Surface-induced alteration of adsorbate electronic structure and intramolecular vibrational coupling: The vibrational spectrum of 2-propoxide on Mo(110) as determined by *ab initio* calculations and experiments

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Interactions with the molybdenum surface have a strong influence on the vibrational spectrum of 2-propoxide on Mo(110). Using *ab initio* electronic-structure calculations the vibrational spectrum of the adsorbed 2-propoxide is determined. All major effects, experimentally observed by electron-energy-loss spectroscopy, are well reproduced by the calculation. Kinematic effects do not explain the observed changes. Calculations indicate that the changes in vibrational spectra are due to alterations of the intramolecular potential function and charge redistribution upon binding to the Mo.

Vibrational spectroscopy is an important tool in surface science. It has successfully probed adsorption and reaction intermediates[1,2] and the dipole selection rule has been applied to infer the orientation of small and large molecules on metal surfaces.[3-5] The ultimate goal of surface vibrational spectroscopy is to determine the origin of the frequency shifts, intensity redistributions, and line-shape changes that occur when a molecule is adsorbed on a surface. The observed changes in chemisorbed ligands can involve a complicated interplay of several factors. Chemical bonding effects lead to vibrational frequency shifts and changes in the intensity of vibrational modes upon adsorption. Coupling effects are usually more subtle, and have been shown to give rise to, for example, vibrational shifts and changes in line shapes.[6]

A necessary condition for a detailed interpretation of the vibrational spectrum is the correct assignment of the individual modes. For complex adsorbates, assignments are usually based on gas-phase data for the same or a similar molecule and an analysis of the reduced symmetry imposed by adsorption.[7] Moreover, it is often assumed that only vibrational modes involving atoms coordinated to the surface are influenced by the adsorption. In this paper, we demonstrate a case where vibrational spectroscopy of polyatomic molecules adsorbed on a surface can be moved from the usual fingerprint approach to a qualitative interpretation using *ab initio* electronic-structure calculations. The case of 2-propoxide constitutes an ideal test case, because the vibrational spectrum is dramatically altered by the coordination to the metal surfaces as compared to the gas phase. Isotopic labeling allows for additional verification of the model, as it induces shifts that cannot be explained in terms of a simple kinematic model.

Differences between the electron-energy-loss spectra of 2-propanol condensed on the Mo surface and of 2-propoxide bound to Mo(110) are clearly evident throughout the entire energy region probed [Figs. 1(a) and 1(b)]. Most dramatic is the appearance of two intense losses at 800 and 910 cm^{-1} in 2-propoxide [Fig. 1(b)]. The intensity redistribution of some modes, e.g., at 1350, 1450, and 2950 cm^{-1}, and the appearance of the loss at 570 cm^{-1} are attributed to the oriented coordination of the alkoxide to the surfaces. 2-propanol in the condensed layer is randomly oriented. Deuterium-substituted species show corresponding changes in the vibrational spectra upon 2-propoxide formation (Fig. 2). There are also two intense losses observed for $(CD_3)_2(H)C$-O (800 and 980 cm^{-1}) and $(CD_3)_2(D)C$-O (800 and 935 cm^{-1}) [Figs. 2(c) and 2(d)]. Only one high-intensity loss is observed for 2-propoxide-d_3 at 880 cm^{-1} [Fig. 2(b)]; the complete spectrum of propoxide-d_3 is shown in Fig. 1(c). The most intense modes for all four isotopically labeled species are dipole scattered rather than impact scattered, as determined by the off-specular electron-energy-loss measurements.[8]

