

Symmetry and orientation of CH₃O on Cu(100)

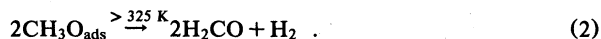
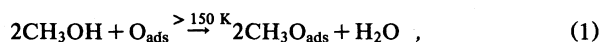
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The C-H stretch vibrational modes of CH₃O chemisorbed on a Cu(100) surface have been studied using infrared spectroscopy. Three absorption peaks were found indicating that the symmetry of the CH₃ group is broken. Comparison with the infrared spectra of free methanol shows that the CH₃O group is rather little perturbed by the chemisorption and that the molecules definitely are tilted on the surface. Thermal desorption spectra indicate that the dehydrogenation of CH₃O to H₂CO goes via the adsorption of a hydrogen atom on the copper surface during a low-frequency bending mode.

A catalytic reaction that has been the subject of a number of investigations is the oxidation of methanol to formaldehyde on a copper surface. The initial thermal desorption work¹ indicated that the reaction proceeds in two steps via the formation of a surface methoxy intermediate, CH₃O, giving



From electron-energy-loss studies one has concluded that the methoxide on Cu(100) is chemisorbed in a hollow position² and bonded to the surface via the oxygen atom.³ In all previous work the CH₃O has been assumed to have a symmetric CH₃ group just as the free methanol molecule. However, it is the purpose of this Rapid Communication to show that free methanol has not a symmetric CH₃ group, that its asymmetry is maintained for chemisorbed CH₃O, that the CH₃ group is rather little perturbed by the chemisorption, that the molecules are tilted on the surface, and finally how one can get some insight into the dehydrogenation mechanism in step (2).

The experimental setup has been described elsewhere.^{4,5} The C-H stretch vibrational spectra was recorded by infrared spectroscopy (IRS). The sensitivity of the spectrometer has been considerably improved since the previous work,⁶ which called for this reinvestigation and indeed exposed new features of this system.

In Figs. 1 (2) we reproduce the new infrared spectra of the C-H (C-D) stretch vibrational modes of different covers of CH₃O(CD₃O) on Cu(100) at 100 K. Because of the better understanding of reaction step (1) that we have obtained,⁷ the reaction procedure was somewhat different from the first work⁶ and a comprehensive discussion of both reaction steps will be given in a forthcoming paper. The striking feature of Fig. 1 is the existence of *three* vibrational modes. For a symmetric CH₃ group with a local C_{3v} symmetry one expects two high-frequency (C-H stretch) modes, one symmetric, and one twofold degenerate antisymmetric mode. The appearance of three modes indicates that this degeneracy is broken. As pointed out in a cluster calculation,⁸ the symmetry of a CH₃O molecule chemisorbed on a Cu(100) surface in a hollow position together with the four nearest-neighbor Cu atoms is at best C_s, that is, with two hydrogen atoms oriented symmetrically with respect to the

substrate. If there were a substantial interaction between the metal and the CH₃ group, this would give rise to two antisymmetric vibrational modes, that is, a total of three, just as we observe.

However, there exists a careful infrared investigation, combined with a valence force-field calculation of gas-phase methanol,⁹ that we were not previously aware of. That study shows that the CH₃ group does not at all have the C_{3v} symmetry and that the infrared spectrum of free methanol does show three C-H stretch modes. The twofold degeneracy of the antisymmetric mode is broken because the C-H bond parallel to the O-H bond is different from the two other C-H bonds.⁹ It would be interesting if this asymmetry were preserved for chemisorbed methoxide. The Cu-CH₃O bond should be quite different, with the oxygen bonding to four metal atoms in the hollow position instead of a single hydroxyl bond.

