Adsorbate symmetry and Fermi resonances of methoxide adsorbed on Mo(110) as studied by surface infrared spectroscopy

P. Uvdal
MAX Chemistry, Department of Chemistry, Lund University, S-22100 Lund, Sweden

M. K. Weldon and C. M. Friend
Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138
(Received 11 July 1994)

It is conclusively demonstrated using surface infrared spectroscopy, in combination with selective isotopic labeling, that methoxy coordinates with C_{3v} symmetry on Mo(110), at coverages below 0.17 ML. The existence of intense Fermi resonances in the C-H stretch region of adsorbed CH_3O is firmly established. By application of these observations to previous studies of methoxy on the low-index planes of copper and nickel, the disparity between the adsorbate geometry predicted by infrared spectroscopy and that deduced from photoelectron studies is removed.

Accurate assignment of vibrational modes of adsorbed species is essential in determining their structure and in probing surface-induced changes in their intramolecular potentials. Among other things, adsorbate structure is important in understanding a variety of surface phenomena, in order to probe the mechanism of complex processes such as heterogeneous methanol synthesis and diamond atomic-layer epitaxy.

Over the last decade, there has been considerable debate over the interpretation of the surface vibrational spectra of adsorbed methoxide due to significant differences from the known spectrum of gaseous or condensed methanol. In particular, there is disagreement regarding the assignment of the symmetric and asymmetric carbon-hydrogen stretching vibrations, which can, in principle, be used to determine the orientation and symmetry of the methoxy moiety. The assignment of these modes is complicated by the existence of additional modes due to anharmonic coupling between overtones of the methyl deformation modes and the stretching fundamentals, such that a normal mode analysis is no longer appropriate. Indeed, strong Fermi resonances are known to be prevalent in methyl-containing compounds and can dominate the 2700–3100-cm^{-1} region of the infrared spectrum.[1–3] Chesters and McCash[4] have previously proposed that the two highest frequency bands in the C-H stretching region in the infrared spectrum of methoxy on Cu(111) were due to overtone and/or combination bands of the methyl deformation modes, based on data for hydrogenated and perdeutero-methoxy. However, a definitive assignment is not possible using such isotopically "pure" methanol, as these overtone modes cannot easily be distinguished from the asymmetric C-H(D) stretching fundamentals, which occur in the same frequency range. Importantly, the resonance results in intensity borrowing by the overtone from the C-H stretch modes, with the result that significant intensity can be observed in the overtone, independent of the oscillator strength of the deformation fundamentals.[1] We were able to eliminate this coupling by partially deuterating the methyl group so that the overtones of the highest frequency-bending modes are no longer near-degenerate with the C-H stretch

modes. This approach has previously been used by McKean and co-workers to remove contributions from Fermi resonances in the infrared spectra of gaseous methyl-containing compounds, including methanol.[2,3] Consequently, we are able to conclusively demonstrate that a single methoxy species with C_{3v} symmetry is present on Mo(110) at 100 K, for a coverage of 0.17 ML. Hence, the intense features observed at 2916 and 2868 cm^{-1} in the infrared spectrum of CH_3O- are not due to the asymmetric C-H stretch, as has been previously proposed for methoxy adsorbed on a variety of surfaces,[5–7] but are due to overtones of the methyl deformation modes mixed with the symmetric C-H stretching fundamental, in agreement with the assignments proposed by Chesters and McCash.[4]

Experiments were performed in an ultrahigh vacuum chamber with a base pressure below 2×10^{-10} Torr, described in detail elsewhere.[8] All infrared reflection absorption spectra were collected using a single-beam, clean-air purged Fourier-transform infrared spectrometer (Nicolet, Series 800) and averaged over 1000 scans using a mercury-cadmium-telluride detector, at 2-cm^{-1} resolution; resulting in a scan time of approximately 15 min. Sample spectra were ratioed against a background taken immediately after the sample scan by flashing the crystal to 900 K. The scan was initiated after the crystal temperature had returned to 100 K. The spectra shown consist of at least two sets of 1000 scans, co-added to improve the signal-to-noise ratio. Methoxy was prepared by exposing the clean Mo(110) surface to a dose of methanol [CH_3OH (Aldrich, 99.9%), CHD_2OH (Cambridge Isotope, 98%)] sufficient to deposit multiple layers, followed by heating to 300 K. Formation of surface methoxy was verified by electron-energy-loss spectroscopy and the methoxy coverage determined by x-ray photoelectron spectroscopy, as described in a subsequent publication.[9]

