ELSEVIER

Surface Science 360 (1996) 144–156

surface science

An FTIR study of the bonding of methoxy on Ni(100): effects of coadsorbed sulfur, carbon monoxide and hydrogen

J.S. Huberty, R.J. Madix *

Departments of Chemical Engineering and Chemistry, Stanford University, Stanford, CA 94305-5062, USA

Received 10 July 1995; accepted for publication 17 January 1996

Abstract

The vibrational spectra of $CH_3O_{(a)}$, $CD_3O_{(a)}$, $CDH_2O_{(a)}$ and $CD_2HO_{(a)}$ on Ni(100) are analyzed and interpreted in terms of resonances between fundamental modes and either combinations or overtones. Analysis of the symmetry of the modes observed suggests that methoxy binds normal to the surface with C_s symmetry, at least at low coverages. Two distinct vibrational bands emerge in the vibrational spectrum of methoxy in the ν(CO) region as the coverage increases which are attributed to bonding in four-fold hollow sites and bridging sites. These bands exhibit blue shifts of about 25 cm^{-1} with increasing coverage up to the saturation coverage. The vibrational bands in the ν(CH) region appear concomitantly at all coverages and shift down 12 cm^{-1} as the coverage is increased. These shifts are attributed to changes in the metal–oxygen bond which are reflected in changes in the strength of the C–O and C–H bonds. Affects on the bonding also appear to occur with the coadsorption of hydrogen or CO with methoxy. Coadsorption of 0.36 ML hydrogen with 0.04 ML methoxy induces blue shifts of 15 and 7 cm^{-1} for the ν(CO) bands at 949 and 984 cm^{-1}, respectively. Adsorbing 0.43 ML of CO with 0.04 ML methoxy (and 0.04 ML hydrogen) causes a red shift of 20 and 12 cm^{-1} for these bands. A drastic drop in mode intensities for methoxy when CO is coadsorbed suggests that the methoxy tilts away from the surface normal. Pre-adsorbing sulfur on the Ni(100) surface reduces the amount of methoxy formed from methanol, but the ν(CO) methoxy bands are unshifted in frequencies relative to their position for the same methoxy coverage on the clean surface.

Keywords: Adhesion; Adsorption kinetics; Alcohols; Catalysis; Chemisorption; Low index single crystal surfaces; Nickel; Reflection spectroscopy; Thermal desorption spectroscopy

1. Introduction

It has been known for some time that methanol decomposes by a series of steps on Ni(100) that first involves the formation of adsorbed methoxy [1–9]. Furthermore, coadsorbed species, such as CO or sulfur, have a profound effect on the kinetics and selectivity of the reaction. At a sulfur coverage of 0.0375 ML, for example, the decomposition produces exclusively formaldehyde. Generally, the kinetics of the activation of the methyl C–H bond, which initiates this reaction, is inaccessible to temperature programmed reaction spectroscopy, because product desorption is the rate-limiting step for evolution of the products into the gas phase. Recently we reported a study of the kinetics of decomposition of methoxy on Ni(100) and the effects of coadsorbed sulfur and CO, determined by time-resolved Fourier transform infrared (TR-FTIR) spectroscopy [10]. In that study we observed band splitting and frequency shifts in the infrared spectra indicative of changes in the bonding of methoxy to the surface either with methoxy

* Corresponding author. Fax: +1 415 7239780; e-mail: rjm@rio.stanford.edu.

0039-6028/96/$15.00 Copyright © 1996 Elsevier Science B.V. All rights reserved

coverage or in the presence of coadsorbed species. These changes are examined further in this paper.

Vibrational modes of the adsorbed methoxy exhibit frequency shifts and intensity changes when compared to methanol. Interpretation of the spectra is further complicated by resonances between the symmetric CH_3 stretch ($\nu_s CH_3$) and combination and overtone modes of the methyl bends, which lead to frequency shifts and a redistribution of intensities [11]. In order to account for these effects, IR spectra of several deuterium-labelled methoxy species were analyzed to assign the complex features of the spectra in the C–H stretch region. A similar approach has also been utilized recently by others [12,13]. The vibrational assignments of methoxy were made by comparison to gas-phase and matrix-isolated methanol in order to minimize the effects of hydrogen bonding in the reference spectra present in solid and liquid-phase methanol. The frequency shifts and band splitting of the methoxy species were examined as a function of the methoxy coverage, using isotopic mixtures of CH_3OH and CD_3OD to separate the chemical shifts from dipole–dipole coupling. The effects of coadsorbed hydrogen, CO and sulfur on the vibrational features of methoxy were also examined in detail.

2. Experimental

The experiments were performed in an ultra-high vacuum chamber that contained a quadrupole mass spectrometer, a retarding field analyzer for both low energy electron diffraction (LEED) and Auger spectroscopy, and an ionizer for argon ion bombardment. The crystal temperature was measured with a chromel–alumel thermocouple spot-welded on the back of the crystal. Following argon ion bombardment, a 0.05 L oxygen dose at 700 K to remove residual carbon, and a 3 min anneal at 1200 K, Auger spectroscopy showed the crystal to be free of contaminants. LEED showed bright diffraction features indicative of the clean Ni(100) surface.

The FTIR spectra were obtained with a Nicolet model 740 infrared spectrometer with a liquid nitrogen-cooled mercury–cadmium–telluride (MCT) detector. 1200 scans at 8 cm^{-1} resolution were collected at 100 K for both sample and background spectra. The ratioed spectra were baseline corrected, but no smoothing was performed.

The sulfided Ni(100) surfaces were prepared by dosing H_2S (Matheson, 99.5%) at room temperature and annealing the crystal at 800 K for 5 min. The sulfur coverages were determined within ± 0.02 ML using the Auger peak-to-peak ratio of S(152 eV)/Ni(848 eV) referenced to the saturation sulfur coverage of 0.50 ML obtained by dosing 30 L of H_2S at 700 K (1 L is equal to 1×10^{-6} Torr·s). This ratio was assumed to be linear with sulfur coverage. The saturation coverage gives a sharp c(2 × 2) LEED pattern.

3. Results and discussion

3.1. Methoxy assignments and orientation

Methoxy overlayers were formed by heating adsorbed methanol to 230 K. In addition to the obvious loss of vibrations associated with the OH bond, the methoxy spectra differ appreciably from the methanol multilayer spectra (Fig. 1). The assignment of the vibrational features in each spectrum is complicated by the Fermi resonances that are observed. A beginning point for the assignments is found by comparison to the frequencies

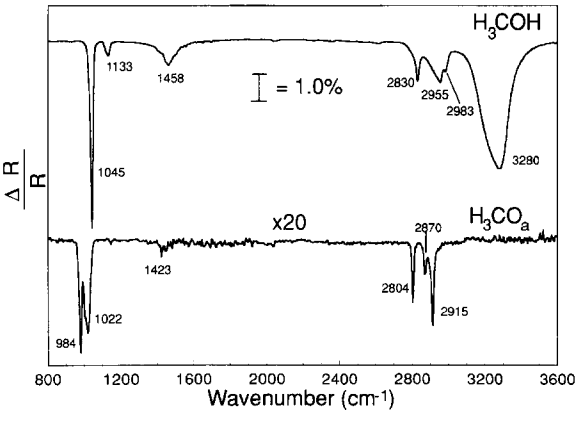


Fig. 1. IR spectra of methanol multilayer and methoxy on Ni(100). Methoxy adlayer formed by annealing multilayer to 230 K. Spectra collected at 100 K.

and assignments given by Serrallach and co-workers for gas phase and argon-matrix-isolated methanol [14]. The assignments of Serrallach et al. were taken since their valence force field calculations using parameters obtained from $CH_3OH(D)$ and $CD_3OH(D)$ could be used to assign the 78 observed fundamentals of the species with partially deuterated methyl groups. The frequencies observed in the condensed multilayer are assigned in Table 1. The broad peak at 1458 cm^{-1} can be attributed to the overlapping asymmetric and symmetric bending modes (Fig. 2). The *s* and *a* indicate whether the mode is symmetric or asymmetric with the molecular plane defined by the HCOH atoms while the prime indicates asymmetry about the C_3 axis of the methyl group. Combinations and overtones of these bending modes in resonance with $\nu_s(CH_3)$ yield a peak at 2955 cm^{-1}. The high frequency shoulder at 2983 cm^{-1} is attributed to $\nu'_s(CH_3)$. $\nu_a(CH_3)$, if it appears at all, most likely coincides with the broad band at 2955 cm^{-1}.

