) | ratio | $O_2/CH_3OH$<br>($O_2/CD_3OD$) | ratio |
|---|---|---|---|---|
| OH stretch | 3355<br>(2482) | 1.35 | 3250(b)<br>(2430(b)) | 1.34 |
| $CH_3$ deg. stretch | 2948<br>(2219) | 1.33 | 2941<br>(2201) | 1.34 |
| $CH_3$ sym. stretch | 2825[b]<br>(2094) | 1.35 | 2823[b]<br>(2085) | 1.35 |
| $CH_3$ deg. deform.<br>$CH_3$ sym. deform.<br>OH in plane bend | 1438<br>(1077) | 1.34 | 1444<br>(1090) | 1.32 |
| CO stretch | 1008<br>(963) | 1.05 | 1023<br>(976) | 1.05 |
| $CH_3$ asym. rock | ~1110[c]<br>(821) | ---- | ----<br>(~800[c]) | |
| $CH_3$ sym. rock | 806<br>(588) | 1.37 | 854<br>(617) | 1.38 |
| OH out of plane bend<br>CO torsion [a] | 585<br>(437) | 1.34 | 520<br>(464) | --- [d] |

[a] mixed mode. The other such mode is predicted to be at 173 $cm^{-1}$ in crystalline methanol (28).

[b] shoulder.

[c] weak shoulder.

[d] broad peak also containing adsorbed oxygen O-M stretching mode (474 $cm^{-1}$).

Table 3. Vibrational frequencies (±10 $cm^{-1}$) of methoxy on Pd(111).

| Assignment | $CH_3O$ | $CD_3O$ | ratio |
|---|---|---|---|
| $CH_3$ deg. stretch | 2933 | 2175 | 1.35 |
| $CH_3$ sym. stretch | 2829 | 2067 | 1.37 |
| $CH_3$ deform. | 1328 | ---- | |
| CO stretch | 1041 | 1024[a] | 1.02 |
| $CH_3$ rock | 770 | ---- | ---- |
| O-Pd stretch | 302 | 277 | 1.09 |

[a] broad peak probably also containing $CH_3$ deformation mode.

Table 4. Vibrational frequencies of chemisorbed methanol on various substrates. Only characteristic modes are given.

| Assignment | Liquid (17) | Pd(111) | $O_2$/Pd(111) | Pd(100) (13) | Pt(111) (8) | Ni(111)[d] (29) |
|---|---|---|---|---|---|---|
| OH stretch | 3328 | 3355 | 3250 | 3345 | 3280 | 3330 |
| $CH_3$ deg. stretch | 2980<br>2946 | 2948 | 2941 | 2945 | 2930 | 2950 |
| $CH_3$ sym. stretch | 2834 | 2825[b] | 2823[b] | 2845 | | 2825 |
| $CH_3$ deg. deform. | 1480 | 1438 | 1444 | 1470 | 1430 | 1460<br>1390 |
| $CH_3$ sym. deform. | 1450 | | | 1400-1500 | | |
| OH in plane bend | 1418 | | | ---- | | |
| CO stretch | 1030 | 1008 | 1023 | 1025 | 1000 | 1030 |
| OH out of plane bend [a]<br>CO torsion | 655 | 585 | 520[c] | 500-800 | 700 | 750 |

[a] mixed mode (28).

[b] shoulder.

[c] broad peak also containing adsorbed oxygen O-Pd stretching mode (~475 $cm^{-1}$).

[d] similar spectrum also reported for methanol on Ni(111) in ref. (6). Author of ref. (29) suggests that earlier spectra were affected by $H_2O$ impurity.

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## Figure Captions

Fig. 1. Vibrational spectra of methanol and deuterated methanol on Pd(111) at 140K. Curves c and f correspond to the condensed phase. The chemisorbed phase is obtained both by heating the condensed layer (b,e) and by using a lower exposure (a,d).

Fig. 2. Vibrational spectra of adsorbed CO obtained after exposure of methanol to Pd(111) at 300K. The top curve is a result of heating chemisorbed methanol to 300K.

Fig. 3. Vibrational spectra of $CH_3OH$ and $CD_3OD$ adsorption on a p(2x2) oxygen covered Pd(111) surface. Curves b and f are identified with the methoxy ($CH_3O$-) species. Decomposition to CO occurs by 300K (a,e).