Methoxy adsorbed on a low-index plane will exhibit either C_{3v}, C_s, or C_1 symmetry, depending on the orientation and the symmetry of the adsorption site. The C_{3v} symmetry requires that the symmetry axis of the molecule be oriented along the surface normal and, formally, that the adsorption
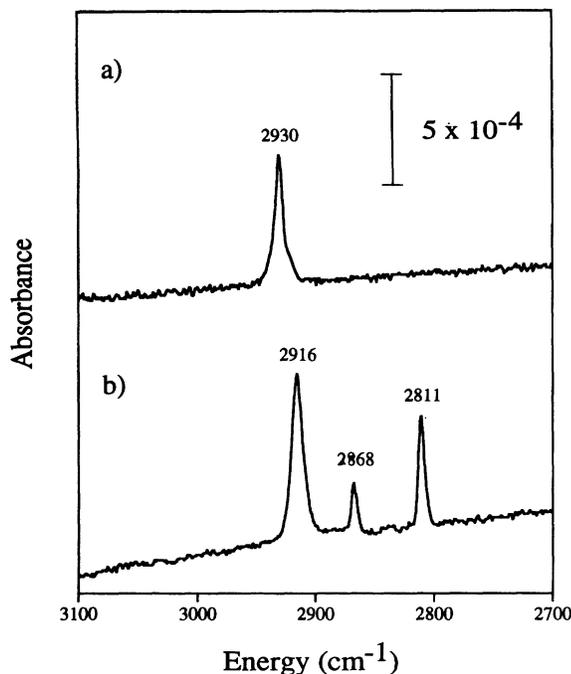
FIG. 1. The C-H stretching region of the infrared spectrum of 0.17 ML of methoxy adsorbed on Mo(110) at 100 K; (a) CHD_2O- and (b) CH_3O-.

site has threefold symmetry or higher. Consequently, methoxy cannot strictly possess C_{3v} symmetry on the twofold-symmetric (110) surface, although, as molybdenum has a body-centered-cubic lattice structure, this surface does possess pseudothreefold sites that are only slightly perturbed from true local threefold symmetry. However, if methoxy is insensitive to the symmetry of the surface beyond the adsorption site, C_{3v} symmetry is possible for the atop site.

The infrared spectra of intermediate coverages of CHD_2O- and CH_3O- adsorbed on Mo(110) conclusively demonstrate that the adsorbate symmetry is C_{3v} (Fig. 1). The presence of only a single feature in the C-H stretching region of CHD_2O- precludes both C_s and C_1 symmetry. Furthermore, the presence of three features in this region of the infrared spectrum of CH_3O- is entirely consistent with the predictions based on C_{3v} molecular symmetry. The fact that only the symmetric deformation mode, at 1424 cm^{-1}, is observed is also consistent with a C_{3v} adsorbate symmetry. The asymmetric deformation, predicted to be at ~ 1445 cm^{-1}, is not observed as it is surface-dipole forbidden for this geometry.[10,11]

Under the surface-dipole selection rule, the only modes that are allowed are those that transform as the totally symmetric representation of the point group. Therefore, for C_{3v} symmetry, the only fundamentals allowed are those with A_1 character: ν(C-O), $\rho(CH_3)$, $\delta_s(CH_3)$, and ν_s(C-H). The $\delta_a(CH_3)$ and ν_a(C-H) modes are degenerate (E character) and are therefore forbidden. Thus, only one fundamental mode, ν_s(C-H), should be observed in the 2700–3100-cm^{-1} region of the vibrational spectrum. For a nondegenerate fundamental, all first overtones (second harmonics) are totally symmetric with respect to the operations of the point

group and are therefore allowed. Hence, the first overtone of the symmetric deformation at 1424 cm^{-1} can contribute intensity in this region. The overtones of the (degenerate) asymmetric deformations have character $A_1 + E$; the only allowed (A_1) part being due to the simultaneous excitation of the fundamental of both degenerate components. Finally, the bands resulting from a combination of the symmetric- and asymmetric-deformation modes have $A_1 \times E = E$ character and are consequently forbidden. Therefore, three bands are allowed under C_{3v} symmetry, in the 2700–3100-cm^{-1} region of the infrared spectrum of CH_3O-: ν_s(C-H), $2\delta_s(CH_3)$, and $2\delta_a(CH_3)$. In contrast, only one C-H stretch mode will have significant intensity for "C_{3v}" CHD_2O-, as all C-H bond coordinates are equivalent and are uncoupled from the overtones and combination bands of the CH_2 bending modes.[3] The degeneracy of the asymmetric modes in CH_3O- is lifted under C_s symmetry, to form two different classes of modes; one having A' symmetry (in plane) and the other A'' symmetry (out of plane). Therefore, the symmetric and in-plane asymmetric C-H stretching modes are allowed under C_s symmetry. Four nonfundamental modes are also allowed: the overtones of the three deformation modes as well as the $\delta_s(CH_3) \times \delta_{a'}(CH_3)$ combination band, giving a total of six allowed bands in the surface infrared spectrum. However, only two features would be observed in this spectral region for C_s CHD_2O^-, formally due to the existence of two different symmetries, C_s and C_1, and corresponding to C-H stretching motions in and out of the Mo-O-C plane present in the molecule.