The simplest approach to interpreting a change in the vibrational spectrum on binding is in terms of a kinematic model; i.e., only the masses and geometry are altered (the mass of hydrogen in OH replaced with the mass of Mo, the C-O-H angle replaced by the linear C-O-Mo angle) in going from propanol to bound propoxide. Kinematic effects do not explain the changes in the experimental vibrational spectra as the vibrational spectra derived from *ab initio* calculations using the force constants for propanol and substitution of the mass of molybdenum (95.94u) for hydrogen do not agree with the experimental results (not shown). Importantly, no enhanced dipole activity of modes related to the C-O stretch resulted from
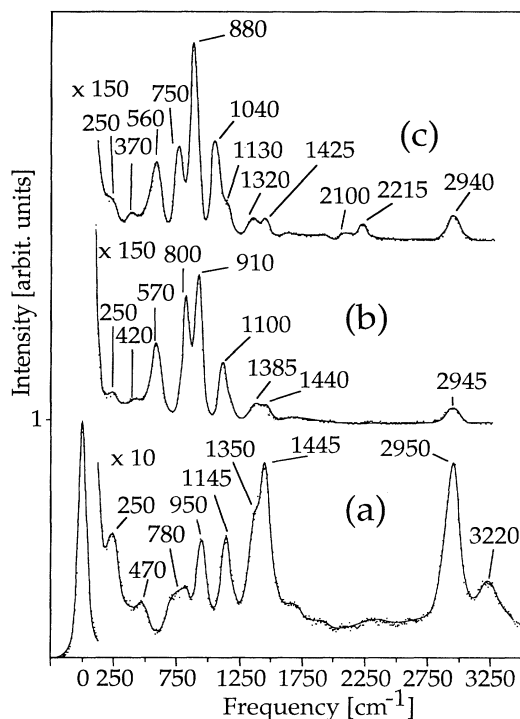
FIG. 1. Electron-energy-loss spectra collected at 120 K of (a) a condensed layer of 2-propanol-d_0, (b) saturation coverage of 2-propoxide-d_0, and (c) saturation coverage of 2-propoxide-d_3. The saturation coverage of 2-propoxide is formed by heating layers of 2-propanol condensed onto Mo(110) to 300 K. The spectra were collected using a LK-2000-14-R electron-energy-loss spectrometer operating at 3-eV primary energy and 55–85-cm^{-1} resolution.
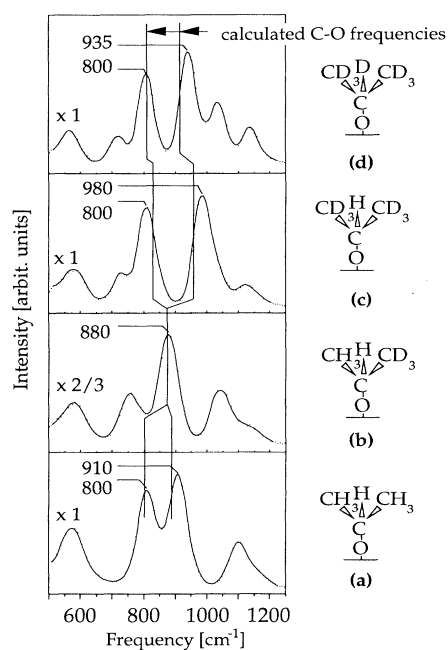

FIG. 2. Electron-energy-loss spectra collected at 120 K of saturation coverage of (a) 2-propoxide-d_0, (b) 2-propoxide-d_3, (c) 2-propoxide-d_6, and (d) 2-propoxide-d_8.

these calculations. Also, the agreement between calculated and observed frequencies was not as good as for the organometallic complex model considered below.

Vibrational coupling is known to be important in higher alcohols due to the similar force constants in the carbon-carbon and carbon-oxygen stretching modes.[9] Hence changes in the C-O bond of 2-propoxide due to interactions with the surface may be reflected in the rest of the vibrational spectrum via coupling to other modes.

Ab initio calculations were performed for the free and bound species to obtain a more detailed understanding of the spectra. Previously, we have successfully applied *ab initio* calculations in the same manner as described below to calculate vibrational spectra of ethanol and ethoxide adsorbed on Mo(110).[10] The perturbation of the molecule due to the coordination to the metal was, however, minor compared to the present case. To determine the effect of the binding of 2-propoxide to the Mo surface on the electronic structure of the alkoxide, the metal was treated as a single Mo atom. Although the surface, as a first approximation, is represented by only a single metal atom, it is expected to provide qualitative information concerning the major effect of metal adsorbate bonding. Previous cluster-model studies have shown that adsorbate vibrations are relatively insensitive to the cluster size as long as the adsorption site is fixed.[11,12] This occurs even though the binding energies often have a strong dependence on cluster size.[13] While changes in the site geometry may be important in the quantitative description of the spectral changes, the one-atom model for the surface interaction used in the present study will provide information about the effect of bonding.