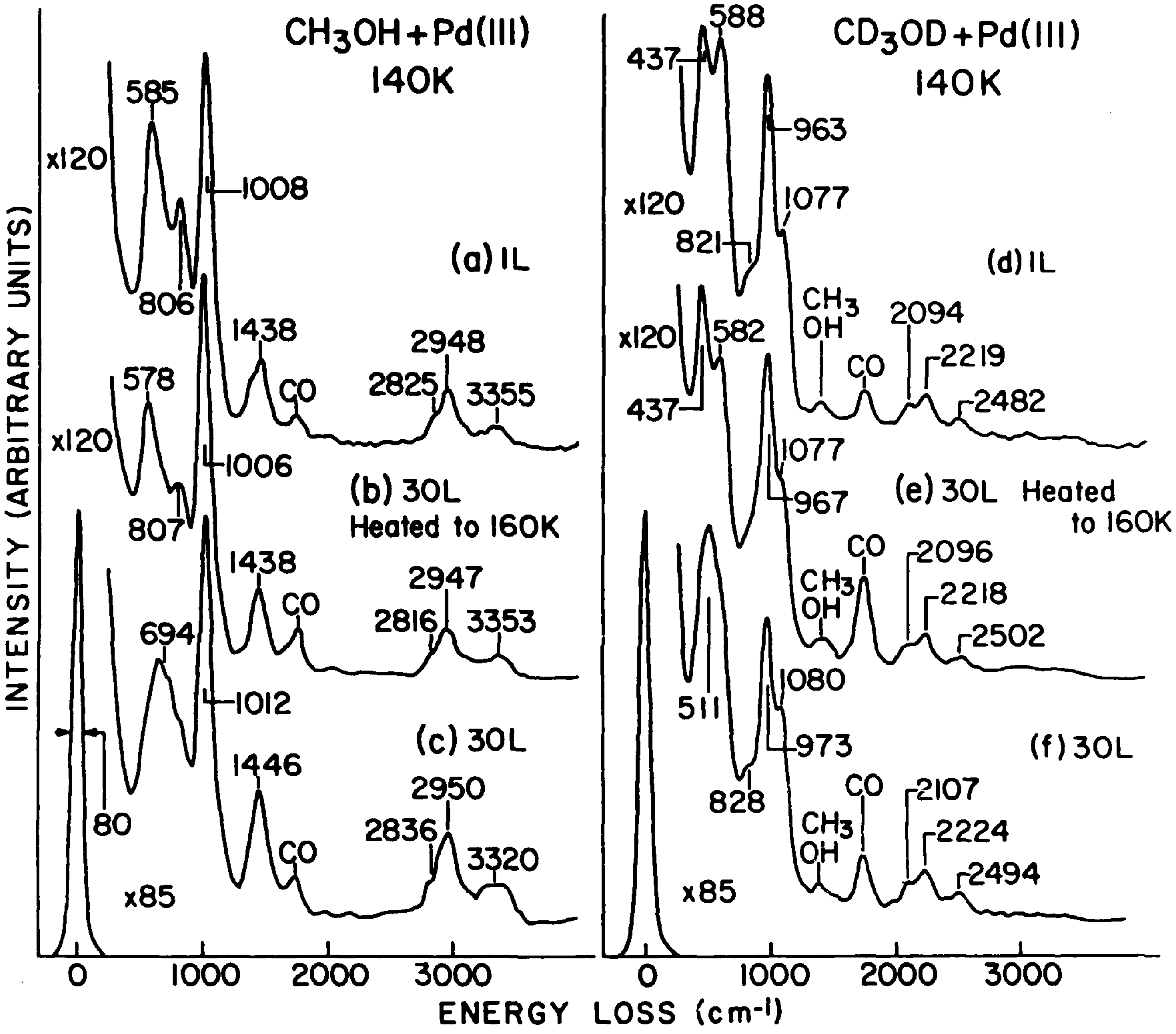

CH3OH+Pd(111)
140K
CD3OD+Pd(111)
140K
INTENSITY (ARBITRARY UNITS)
ENERGY LOSS (cm-1)
x120
585
1008
806
(a) 1L
1438
CO
2825
2948
3355
x120
578
1006
807
(b) 30L
Heated to 160K
1438
CO
2816
2947
3353
694
1012
80
(c) 30L
1446
CO
2836
2950
3320
x85
437
588
963
x120
1077
821
(d) 1L
CH3
OH
2094
CO
2219
2482
x120
582
437
1077
967
(e) 30L Heated
to 160K
CO
CH3
OH
2096
2218
2502
511
1080
973
(f) 30L
828
CO
CH3
OH
2107
2224
2494
x85
0
1000
2000
3000
0
1000
2000
3000