Table 1
Vibrational assignments for CH_3O_a by comparison to the values of CH_3OH by Serrallach et al. [14][a]

CH_3OH assignments	Ar matrix 15 K (cm^{-1})±0.5	Multilayer (cm^{-1})	Methoxy (cm^{-1})
$\nu_1(a')$, $\nu(OH)$	3667 m	3280	–
$\nu_2(a')$, $\nu'_s(CH_3)$	3005 m	2983	–
$\nu_9(a'')$, $\nu_a(CH_3)$	2961 m	–	–
$2\nu_4(A')$	2956 m	2955	2915[b]
$\nu_4+\nu_{10}(A'')$	2930 m	–	–
$\nu_4+\nu_5(A')$	2915 w	–	–
$\nu_5+\nu_{10}(A'')$	2908 vw	–	–
$2\nu_5(A')$	2893[v] w	–	2870[b]
$\nu_3(A')$, $\nu_s(CH_3)$	2847 m	2830	2804[b]
$\nu_4(a')$, $\delta'_s(CH_3)$	1473 w	–	–
$\nu_{10}(a'')$, $\delta_a(CH_3)$	1466 w	1458	–
$\nu_5(a')$, $\delta_s(CH_3)$	1452 vw	–	1423
$\nu_6(a')$, $\delta(COH)$	1334	–	–
$\nu_{11}(a'')$, $\gamma_\perp(CH_3)$	1145[v]	1133	1130
$\nu_7(a')$, $\gamma_\perp(CH_3)$	1077 w	–	–
$\nu_8(a')$, $\nu(CO)$	1034 vs	1045	1022 984

[a]Abbreviations are: [v], vapor; s, strong; m, medium; w, weak; v, very.
[b]According to Lavelley and Sheppard the assignments are: ν_3, 2915 cm^{-1}; $2\nu_4$ and $2\nu_{10}$, 2870 cm^{-1}; $2\nu_5$, 2804 cm^{-1} in Fermi resonance.

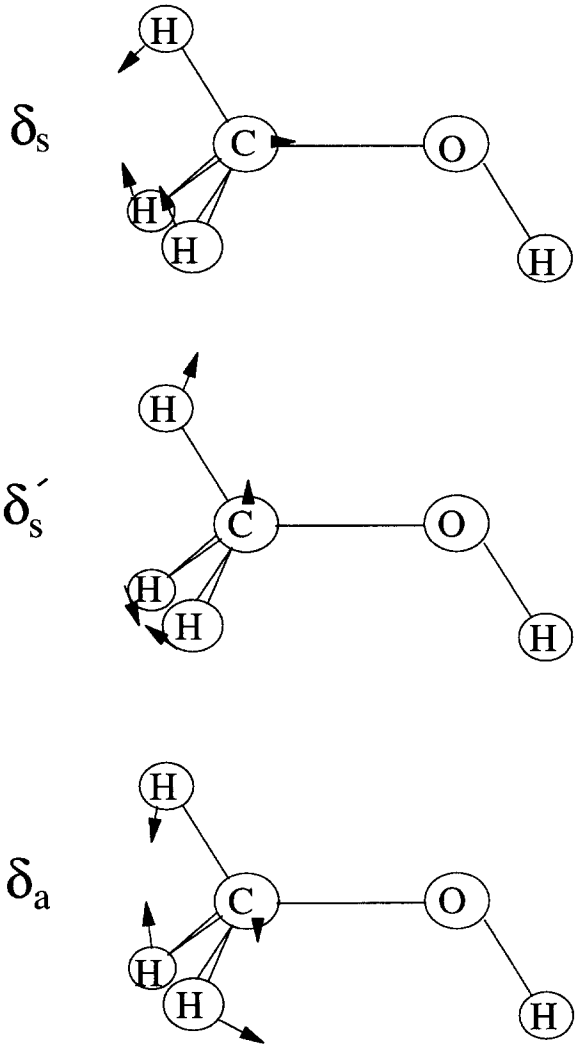


Fig. 2. CH_3 bending modes of methanol. "s" and "a" refer to symmetry with respect to the HCOH plane. The prime refers to the asymmetry with respect to the methyl group.

The methoxy spectrum shows three sharp features in the CH stretch region which are assigned to the overtones of the symmetric and asymmetric CH_3 bends in resonance with $\nu_s(CH_3)$ (Table 1). Resonance can take place between modes of the same symmetry. The first overtone of modes with a′ and a″ symmetries will have a′ symmetry. Combination bands of two a″ or two a′ modes will also have a′ symmetry. However, the combination of an a′ and a″ mode has a″ symmetry. The splitting of ν(CO) to yield peaks at 1022 and 984 cm^{-1} is

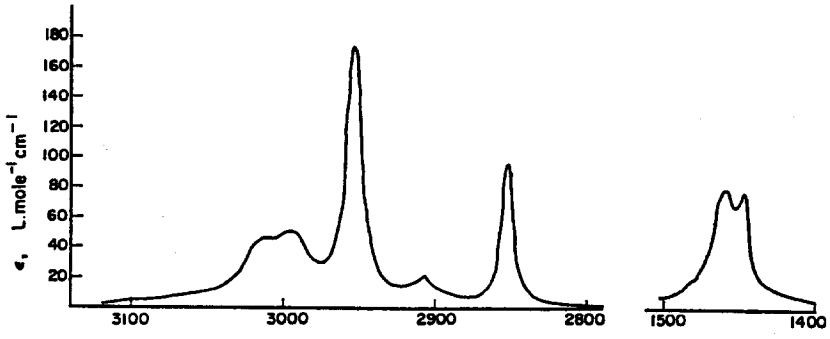


Fig. 3. Infrared spectrum of $OP(OCH_3)_3$ in solution of CCl_4. The bands are assigned as follows: 2955 cm^{-1}, $\nu_s(CH_3)$; 2909 cm^{-1}, $2\delta_a$; 2854 cm^{-1}, $2\delta_s$; 1461 cm^{-1}, δ_a; 1448 cm^{-1}, δ_s. Used with permission [6].

attributed to chemically different adsorption sites. The peaks in the CH stretch region are not influenced by this splitting, as will be shown later in this paper.