Hartree-Fock calculations were performed using GAUSSIAN90 (Ref. 14) with the Los Alamos effective core potential for Mo[Kr]$4d^5$, $5s^1$ and a double-zeta basis set[15,16] on all other atoms. Three charge states were considered for the 2-propoxide-Mo complex in our calculations: -1, 0, and $+1$. The electron configuration of Mo is [Kr]$4d^5$,$5s^1$; six electrons are therefore required to fill the $4d$ and $5s$ orbitals. Since oxygen contains five valence electrons, the use of a 0 charge state for the complex would yield an unpaired electron. Due to difficulties in performing the open-shell calculations required for unpaired electrons, the 0 charge state was not considered further. Results of calculations using the -1 charge state were in poor agreement with the experimental results (data not shown) and are therefore not considered further.

Since a total charge of $+1$ for the complex, in principle, is unphysical, the influence of the charge was also investigated by additional *ab initio* calculations. Calculations of methoxy-Mo, $+1$ charge and methoxy-Rh, 0 charge, were performed in order to evaluate the effect of different charge states.[17] Analysis of the Mulliken charge population of the methoxy-Rh complex revealed a charge distribution close to the one determined by Hermann and Meyer[18] for a CH_3O-Cu_3 cluster. The latter resulted in a CH_3O charge between -0.64 and -0.67 depending on the adsorption site, in good agreement with the corresponding value for the rhodium complex: -0.52. The corresponding $+1$ charged molybdenum complex result-

ed in a Mulliken charge of -0.1 for the methoxy. Furthermore, the calculations of the CH_3O-Rh complex resulted in a methoxy with a metal-O-C bond of $127°$ as compared to $180°$ for the corresponding molybdenum complex. In spite of these differences the ν(C-O) stretch was up-shifted by only 3% for the 0 charge complex, demonstrating the relative insensitivity of the vibrational frequencies to the charge state of the metal. The results are both in good agreement with experimental observations of the ν(C-O) stretch on the majority of single-crystal metal surfaces (see, e.g., Ref. 19 and reference therein). Since the structure of methoxy-Rh species is incompatible with experimental observations of the orientation of 2-propoxide adsorbed on Mo(110),[5] calculations of the 2-propoxide-Rh species were not performed. The [2-propoxide-Mo]$^-$ complex resulted in a qualitatively different charge distribution from the $+1$ charged propoxide and methoxide complexes of Mo and zero charge states methoxide complexes of Rh and Cu_3.[18] This explains the poor agreement between this state and experimental spectra. For the -1 charge state both the metal and the ligand are negatively charged, and the difference in charge between the ligand and the metal is only 0.24, whereas the corresponding values for [Rh]^0, [Mo]$^{+1}$, and [Cu_3]^0 (Ref. 18) complexes are between 1.04 and 1.40 (Fig. 3). The qualitative similarities between $+1$ and 0 charge states is consistent with the substantial increase of the dipole activity of modes with a contribution from the C-O stretch for the $+1$ and 0 charge states and not for the -1 charge state, upon coordination to the metal. The -1 charge state is qualitatively different from the 0 and $+1$ charge states (Fig. 3).

Full geometry optimization was performed to default tolerances and frequency and intensity determinations were done via numerical differentiation of the dipole moment. Final rms gradients were 0.000 101 and 0.000 114

FIG. 3. Mulliken charges for different alkoxide-metal complexes.

hartree/bohr or rad for 2-propanol and the 2-propoxide-Mo complex, respectively. Since the correlated motion of electrons are neglected, the computed vibrational frequencies are expected to be higher than those observed experimentally.[20] The discrepancies are, however, sufficiently systematic to permit a general scaling, which is a standard procedure for these types of calculations.[21] The calculated frequencies were scaled by 0.9 in accordance with earlier work.[22] Potential-energy distributions, which serve to determine the contribution of the internal coordinates to the calculated normal modes were calculated using the MOLVIB program[23] as described previously.[24] Internal coordinates were assigned as in Pulay et al.[25] Vibrational spectra of the deuterated species were calculated using the Wilson GF method[24] using optimized geometry and the force-constant matrix of the parent compounds.

The scaled calculated frequencies for gas-phase 2-propanol are all in good agreement with the experimental results for the gas phase and condensed propanol (data not shown). The only substantial differences between the condensed and gas-phase frequencies occur for modes related to the OH group. This can be attributed to hydrogen bonding in the condensed phase. For instance ν(H-O) was observed at 3220 cm^{-1} but calculated to be 3643 cm^{-1}. The latter value is in agreement with observed gas-phase value at 3659 cm^{-1}.