Finally, the out-of-plane component of the asymmetric stretch and the $\delta_s(CH_3) \times \delta_{a''}(CH_3)$ and $\delta_{a'}(CH_3) \times \delta_{a''}(CH_3)$ combination bands also become allowed for CH_3O- under C_1 symmetry, giving a total of nine possible bands in the 2700–3100-cm^{-1} region. In contrast, three C-H stretch modes would be observed in this region for CHD_2O-, as all C-H coordinates become inequivalent on removal of the σ_h symmetry element present under C_s symmetry.

By reference to our data for CHD_2O-, we assign the features observed in the C-H stretch region of the spectrum of 0.17-ML CH_3O^- to $2\delta_s(CH_3)$ and $2\delta_a(CH_3)$ in Fermi resonance with the symmetric C-H stretching fundamental ν_s(C-H). However, these features can only be approximately described in terms of these normal modes. The anharmonic coupling allows mixing of the vibrational wave functions to form modes with partial ν_s and partial δ_s/δ_a character, resulting in "intensity borrowing" by the overtone states from the fundamental, so that the observed intensity is independent of the transition dipole moment of deformation fundamentals. Therefore, a more accurate description is that the modes at 2916 and 2811 cm^{-1} are due to a Fermi resonance between ν_s(C-H) and an in-phase combination of $2\delta_s(CH_3)$ and $2\delta_a(CH_3)$, whereas the mode at 2868 cm^{-1} results in an out-of-phase combination of $2\delta_s(CH_3)$ and $2\delta_a(CH_3)$, with considerably less admixture of ν_s(C-H).[1]

The above assignments may be generally applicable for adsorbed methoxide, based on the excellent agreement between our data and those reported for a wide variety of different surfaces (Table I). An early infrared reflection absorption study of methoxy adsorbed on Cu(100) attributed the observation of three modes at 2787, 2861, and 2901 cm^{-1} to

TABLE I. Vibrational assignments for CH_3O- on various surfaces.

Mo(110) (cm^{-1})	Cu(100) (cm^{-1})	Cu(111) (cm^{-1})	Ni(111) (cm^{-1})	Assignment
2916	2901	2918	2921	$2\delta_a(CH_3)$
2868	2861	2882	2878	$2\delta_s(CH_3)$
2811	2787	2818	2817	ν_s(C-H)
1424		1435		$\delta_s(CH_3)$
1007		1036	1027	ν(C-O)

the symmetric and asymmetric stretching modes, respectively, of a single, tilted (C_1 symmetry) species.[7] However, a subsequent study determined that the C-O axis is actually perpendicular to the Cu(100) plane, using x-ray absorption and backscattering photoelectron diffraction measurements,[12] consistent with our assignment of the three bands in the infrared spectrum to the symmetric C-H stretch and two overtone modes (Table I). Similarly, for methoxy adsorbed on Cu(111), a perpendicular C-O bond orientation has been derived from forward-scattering photoelectron diffraction,[13] whereas three modes are observed at 2818, 2882, and 2918 cm^{-1} in the 2700–3100-cm^{-1} region of the surface infrared spectrum.[4] There is also excellent agreement between our data and that observed for methoxy adsorbed on Ni(111), for which the 2921-cm^{-1} mode was previously attributed to ν_a(C-H), implying that the molecular symmetry axis was tilted away from the surface normal, as proposed in an earlier electron-energy-loss study of this system.[6,14] The C_{3v} geometry predicted for CH_3O-Ni(111) based on our assignments, is in agreement with the conclusions of ultraviolet photoemission studies of methoxy on Ni(111) and ab initio valence-orbital calculations of methoxy adsorbed in a threefold site on a 28-atom Ni(111) cluster, which indicated that a perpendicular C-O bond orientation was most favorable (Table I).[15,16] Clearly, infrared studies using CHD_2O- on these surfaces would be valuable, in order to further justify the generality of our assignments. Finally, in a subsequent publication we will show that, other than the appearance of ν_a(C-H) at ~ 2950 cm^{-1}, the vibrational spectrum of a tilted methoxy species, formed at higher coverages, is essentially identical to that for C_{3v}, implying that Fermi resonances also give rise to the intense features at around 2900 cm^{-1} in

tilted methoxy species,[9] in contrast to the recent assignment of these features to $\nu_{a'}$(C-H) for methoxy on Ni(110), based on rhenium cluster data.[5,17]