Further evidence for not assigning $\nu_a(CH_3)$ or $\nu_s'(CH_3)$ to any of the observed bands in the methoxy spectrum is provided by a study of the anharmonicity of the deformation vibrations $\delta(CH_3)$ in methyl compounds conducted by Lavalley and Sheppard [15]. In this study a number of methyl containing molecules with C_s or C_{3V} symmetry were examined to show how the overtone frequencies of the deformation modes (2δ) were shifted from their expected values due to Fermi resonance with $\nu_s(CH_3)$. When $\delta_s(CH_3)$ exceeds 1400 cm^{-1} there is a strong Fermi resonance perturbation between $\nu_s(CH_3)$ and $2\delta_s$. In fact, when δ_a or δ_s' and δ_s have similar values, the interaction between ν_s and $2\delta_s$ is greater than that between ν_s and $2\delta_a$ or $2\delta_s'$. This is shown clearly by a spectrum of $OP(OCH_3)_3$ in solution with CCl_4 (Fig. 3). The bands at 2955, 2909 and 2854 cm^{-1} are assigned to ν_s, $2\delta_a$, and $2\delta_s$, while the bands at 1461 and 1448 cm^{-1} are assigned to δ_a and δ_s. The value for $(2\times\delta_a-2\delta_a)$ is 13 cm^{-1} while $(2\times\delta_s-2\delta_s)$ equals 42 cm^{-1}[1]. The greater absorption intensity in the $2\delta_s$ band compared to the $2\delta_a$ (and $2\delta_s'$) band also indicates the greater interaction between ν_s and $2\delta_s$. Note that the $\nu(CH)$ region of the spectrum of methoxy on Ni(100) compares favorably with the $OP(OCH_3)_3$ spectrum. The methoxy on Ni(100) spectrum simply lacks the $\nu_a(CH_3)$ bands near 3000 cm^{-1}, and the $\nu_s(CH_3)$, $2\delta_a(CH_3)$ and $2\delta_s(CH_3)$ bands are shifted to lower frequencies by 40, 39 and 50 cm^{-1}, respectively. The modes at 2915 cm^{-1} and 2804 cm^{-1} are assigned to Fermi resonance between the first overtone of the symmetric deformation and the symmetric methyl stretch. The value of $(2\times\delta_s-2\delta_s)$ equals 42 cm^{-1}, exactly as for $OP(OCH_3)_3$.

Deuterated methoxy spectra (Fig. 4 and Table 2) provide further evidence for assigning vibrations of CH_3O_a to the overtones in Fermi resonance with $\nu_s(CH_3)$. Since the overtone of the $\delta_s(CD_3)$ band is farther from the frequency of $\nu_s(CD_3)$ than

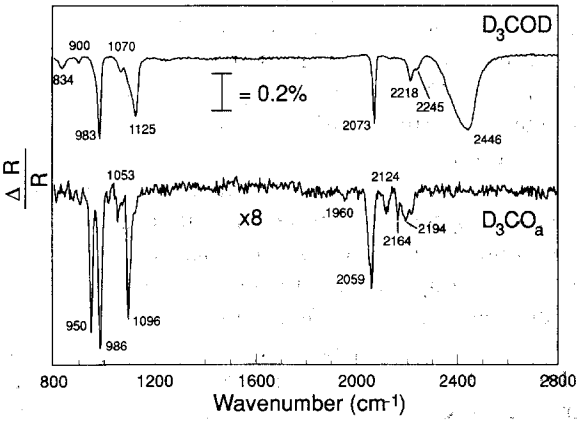


Fig. 4. D_3COD multilayer and D_3CO_a spectra on Ni(100) collected at 100 K. $D_3CO_{(a)}$ formed by annealing to 230 K.

[1] The degeneracy splitting of the perpendicular methyl deformation vibrations of δ_s' (symmetric with the local symmetry plane) and δ_a (asymmetric with the plane) is too small to be observed in $OP(OCH_3)_3$. This also appears to be the case for methoxy adsorbed on the nickel surface.

Table 2
Vibrational assignments for CH_3O_a by comparison to the values of CD_3OD by Serrallach et al. [14]

CD_3OD assignments	Ar matrix 15 K (cm^{-1})±0.5	Multilayer (cm^{-1})	Methoxy (cm^{-1})
$\nu_1(a')$, $\nu(OD)$	2705 s	2446	–
$2\nu_4(A')$	2266 w	2245	2194
$\nu_2(a')$, $\nu_s'(CD_3)$	2254 m	–	–
$\nu_9(a'')$, $\nu_a(CD_3)$	2218 s	2218	–
$\nu_4+\nu_5(A')$	2209[v] m	–	2164
$\nu_4+\nu_6(A')$	2158 vw	–	–
$\nu_5+\nu_{10}(A'')$	2138 vw	–	–
$2\nu_{10}(A')$	2132 vw	–	2124
$\nu_3(a')$, $\nu_s(CD_3)$	2078 s	2073	2059
$2\nu_7(A')$	1956 w	–	1960
$\nu_4(a')$, $\delta_s(CD_3)$	1132 vs	1125	1096[f]
$\nu_5(a')$, $\delta_s'(CD_3)$	1080 vw	1070	1053[f]
$\nu_{10}(a'')$, $\delta_a(CD_3)$	1068 m	–	–
$\nu_6(a')$, $\gamma_\perp(CD_3)$	1031 s	–	–
$\nu_7(a')$, $\nu(CO)$	983 vs	983	986[f]
			950
$\nu_{11}(a'')$, $\gamma_\parallel(CD_3)$	895 vw	900	–
$\nu_8(a')$, $\delta(COD)$	776 vs	834	–

[f]Resonance likely between these modes.

the overtone of the $\delta_s(CH_3)$ is from $\nu_s(CH_3)$, the Fermi resonance is reduced and only one strong mode, attributed to $\nu_s(CD_3)$, appears in the $\nu(CD)$ region. The overtone is expected near 2192 cm^{-1}, in agreement with the observed band at 2194 cm^{-1}. The strong band at 1096 cm^{-1} is attributed to resonance of the $\delta_s(CD_3)$ band with the $\nu(CO)$ mode. The mode at 2124 cm^{-1} is assigned to the first overtone of the asymmetric methyl deformation. The origin of the mode at 2164 cm^{-1} is unclear. The CD_3O_a band at 1053 cm^{-1} is assigned to the $\delta_s'(CD_3)$ mode of a′ symmetry and will be discussed further with regard to the methoxy orientation.

The bands from the partially deuterated methoxy species are more difficult to assign. For methanol with an asymmetrically deuterated methyl group there are two spectroscopically equivalent enantiomorphic rotamers of C_1 symmetry and a symmetric rotamer of C_s symmetry (Fig. 5). The relative populations of the two symmetries, $n(C_s)/n(C_1)$, can be calculated from the zero point energies to be 0.44 at 100 K [14]. However, there is no clear spectroscopic evidence

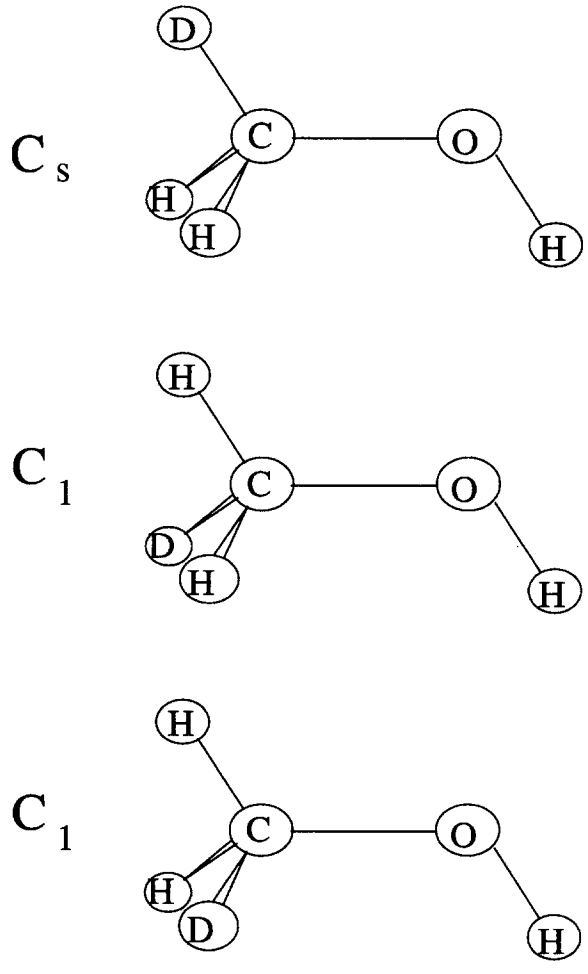


Fig. 5. The two enantiomers of DH_2COH.

for the C_s species in the DH_2COH multilayer spectrum or the DH_2CO_a spectrum (Fig. 6 and Table 3). Each of the observed modes in the multilayer may be assigned to the fundamentals and combination modes of the C_1 species alone. The methoxy bands at 2852 and 2919 cm^{-1} are assigned to the overtone of $\delta(CH_2)$ and $\nu_s(CH_2)$ in Fermi resonance, and the band at 2204 cm^{-1} is assigned to the overtone of $\gamma_r(CH_2)$ in resonance with $\nu(CD)$ at 2152 cm^{-1}.