In Table I we compare the vibration frequencies of the three C-H stretch modes of ordinary and deuterated

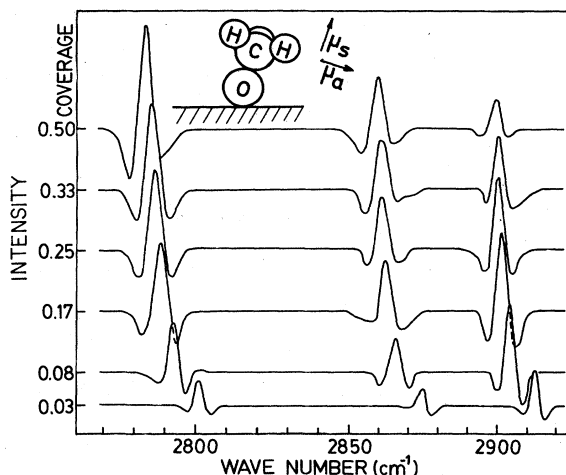


FIG. 1. Infrared spectra of C-H stretch vibrational modes of different covers of CH₃O on Cu(100) at 100 K. The reproduced spectrometer signal is proportional to the second derivative of the absorbance. Insert shows a chemisorbed CH₃O molecule and the orientation of the dynamical dipole moments μ of the symmetric and antisymmetric modes.

TABLE I. Vibration frequencies (in cm^{-1}) and isotopic shift ratios of the symmetric (ν_s) and the two antisymmetric (ν_a) C-H stretch modes of free methanol (Ref. 9) and a coverage of 0.25 of methoxide on Cu(100).

	ν_s	ν_a''	ν_a'
CH ₃ OD	2841	2970	3001
CD ₃ OD	2078	2213	2250
CH ₃ O	2787	2861	2901
CD ₃ O	2054	2127	2178
CH ₃ OD/CD ₃ OD	1.37	1.34	1.33
CH ₃ O/CD ₃ O	1.36	1.35	1.33

methanol and methoxide and the ratios of these isotope shifts. The ratios are very similar for CH₃OH and Cu-CH₃O, indicating that the vibrational modes preserve their character, and that the asymmetry of the CH₃ group is not caused by an interaction with the substrate but is an inherent property of the CH₃O group. So the methoxide not only maintains the asymmetry, but, except for a general chemisorption shift of about 100 cm^{-1} , the CH₃ group is also rather little perturbed by the chemisorption (that there is some direct and/or indirect molecule-molecule interaction is seen by the intensity variations of the different modes in Figs. 1 and 2).

In a rather recent work Stöhr *et al.*¹⁰ have used an x-ray photoemission technique to determine the molecular orientation for CO, CH₃O, and HCO₂ on Cu(100). They argue that methoxide is oriented with the C-O axis normal to the surface. This is in contradiction to our present work because both the symmetric and the antisymmetric C-H modes are seen in the infrared spectra. The so-called infrared selection rule says, namely, that if the substrate is a good conductor the component of the incident electric field parallel to the surface is screened. Consequently, for a particular vibrational mode it is only the component of its dynamical dipole moment normal to the surface that causes

absorption of the infrared radiation. As the dynamical dipole moments of the symmetric and the antisymmetric C-H modes are orthogonal (Fig. 1) and as they all are seen in the infrared spectra, this shows definitely that the molecules are tilted on the surface (with the orientation suggested by Stöhr *et al.*¹⁰ only the symmetric mode would be excited). If the magnitudes of the dynamical dipole moments of the different modes were known, one could from the relative absorption intensities determine the tilt angle. However, one cannot simply use the gas phase values, as the dipole moments, in general, are changed upon chemisorption. An interesting observation in Figs. 1 and 2 is that the antisymmetric modes are much weaker for CD₃O. If for comparison we use the *calculated* gas phase values⁹ we get for the ordered $c(2 \times 2)$ structure a tilt angle of 30° for CH₃O (using either of the antisymmetric modes) and only 13° for CD₃O. However, as there exist no *measured* gas phase values and as the absorption of the antisymmetric C-D modes are so weak, there is a large uncertainty even in these relative figures and we are not able at this point to establish whether or not this is a real effect.