Our data clearly indicate that the vibrational spectrum of methoxide is not sensitive to substrate symmetry. Formally, the only coordination site on the Cu(100) and Mo(110) surfaces compatible with a C_{3v} adsorbate symmetry is the atop site, provided that the symmetry of the surface beyond the adsorption site can be neglected. However, this site can be excluded for Cu(100), based on the symmetry properties of the observed surface phonons.[18] Therefore, the highest symmetry possible for methoxide is C_s, when coordination to an unreconstructed surface is taken into account. In a previous publication, we have discussed the possibility of a surface reconstruction occurring upon adsorption of CH_3S-, resulting in a local C_{3v} symmetry of the pseudothreefold-hollow sites.[19] However, no reconstruction of the Mo(110) occurs on adsorption of CH_3O-, based on low-energy electron-diffraction data. We therefore conclude that formal group theory is not always applicable when determining the symmetry of methoxy on these surfaces, even when only the symmetry of the coordination site is considered.

In conclusion, we have shown by surface infrared spectroscopy in combination with selective isotopic labeling, that methoxy coordinates in an upright or "pseudo-C_{3v}" geometry on Mo(110), at coverages below 0.17 ML. Consequently, the intense features at 2868 and 2916 cm^{-1} in the infrared spectrum of methoxy can only be assigned to overtones of the methyl deformation modes, gaining virtually all intensity from Fermi resonances with the symmetric C-H stretching vibration. Furthermore, we propose that the predominance of the overtone modes in the infrared spectrum is not restricted to molybdenum, but is generally the case for methoxy adsorbed on transition-metal surfaces, based on the excellent agreement between our data and that for the low-index planes of copper and nickel. Indeed, reassignment of the three bands in the infrared spectrum of methoxy adsorbed on these surfaces to the symmetric carbon-hydrogen stretch and two overtones of the methyl deformations of a C_{3v} moiety, removes the disparity between the structure predicted by infrared spectroscopy and that deduced by a variety of other techniques.

[1] J. P. Champion, A. G. Robiette, I. M. Mills, and G. Graner, J. Mol. Spectrosc. **96**, 422 (1982).

[2] P. D. Mallinson and D. C. McKean, Spectrochim. Acta, Part A **30**, 1133 (1974).

[3] D. C. McKean, Spectrochim. Acta, Part A **29**, 1559 (1973).

[4] M. A. Chesters and E. M. McCash, Spectrochim. Acta, Part A **43**, 1625 (1987).

[5] H. E. Dastoor, P. Gardner, and D. A. King, Chem. Phys. Lett. **209**, 493 (1993).

[6] R. Zenobi, J. Xu, J. T. Yates, B. N. J. Persson, and A. I. Volokitin, Chem. Phys. Lett. **208**, 414 (1993).

[7] R. Ryberg, Phys. Rev. B **31**, 2545 (1985).

[8] M. K. Weldon and C. M. Friend, Surf. Sci. **310**, 95 (1994).

[9] M. K. Weldon, P. Uvdal, C. M. Friend, and J. G. Serafin (unpublished).

[10] The frequency of the asymmetric stretch is predicted by applying the same adsorption-induced frequency shift from the value in matrix-isolated methanol, as was observed for the symmetric deformation mode. This approach is justified by reference to data for a tilted methoxy species on Mo(110), for which both modes are observed and are similarly shifted from the matrix-isolated methanol reference state (Ref. 9).

[11] The signal-to-noise ratio for the symmetric-deformation mode is approximately 10:1 for 0.17 ML of methoxy compared to a symmetric-to-asymmetric intensity ratio of approximately 4:1 for methoxy in a tilted geometry, identified at higher coverage

(Ref. 9). Therefore, the lack of observed intensity in the asymmetric-deformation mode is not detection limited.

[12] Th. Lindner, J. Somers, A. M. Bradshaw, A. L. D. Kilcoyne, and D. P. Woodruff, Surf. Sci. **203**, 333 (1988).

[13] M. Witko, K. Hermann, D. Ricken, W. Stenzel, H. Conrad, and A. M. Bradshaw, Chem. Phys. **177**, 363 (1993).

[14] J. E. Demuth and H. Ibach, Chem. Phys. Lett. **60**, 395 (1979).

[15] J. L. Erskine and A. M. Bradshaw, Chem. Phys. Lett. **72**, 260 (1980).

[16] H. Yang, J. L. Whitten, and C. M. Friend, Surf. Sci. **313**, 295 (1994).

[17] U. A. Jayasooriya, C. E. Anson, O. Al-Jowder, G. D'Alfonso, P. L. Stanghellini, and R. Rossetti, Surf. Sci. **294**, 131 (1993).

[18] S. Andersson and M. Persson, Phys. Rev. B **24**, 3659 (1981).

[19] B. C. Wiegand, P. Uvdal, and C. M. Friend, Surf. Sci. **279**, 105 (1992).