Modes of C_s symmetry appear to be observed for HD_2COH although with very small intensity. The modes at 982 and 1120 cm^{-1} in the multilayer spectrum are assigned to $\nu(CO)$ and $\delta(CD_2)$ of C_s symmetry (Fig. 7 and Table 4). The high frequency

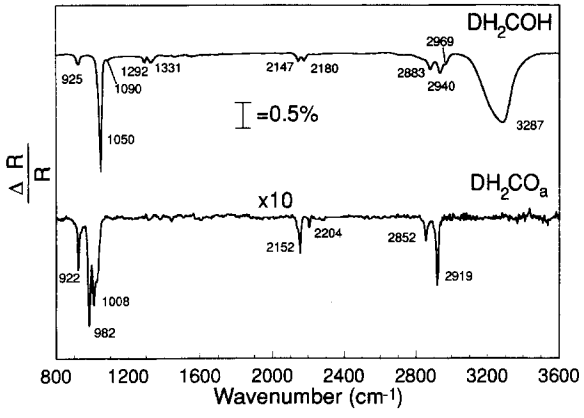


Fig. 6. DH_2COH multilayer and methoxy adlayer spectra on Ni(100) at 100 K. Methoxy adlayer formed by annealing to 230 K.

shoulder of the 2911 cm^{-1} peak at 2940 cm^{-1} may be due to ν(CH) of C_s symmetry. The fact that these features are not found in the methoxy spectrum may be due to the expected reduction of intensity with decreased coverage or the absence of the species of this symmetry. The modes for methoxy are assigned as follows. Since no combinations or overtones are in resonance with ν(CH), the single peak occurs at 2921 cm^{-1} for this isotope. The modes at 2147 cm^{-1} and 2102 cm^{-1} are assigned to $\nu_s(CD_2)$ and the overtone of $\delta(CD_2)$ in Fermi resonance. The $\nu_a(CD_2)$ bands are expected to be closer to 2200 cm^{-1}. The high intensity of the band at 1068 cm^{-1} is suggestive of Fermi resonance between $\delta(CD_2)$ and ν(CO).

The spectrum for CH_3O following the anneal of the methanol multilayer to 230 K (Fig. 1) suggests that methoxy may be tilted at the highest coverages studied. In particular, the persistence of a feature at 1130 cm^{-1}, a weak feature at 1423 cm^{-1} and a shoulder on the high frequency side of the mode at 2915 cm^{-1} are all consistent with a tilted species, because they are symmetry unallowed for the upright methoxy (Table 1). Further, the mode at 1053 cm^{-1} in the D_3CO_a spectrum (Fig. 4) is assigned to $\delta'_s(CD_3)$ of a′ symmetry from the C_s symmetry group, though association of this mode with the geometry of the adsorbed species is subject to question. Under C_{3v} symmetry, this mode is degenerate with the $\delta_a(CD_3)$ mode and both are unallowed for the species normal to the surface

Table 3
Vibrational assignments for DH_2CO_a by comparison to the values of DH_2COH by Serrallach et al. [14]

DH_2COH assignments	Ar matrix 15 K (cm^{-1})±0.5	Multilayer (cm^{-1})	Methoxy (cm^{-1})
$\nu_1(C_1)$, $\nu_1(a', C_s)$, ν(OH)	3668 s	–	–
$\nu_2(C_1)$, $\nu_a(CH_2)$	2996 m	2969	–
$\nu_9(a'', C_s)$, $\nu_a(CH_2)$	2948 s	–	–
$2\nu_5(C_1)$	2931 w	2940	2919[f]
$\nu_3(C_1)$, $\nu_s(CH_2)$	2908[e]	–	2852[f]
$\nu_2(a', C_s)$, $\nu_s(CH_2)$	2890 s	2883	–
$\nu_3(a', C_s)$, ν(CD)	2193 w	–	–
$2\nu_9(C_1)$	–	2180	2204[f]
$\nu_4(C_1)$, ν(CD)	2165 ms	2147	2152[f]
$\nu_6+\nu_8(A', C_s)$	2138 w	–	–
$\nu_5(C_1)$, $\delta(CH_2)$	1468 w	–	–
$\nu_4(a', C_s)$, $\delta(CH_2)$	1462 w	–	–
$\nu_5(a', C_s)$, $\gamma_w(CH_2)$	1378 w	–	–
$\nu_6(C_1)$, $\gamma_w(CH_2)$	1368 m	–	–
$\nu_7(C_1)$, $\gamma_t(CH_2)$	1345 w	1331	–
$\nu_{10}(a'', C_s)$, $\gamma_t(CH_2)$	1301 vw	–	–
$\nu_8(C_1)$, δ(COH)	1257 m	1292	–
$\nu_6(a', C_s)$, δ(COH)	1241 ms	–	–
$\nu_{11}(a'', C_s)$, $\gamma_r(CH_2)$	1113[e]	–	–
$\nu_9(C_1)$, $\gamma_r(CH_2)$	1070 m	1090	–
$\nu_7(a', C_s)$, ν(CO)	1052 s	–	–
$\nu_{10}(C_1)$, ν(CO)	1025 vs	1050	1008
	–	–	982
$\nu_{11}(C_1)$, δ(OCD)	919 vw	925	922
$\nu_8(a', C_s)$, δ(OCD)	892 s	–	–

[f]Resonance likely between these modes.

according to the surface dipole selection rule. However, under C_s symmetry this mode would belong to the same symmetry class as ν(CO), a′, and could gain intensity through resonance with ν(CO), as the $\delta_s(CD_3)$ at 1096 cm^{-1} appears to do. The appearance of this mode need not signify methoxy is tilted, only that it is not in C_{3v} symmetry. The origin of this symmetry reduction could be that the Ni(100) surface contains Ni atoms square symmetry, and no C_{3v} sites exist. The absence of other observable asymmetric a′ modes (ν'_s and δ'_s) may be due to their small dynamic

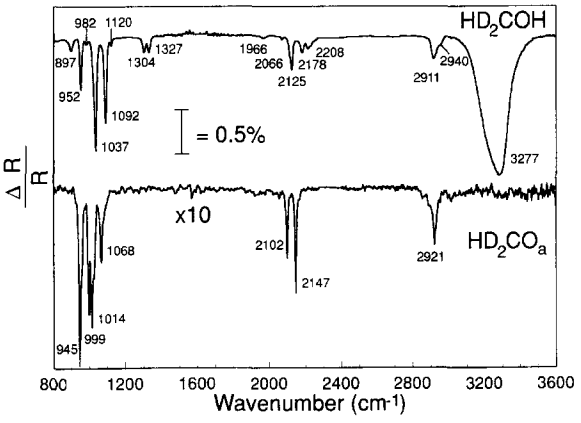


Fig. 7. HD_2COH multilayer and methoxy adlayer spectra on Ni(100) collected at 100 K. Methoxy adlayer formed by annealing to 230 K.

dipoles in the normal direction. In fact, without a resonance with ν(CO), the mode at 1053 cm^{-1} may not have been observed. Nonetheless, there is distinct evidence for a tilted geometry at these high coverages, and it cannot be ruled out. However, at lower coverages none of these modes are observed (see Fig. 10 below). The absence of modes above 2915 cm^{-1} [$\nu_a(CH_3)$] (see also Fig. 10 below) is consistent with the methoxy orientation normal or near normal to the surface. In such an orientation the $\nu_a(CH_3)$ mode of a″ symmetry is not allowed according to the dipole selection rule, and the ν_s' (CH_3) mode of a′ symmetry would likely not appear since its dynamic dipole would lie perpendicular to the surface normal. However, this mode of methoxy may remain totally symmetric with respect to a mirror plane when adsorbed on the surface, as will be discussed further below. It is then concluded that the O–C bond of the methoxy species lies normal or nearly normal to the surface at low coverages but may tilt slightly at high coverage.