Finally, let us consider reaction step (2), the dehydrogenation of CH₃O to H₂CO. One may think of three possible mechanisms. Firstly, as the temperature is raised there could be a more or less continuous weakening of a C-H bond by the filling of an antibonding molecular orbital.¹¹ This should be manifested by an increased vibrational damping, possibly observed as a broadening of the absorption peak and a simultaneous downward frequency shift. However, our infrared spectra show no such variation with temperature in the range 100–320 K. Secondly, as the CH₃O molecules become more mobile with increasing temperature⁷ they may during a collision form a short-lived, unstable (CH₃O)₂ complex on the surface. But Wachs and Madix¹ showed that the reaction was a first-order process. They also suggested that the molecules make some kind of bend motion, bind at a certain inclination a hydrogen atom to the surface, and desorb as H₂CO.

To test this idea, a thermal desorption study was undertaken for CH₃O and CD₃O; the results are shown in Fig. 3. The interesting observation was that the reaction occurred at 16 ± 2 K lower temperature for CH₃O than for CD₃O. Suppose that the hydrogen atom binds to the surface because of

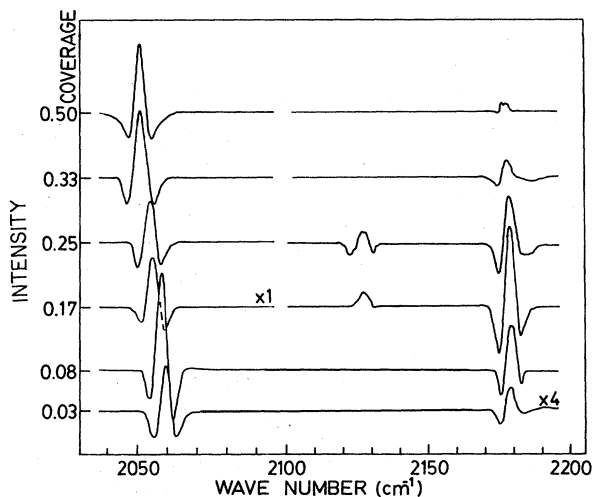


FIG. 2. Infrared spectra of C-D stretch vibrational modes of different coverages of CD₃O on Cu(100) at 100 K.

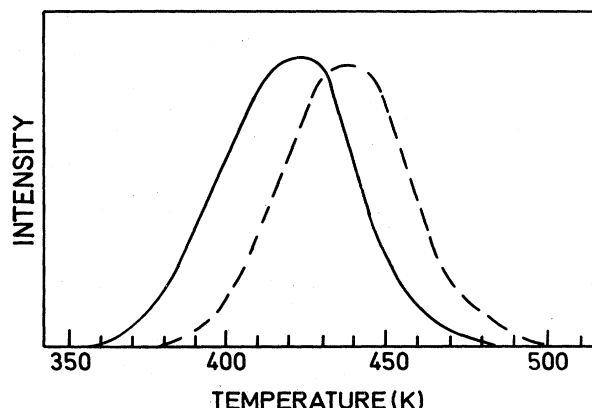


FIG. 3. Thermal desorption spectra for H₂CO ($m = 30$) solid line and D₂CO ($m = 32$) broken line. Heating rate about 2 K/s.

a low-frequency bending mode (a frustrated motion), then it is a reasonable assumption that the important parameter is the Cu-H distance. If we assume a pure harmonic bending mode with a small angular amplitude ψ_0 then

$$\psi_0^2 \sim \frac{1}{\Omega I},$$

where I is the moment of inertia and Ω is the bending frequency. This gives a bend mode amplitude $Q_0 \sim I^{-1/4}$ (cf. Ref. 11). Using the molecular configuration in Ref. 9 and placing the origin of the motion at the oxygen atom, we get

an isotope effect of 7.7%, in this case about 30 K, which obviously is of the right order. Furthermore, as the molecules are tilted on the surface the Cu-CH₃O stretching and bending modes are not orthogonal and will therefore mix. As the stretch mode has the higher frequency of the two, the mixed mode that has a predominantly bending character will lower its energy, making the agreement with the observed temperature shift still better.

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