Fig. 1

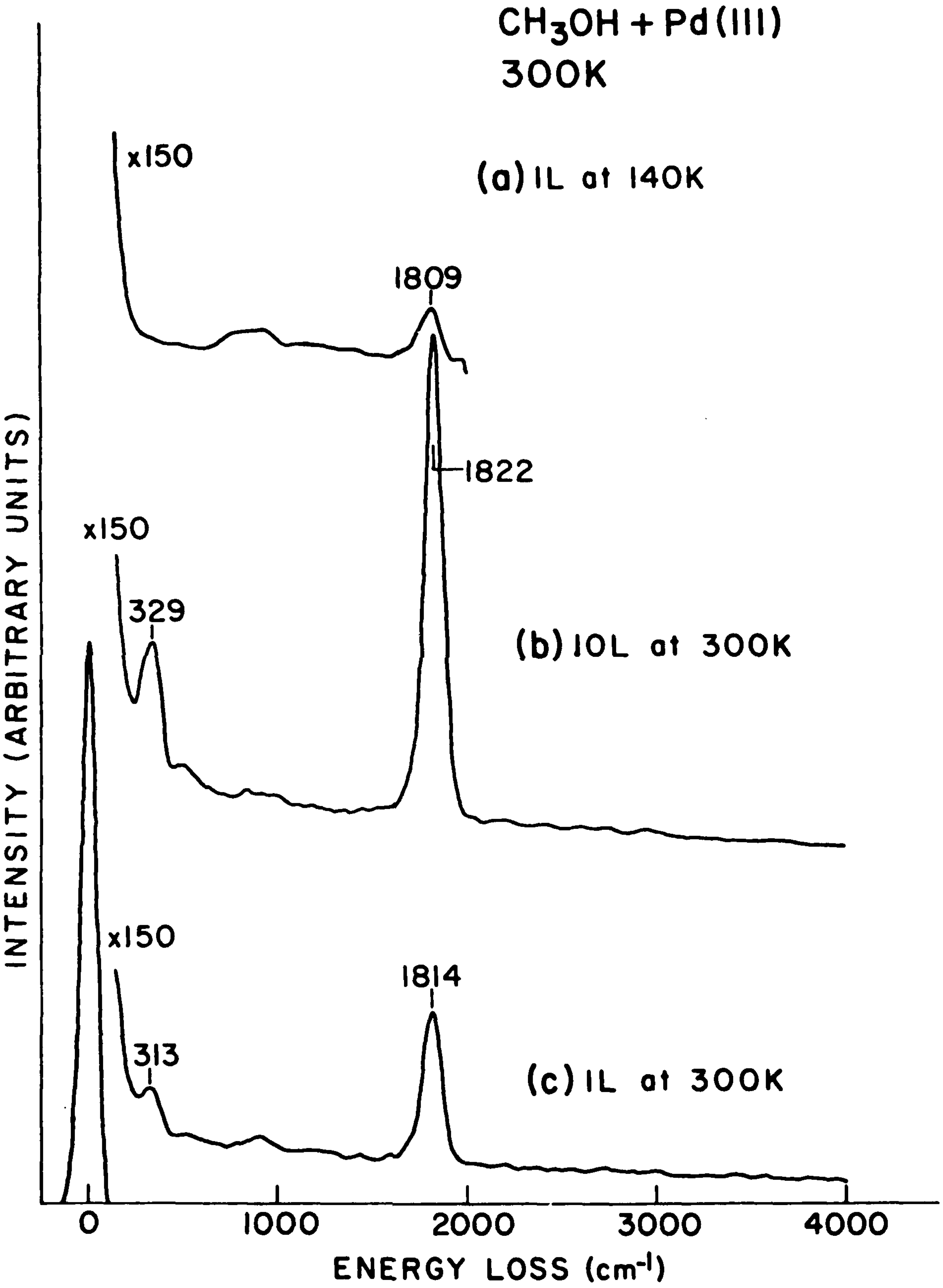
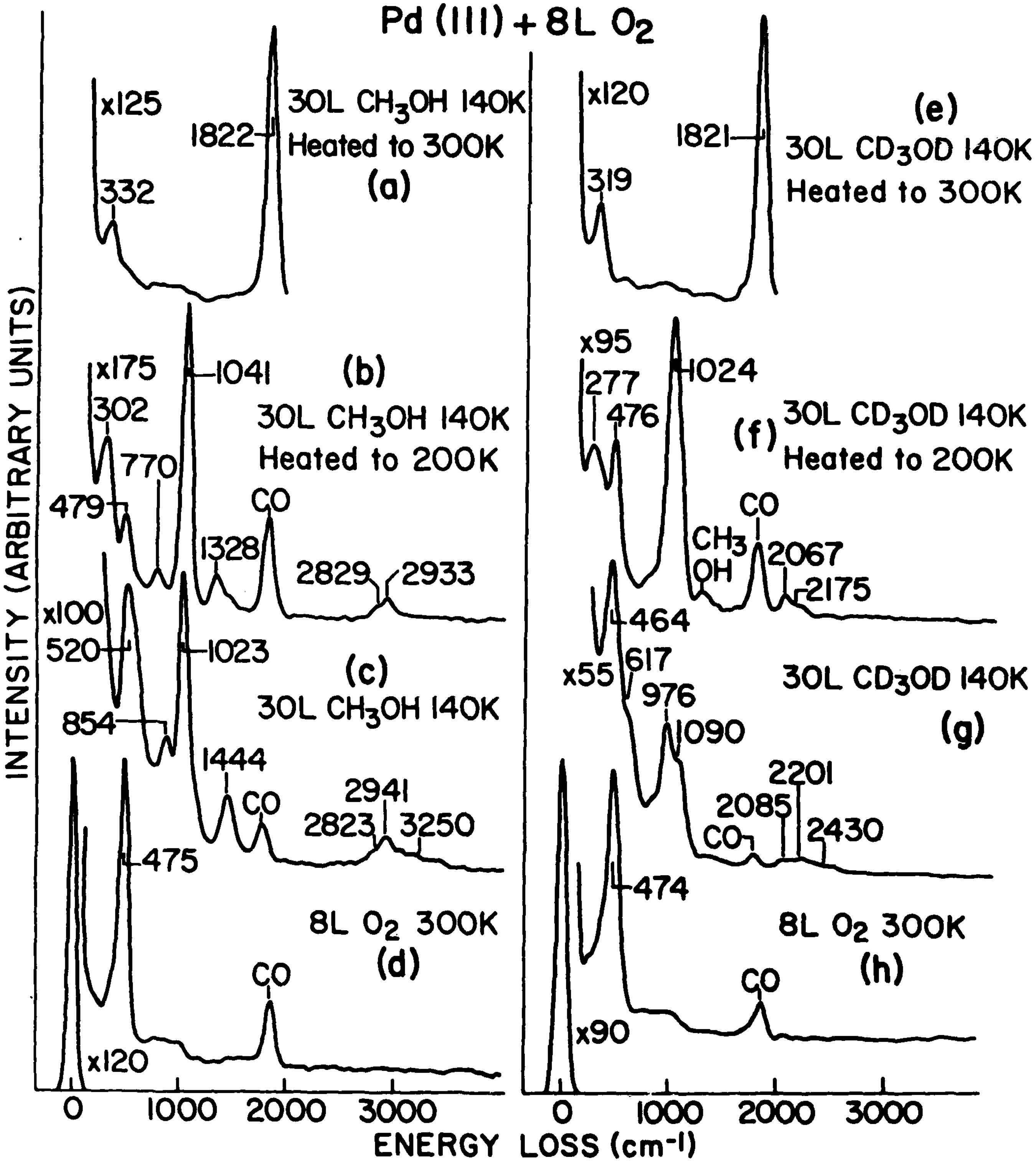