The extent to which a tilted methoxy species would change the observed spectra is critical to understanding the limitations of this measurement. At least to the first approximation, the intensities of the ν(CO) and $\nu_s(CH_3)$ bands of CH_3O_a would be diminished by a factor of $\cos^2\theta$, where θ is the angle between the C–O axis and the surface normal. However, even in the methanol multilayer,

Table 4
Vibrational assignments for D_2HCO_a by comparison to the values of D_2HCOH by Serrallach et al. [14]

D_2HCOH assignments	Ar matrix 15 K (cm^{-1})±0.5	Multilayer (cm^{-1})	$CH_3O_{(a)}$ (cm^{-1})
$\nu_1(C_1)$, $\nu_1(a', C_s)$, ν(OH)	3668 s	3277	–
$\nu_2(a', C_s)$, ν(CH)	2988 m	2940	–
$\nu_2(C_1)$, ν(CH)	2931 s	2911	2921
$\nu_3(C_1)$, $\nu_8(CD_2)$	2242 m	–	–
$\nu_3+\nu_{11}(C_1)$, $\nu_7+\nu_{10}(C_1)$	2217 vw	–	–
$\nu_9(a'', C_s)$, $\nu_s(CD_2)$	2208 m	2208	–
$2\nu_6(A', C_s)$	2198 w	–	–
$2\nu_8(C_1)$	2187 m	2178	2147[f]
$\nu_7+\nu_{11}(C_1)$, or $\nu_8+\nu_9(C_1)$	2143 m	–	–
$\nu_4(C_1)$, $\nu_s(CD_2)$	2134 m	2125	2102[f]
$\nu_3(a', C_s)$, $\nu_s(CD_2)$	2114 m	–	–
$\nu_6+\nu_7(A', C_s)$	2101 w	–	–
$2\nu_9(C_1)$	2068 w	2066	–
$\nu_9+\nu_{10}(C_1)$	1977 w	1966	–
$\nu_4(a', C_s)$, δ(OCH)	1377 m	1327	–
$\nu_5(C_1)$, δ(OCH)	1356 m	1304	–
$\nu_6(C_1)$, $\gamma_r(CD_2)$	1319 m	–	–
$\nu_{10}(a'', C_s)$, $\gamma_r(CD_2)$	1310 w	–	–
$\nu_9+\nu_{12}(C_1)$	1305 w	–	–
$\nu_5(a', C_s)$, δ(COH)	1276 w	–	–
$\nu_7(C_1)$, δ(COH)	1268 m	–	–
$\nu_6(a', C_s)$, $\delta(CD_2)$	1095 ms	1120	–
$\nu_8(C_1)$, $\delta(CD_2)$	1091 vs	1092	1068[f]
$\nu_9(C_1)$, δ(CO)	1041 vs	1037	1014[f]
	–	–	999
$\nu_7(a', C_s)$, ν(CO)	1013 vs	982	–
$\nu_{10}(C_1)$, $\gamma_w(CD_2)$	946 s	952	945
$\nu_8(a', C_s)$, $\gamma_w(CD_2)$	925 w	–	–
$\nu_{11}(a'', C_s)$, $\gamma_t(CD_2)$	898 w	897	–
$\nu_{11}(C_1)$, $\gamma_t(CD_2)$	870 s	–	–

[f]Resonance likely between these modes.

these are the most intense bands observed with the exception of ν(OH). In the case of the a″ modes a tilt of only 30 degrees yields intensities for $\nu_a(CH_3)$ or $\delta_a(CH_3)$ of only 25% of their maximum possible intensity. From their relative intensities in the multilayer we estimate 30 degrees to be the limit

to which it can be determined that the C–O axis is normal to the surface at the lower coverages.

A comparison to studies of the orientation of methoxy on other surfaces is useful. IR spectra of CH_3O_a and CD_3O_a on Cu(100) obtained by Ryberg [16] are very similar to those observed here. Further, the band assignments of Ryberg led to the conclusion that methoxy was tilted, but Stohr estimated the methoxy to tilt 32 ± 10 degrees from the surface normal by near-edge X-ray absorption fine structure analysis [17,18]. Most recently, Lindner et al. used photoelectron diffraction and O and C K-edge NEXAFS to show that the C–O bond is oriented essentially parallel to the surface normal (with a possible tilt of about 10 degrees only) [19]. Also, the theoretical calculations of Wander and Holland [20] indicate that the system energy increases monotonically with tilt angle and suggest the methoxy is untilted from the surface normal. By the similarity between the spectra of methoxy on Cu(100) and Ni(100), we conclude that the methoxy on Ni(100) is oriented with its CO bond along the surface normal at low coverage. This result is in agreement with theoretical calculations of methoxy on Ni(100), which give a tilt of 5 degrees [21].

3.2. Methoxy coverage variation

IR spectra for increasing methoxy coverages show the sequential growth of different ν(CO) bands accompanied by frequency shifts. Spectra were collected at 100 K after dosing methanol at 100 K and annealing to 230 K to form methoxy. Annealing to higher temperatures leads to methoxy decomposition. TPRS was performed after each IR spectrum to obtain the methoxy coverage from the CO desorption peak areas resulting from methoxy decomposition; the peak area of the 0.68 ML saturated CO coverage at 100 K on Ni(100) was used as a coverage standard (Fig. 8). Fig. 9 shows that the three ν(CO) bands grow in intensity as the methoxy coverage increases. The middle band at 982 cm^{-1} appears first and shifts to 1003 cm^{-1} with increasing coverage. This band appears to saturate in intensity near a total

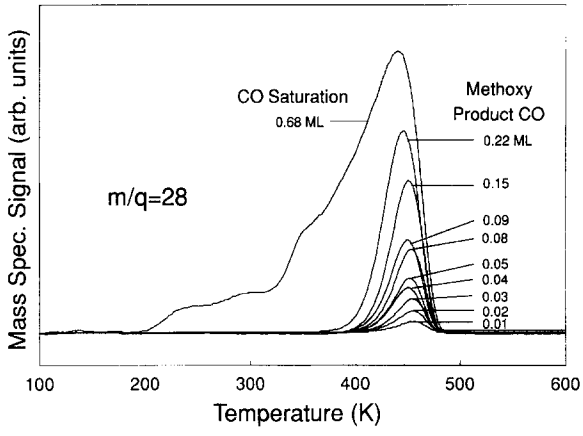


Fig. 8. CO TPD and TPRS spectra of the 100 K saturated CO adlayer and methoxy product desorption. TPRS spectra were collected after anneals to 230 K with IR data collection at 100 K.

methoxy coverage of 0.08 ML. The lowest frequency band first appears at 0.03 ML and shifts from 951 cm^{-1} at this coverage to 977 cm^{-1} at the highest attainable methoxy coverage (0.22 ML). This band grows in intensity continuously until the maximum coverage is attained. The highest frequency ν(CO) band appears as a shoulder to the middle band at a 0.04 ML methoxy coverage. This band grows most rapidly at the higher coverages. All three bands blue shift by roughly 20 cm^{-1} between the coverages at which they first appear and the saturation coverage.

The three bands must be attributed to three chemically different adsorbed species. No new LEED patterns have been observed for methoxy on the Ni(100) surface, which suggests that methoxy does not form well-ordered long range structures on this surface. This is consistent with our vibrational spectra that show that, except for methoxy coverages below 0.03 ML, more than one adsorbed species exists on the surface. On a Ni(100) surface the atop, bridge and four-fold hollow are the three high symmetry binding sites available. Additionally, there are defect sites and sites that may be affected by coadsorbed hydrogen. From theoretical calculations, methoxy is thought to bind in the four-fold hollow site with a binding energy of 95.7 kcal/mol [21]. The binding energy for the bridge site is calculated to be 89.0 kcal/mol. When hydrogen and methoxy are coadsorbed at

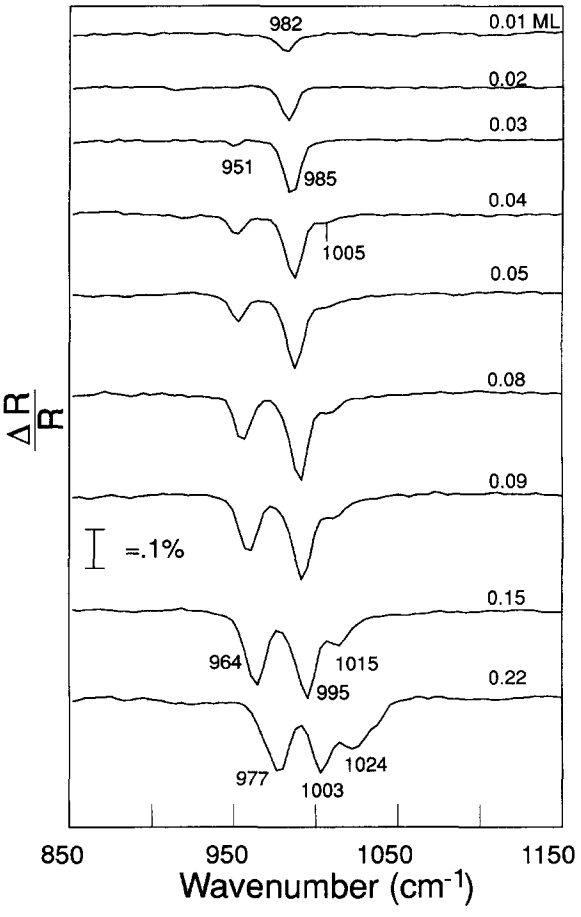


Fig. 9. The ν(CO) bands of methoxy after 230 K anneals for increasing methanol doses at 100 K. Spectra collected at 100 K. IR spectra correspond to TPRS spectra shown in Fig. 8.

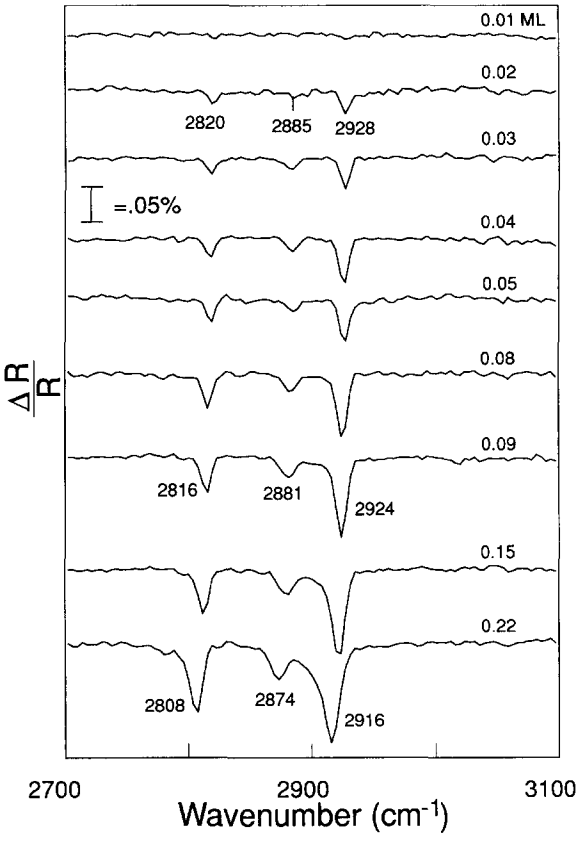


Fig. 10. The $\nu_s(CH_3)$, $2\delta_a(CH_3)$, and $2\delta_s(CH_3)$ bands of methoxy as a function of increasing coverage after annealing methanol to 230 K. Spectra correspond with TPRS data in Fig. 8.

nearest neighbor four-fold hollow sites, the binding energy drops to 90.1 kcal/mol. These calculations also indicate that the frequency of ν(CO) at a bridge site is expected to be lower than its frequency at a four-fold hollow site and that coadsorbed hydrogen raises the frequency [21]. We have shown previously that chemisorbed methanol continues to desorb at the temperature at which methoxy decomposition begins. This result suggests that the high frequency band is due either to chemisorbed methanol or to methoxy influenced by the coadsorbed hydrogen. However, coadsorbing additional hydrogen after a small amount of methoxy is formed leads only to a blue shift for the ν(CO) bands, not the high frequency band (see below). Therefore, we assign the lowest frequency peak to methoxy in the bridge site, the middle peak to methoxy in the four-fold hollow site, and the high frequency peak to chemisorbed methanol.

A comparison of the results with calculations for methoxy on Cu(100) supports our assignments. Theoretical calculations by Wander and Holland comparing the atop, bridge and four-fold hollow site of methoxy on Cu(100) indicate that a four-fold hollow site is most energetically preferred, and a potential barrier exists for transfer of the methoxy between the bridge and four-fold hollow sites [20]. The SEXAFS results of Stöhr et al. [9] support a bridge or four-fold hollow adsorption site, as do the photoelectron diffraction results of Lindner et al., which indicate adsorption at a low symmetry site between the bridge and four-fold hollow site

with the oxygen atom displaced approximately 0.3 Å parallel to the surface from the bridge site and 0.4 Å from the four-fold hollow site [19]. New LEED patterns were not observed by Lindner and co-workers in their study. The existence of both bridge and atop methoxy species is a plausible explanation for the observed results and supports our given assignment for methoxy on Ni(100).

3.3. Chemical shifts and dipole coupling

In contrast to the ν(CO) bands, the bands in the ν(CH) region continuously increase in intensity up to the saturation coverage of methoxy and shift to lower frequencies (Fig. 10) by roughly 10 cm^{-1} between 0.02 and 0.22 ML. Since dipole–dipole interactions lead to shifts to higher frequencies [22], the shift to lower frequencies with increasing coverage implies that a chemical shift is involved.

In order to decouple the effects of chemical and dipole shifts, experiments were performed with isotopic mixtures of 10 and 20% D_3COD in H_3COH. The 10% and 20% samples were considered dilute enough to minimize dipole coupling among absorbed CD_3O. The chemical shift will be the same as for the pure samples, while the dipole coupling will be minimized since the similar bands of the two different methoxy isotopes are separated by 25 cm^{-1}. Fig. 11 shows that the pure $D_3CO_{(a)}$ also exhibits the three ν(CO) bands although the two higher bands are not as well resolved as they were for $CH_3O_{(a)}$. The band near 1090 cm^{-1} is assigned to $\delta_s(CD_3)$ and is not of consequence in this analysis. The lowest frequency band which occurs at 953 cm^{-1} in the spectrum for saturation $D_3CO_{(a)}$ coverage appears as a shoulder in the spectra shown in Fig. 12 for saturated adlayers of methoxy with 10% and 20% $CD_3O_{(a)}$, respectively. This figure also shows the deconvolution of the absorption bands. Ideally, the absorption bands from $CH_3O_{(a)}$ could be subtracted from the spectra to leave only the $CD_3O_{(a)}$ bands. Small frequency shifts in these features made this approach impractical. However, the lowest frequency $D_3CO_{(a)}$ peak could be deconvoluted in both cases to yield bands at 949 and 950 cm^{-1}. The higher frequency D_3CO_a peak could not be deconvoluted from the H_3CO_a peaks occurring near the same frequency. The three