$CH_3OH$ + Pd(111)
300K
x150
(a) 1L at 140K
1809
1822
x150
329
(b) 10L at 300K
x150
1814
313
(c) 1L at 300K
INTENSITY (ARBITRARY UNITS)
0
1000
2000
3000
4000
ENERGY LOSS ($cm^{-1}$)

Fig. 2



Pd (111) + 8L $O_2$
x125
332
1822
30L $CH_3OH$ 140K
Heated to 300K
(a)
x120
319
1821
(e)
30L $CD_3OD$ 140K
Heated to 300K
x175
302
770
479
1041
(b)
30L $CH_3OH$ 140K
Heated to 200K
1328
CO
2829
2933
x95
277
476
1024
(f)
30L $CD_3OD$ 140K
Heated to 200K
CO
$CH_3$
OH
2067
2175
x100
520
1023
(c)
30L $CH_3OH$ 140K
854
1444
CO
2941
2823
3250
464
x55
617
976
1090
30L $CD_3OD$ 140K
(g)
2201
2085
CO
2430
475
8L $O_2$ 300K
(d)
CO
x120
474
8L $O_2$ 300K
(h)
CO
x90
INTENSITY (ARBITRARY UNITS)
0
1000
2000
3000
ENERGY LOSS ($cm^{-1}$)

Fig. 3

FILM

5-8