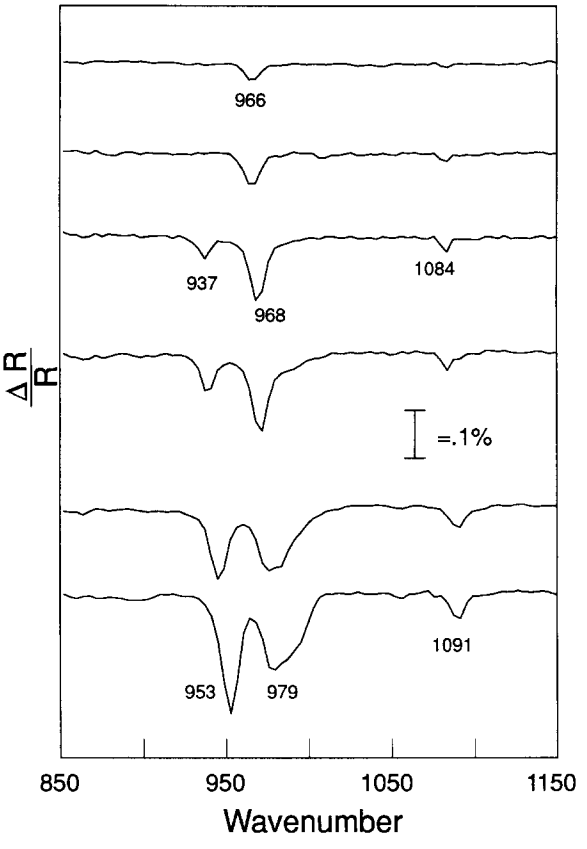


Fig. 11. IR spectra for increasing $D_3CO_{(a)}$ coverages obtained following anneals to 230 K. Coverages range from 0.02 ML to 0.22 ML.

deconvoluted peaks above the 950 cm^{-1} peak are formed from the three H_3CO_a peaks and two D_3CO_a peaks.

The primary cause of the frequency shift appears to be from chemical effects. Instead of appearing at 937 cm^{-1} where the low coverage D_3CO_a ν(CO) peak is expected if dipole coupling were the only effect (Fig. 11), this peak appears at 950 cm^{-1}. The maximum frequency expected is 953 cm^{-1} if only chemical shifts were present. Very little frequency shift is observed between 0.01 and 0.04 ML methoxy coverages for the pure samples. And if the lowest frequency peak has roughly a third of total site distribution, this peak in the mixtures only accounts for 0.01–0.02 ML. Therefore, to the extent that dipole–dipole coupling is removed by

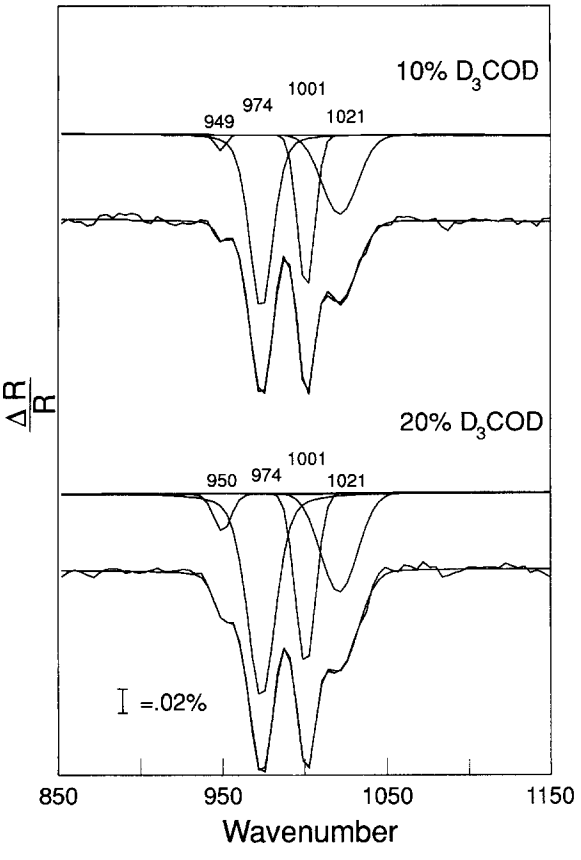


Fig. 12. IR spectra and curve fits for 10 and 20% $D_3CO_{(a)}$ methoxy adlayers formed by anneals to 230 K.

the isotopic substitution, roughly 80% of the shift appears to be caused by chemical effects.

This may also be the case for methoxy adsorbed on other surfaces. Ryberg proposed that since the dynamic dipole of methoxy ν(CO) is similar to that for ν(CO) of adsorbed CO and the dipole shift for CO on Cu(100) was 43 cm^{-1}, the 37 cm^{-1} increase in ν(CO) observed for methoxy on Cu(100) was due to dipole coupling [23]. However, Chesters and McCash observe that the frequency of methoxy ν(CO) on Cu(111) continues to increase with oxygen pre-coverage (1032 cm^{-1} for a 50 L pre-dose to 1046 cm^{-1} for a 300 L pre-dose) and suggest a chemical shift due to the interaction with the adsorbed oxygen [12]. Coadsorbed methoxy on Ni(100) would be expected to produce similar perturbation in the local electronic structure.

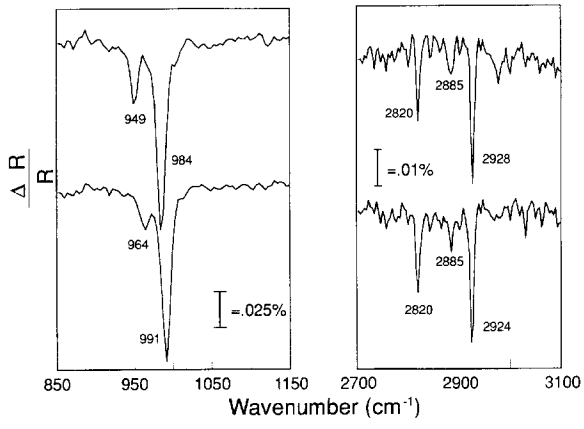


Fig. 13. Spectra for 0.04 ML methoxy with (bottom spectra) and without (top spectra) 0.32 ML hydrogen added. Hydrogen adsorbed following the anneal to 230 K.

3.4. *The effects of coadsorbed hydrogen, CO and sulfur*

The addition of 0.32 ML of hydrogen to 0.04 ML of methoxy and 0.04 ML hydrogen formed from the decomposition of methanol leads to a 15 and 7 cm^{-1} blue shift in the methoxy ν(CO) for the bridge and four-fold hollow species as shown in Fig. 13. The shift of the ν(CO) bands to higher frequencies with coadsorbed hydrogen agrees with the trend predicted by the theoretical calculations mentioned previously [21]. The frequency shifts are also in the same direction as those observed with increasing methoxy coverage (Fig. 9). Therefore, the chemical shifts reported above are a function of both the hydrogen and the methoxy coverages although the hydrogen coverages were lower (less than 0.22 ML hydrogen for the highest coverages when dosing methanol alone). The stretching frequencies in the ν(CH) region show little change; the highest frequency band shows at most a 4 cm^{-1} red shift.

The effects due to coadsorbed CO are much more dramatic. Red shifts of 20 and 12 cm^{-1} are observed for the bands at 950 and 987 cm^{-1}, respectively, when 0.43 ML CO is coadsorbed with 0.04 ML of methoxy and 0.04 ML hydrogen (Fig. 14). Theoretical calculations for methoxy and CO coadsorbed in nearest-neighbor four-fold hollow sites predict a red shift of the methoxy

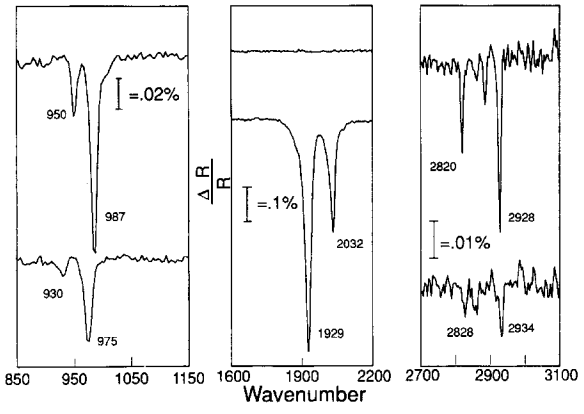


Fig. 14. Spectra for 0.04 ML methoxy with (bottom spectra) and without (top spectra) 0.43 ML additional CO. CO adsorbed following the anneal to 230 K.

ν(CO) of 60 cm^{-1} and an increase in the methoxy adsorption energy from 96.2 kcal/mol on the clean surface to 99.8 kcal/mol in the presence of CO [21]. The increased bonding of the oxygen to the surface lowers the methoxy C–O bond strength. Although the CO in our experiment is adsorbed only in bridge and atop sites, the shift is in the correct direction. Blue shifts of approximately 7 cm^{-1} occur in the ν(CH) region. These compensatory shifts are expected; as the C–O bond strength decreases, the C–H bond strength increases.

In addition to the frequency shifts, the integrated intensities for methoxy are drastically reduced in the presence of CO. If the dynamic dipole remains constant for the methoxy ν(CO) upon CO adsorption, the loss of intensity can be attributed to the tilting of the methoxy species. Assuming the methoxy C–O stretch is orientated along the surface normal when CO is not present and that the dynamic dipole moments are unchanged, the addition of CO leads to a tilt of 48 degrees and reduces the integrated intensity by 0.44. This is a maximum tilt. If the dynamic dipole of the methoxy ν(CO) is reduced or screened by the coadsorbed CO or reduced by a change in binding caused by the tilting itself, the tilt would be less than 48 degrees. In contrast to the case for hydrogen, CO can be adsorbed on a methoxy saturated surface. It is probably adsorbed close to the methoxy species in this experiment. This leads to the interactions necessary to cause tilting.

Theoretical calculations predict that CO adsorbed at the nearest-neighbor four-fold hollow site would lead to methoxy tilt of 25 degrees from normal [21]. They also suggest that it is the repulsive interactions between the CO oxygen atom and the methoxy hydrogens which govern this effect. It is noted that the only new vibrational features to appear in the spectrum are assigned to CO in bridge and four-fold hollow sites. All the methoxy modes decrease in intensity as expected for a′ modes no longer orientated along the surface normal. Asymmetric vibrational modes could be expected to increase in intensity with the tilting, but the signal to noise is too limited to allow any definite conclusions concerning their presence.

The maximum methoxy coverage formed on Ni(100) is decreased by the presence of sulfur on the surface as shown in Fig. 15. The sulfur blocks the sites for methoxy formation. 0.12 ML of sulfur reduces the maximum methoxy concentration to $0.10 \pm .02$ ML. Very little methoxy is formed at sulfur concentrations above 0.20 ML. (The small amounts that do form are likely to be on patches of "clean" surface which have been shown to exist [24].) The pre-adsorbed sulfur does not cause any clear significant frequency shifts in the methoxy spectra. However, the ν(CO) bands are broadened

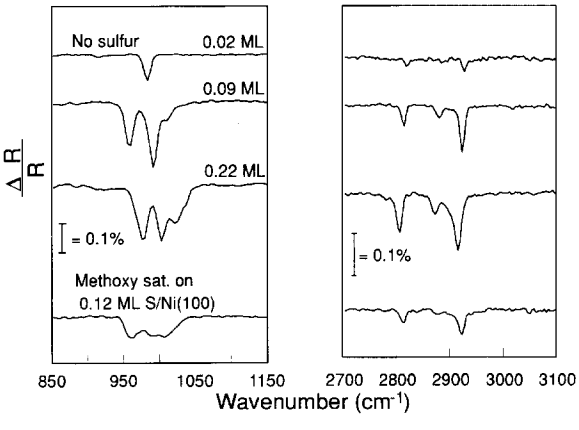


Fig. 15. IR spectra for methoxy of clean Ni(100) (shown previously) and 0.12 ML S/Ni(100). Adlayers were formed by annealing methanol doses to 230 K. Methoxy coverage on 0.12 ML S/Ni(100) surface is 0.10 ± 0.02 ML.

when sulfur is coadsorbed and resemble the shape of the same bands for the maximum methoxy coverage on the clean surface, indicative of inhomogeneities in the adsorbed layer.

4. Conclusions

Methoxy orients with its C–O bond nearly normal to the surface, at least at low coverage. The three ν(CO) bands observed are attributed to methoxy in a four-fold hollow site, methoxy adsorbed at a bridge site, and chemisorbed methanol. Coadsorption of CO causes the methoxy to tilt away from the surface normal. Coadsorbed sulfur or hydrogen do not drastically influence the orientation. The blue shift in ν(CO) for methoxy with the increasing methoxy coverage is attributed 80% to a chemical shift and 20% to dipole coupling. Coadsorbed CO shifts the methoxy ν(CO) peaks to lower frequencies, while hydrogen shifts the peaks upwards in agreement with theoretical predictions.

Acknowledgements

The authors gratefully acknowledge the support of the National Science Foundation (NSF CTS 9005135) and the partial support through the Center for Materials Research at Stanford, without which this research could not have been accomplished. We also appreciate helpful discussions with Dr. Marcus Weldon.

References

[1] S.W. Johnson and R.J. Madix, Surf. Sci. 103 (103) 361.
[2] R.B. Hall, A.M. DeSantolo and S.J. Bares, Surf. Sci. 161 (1985) L533.
[3] R.B. Hall and A.M. DeSantolo, Surf. Sci. 137 (1984) 421.
[4] R.B. Hall, A.M. DeSantolo and S.G. Grubb, J. Vac. Sci. Tech. A 5(4) (1987) 865.
[5] J. Miragliotta, R.S. Polizzotti, P. Rabinowitz, S.D. Cameron and R.B. Hall, Chem. Phys. 143 (1990) 123.
[6] F.L. Baudais, A.J. Borschke, J.D. Fedyk and M.J. Dignam, Surf. Sci. 100 (1980) 210.
[7] L. Westerlund, L. Jönsson and S. Andersson, Surf. Sci. 199 (1988) 109.
[8] G.E. Mitchell, J.L. Gland and J.M. White, Surf. Sci. 131 (1983) 167.
[9] L. Westerlund, L. Jönsson and S. Andersson, Surf. Sci. 187 (1987) L669.
[10] J.S. Huberty and R.J. Madix, Surf. Sci. 334 (1995) 77.
[11] S. Pinchas and I. Laulicht, Infrared Spectra of Labelled Compounds, 2nd ed. (Academic Press, New York, 1971).
[12] M.A. Chesters and E.M. McCash, Spectrochim. Acta A 43 (1987) 1625.
[13] P. Uvdal, M.K. Weldon and C.M. Friend, Phys. Rev. B 50 (1994) 12258.
[14] A. Serrallach, R. Meyer and Hs.H., Günthard, J. Molec. Spect. 52 (1974) 94.
[15] J.C. Lavalley and N. Sheppard, Spectrochim. Acta A 28 (1972) 2091.
[16] R. Ryberg, Phys. Rev. B 31 (1985) 2545.
[17] J. Stöhr, J.L. Gland and W. Eberhardt et al., Phys. Rev. Lett., 51 (1983) 2414.
[18] D.A. Outka, R.J. Madix and J. Stöhr, Surf. Sci. 164 (1985) 235.
[19] Th. Lindner, J. Somers, A.M. Bradshaw, A.L.D. Kilcoyne and D.P. Woodruff, Surf. Sci. 203 (1988) 333.
[20] A. Wander and B.W. Holland, Surf. Sci. 203 (1988) L637.
[21] H. Yang, J.L. Whitten J.S. Huberty and R.J. Madix, to be published.
[22] F.M. Hoffman, Surf. Sci. Rep. 3 (1983) 107.
[23] R. Ryberg, Phys. Rev. Lett. 49 (1982) 1579.
[24] N. Vasquez, A. Muscat and R.J. Madix, Surf. Sci. 339 (1995) 29.