The potential-energy distributions show that the C-O stretch in 2-propanol is coupled to other modes and, in particular, to the C-C stretch, in agreement with previous work.[9] The mode at 938 cm^{-1} is calculated to have 47% ν(C-O) character, 30% ρ_s(CH_3) character, and 22% ν_s(C-C) character for 2-propanol, and the mode at 779 cm^{-1} is 60% ν_s(C-C) and 28% ν(C-O) (Fig. 1). The coupling of the C-O stretch is sensitive to the isotopic substitution in the molecule. For example, the mode at 913 cm^{-1} in the 2-propanol-2,2,2-d_3 spectrum is 37% ν(C-O) and 34% ρ(CH_3).

The experimental results for 2-propoxide bound to Mo(110) and the calculated values for the model system are compared in Table I. There is very good agreement between the two. As observed experimentally, there are only small shifts in the calculations of the modes above 1300 cm^{-1}, which arise entirely from ρ(C-H), δ(CH_3), and ν(C-H) vibrations (data not shown). The calculated shifts that occur above 1300 cm^{-1} upon alkoxide formation are too small to be observed experimentally. Also, the OH stretching mode at 3220 cm^{-1} is absent in the propoxide spectrum. Furthermore, a new loss is observed at 570 cm^{-1}, attributed to the metal-oxygen stretch.

The most striking experimental difference between the spectrum of propanol and 2-propoxide-Mo(110) is the presence of two intense bands at 800 and 910 cm^{-1} in the alkoxide. This is reproduced well by the calculations, which show a high dipole intensity for the two modes. According to the calculations, the intramolecular coupling within 2-propoxide on Mo(110) is dramatically different than that for 2-propanol. The scaled vibrational energies and calculated relative intensities of dipole scattered modes reproduce the data well (Table I). The ν(C-
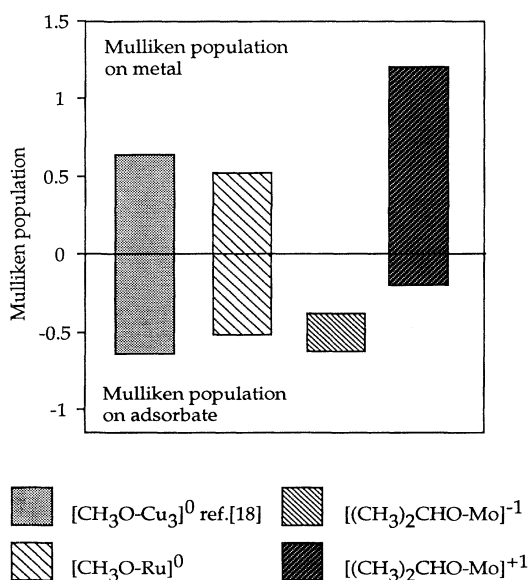
TABLE I. Comparison of experimental data and *ab initio* calculation of ν(C-O) modes of 2-propanol and 2-propoxide-Mo isotopomers.

		Vibrational frequencies [cm^{-1}]				Calculated mode contributions ($\geq 10\%$)			
		No.	EELS	Calc.	IR int. arb. units	Mode (%)	Mode (%)	Mode (%)	Mode (%)
d_0	(CH$_3$)$_2$(H)C-OH	7	~780	779	18	ν_sC-C 60	νC-O 26		
		9	950	938	17	νC-O 47	ρ_sCH$_3$ 30	ν_sC-C 22	
	(CH$_3$)$_2$(H)C-OMo	9	800	803	456	ν_sC-C 38	νC-O 28	νO-Mo 23	
		10	910	889	492	ν_sC-C 45	νC-O 38	νO-Mo 10	
d_3	(CD$_3$)(CH$_3$)(H)C-OH	10	915	913	14	νC-O 37	ρ_{as}CH$_3$ 34	ν_sC-C 16	
	(CD$_3$)(CH$_3$)(H)C-OMo	12	880	874	526	νC-O 40	ν_sC-C 19	ρ_{as}CH$_3$ 16	νO-Mo 12
d_6	(CD$_3$)$_2$(H)C-OH	10	~800	801	2	ρ_sCD$_3$ 56	νC-O 29		
		13	1050	1054	87	νC-O 36	δ_sCD$_3$ 29	ρ_sCD$_3$ 15	
	(CD$_3$)$_2$(H)C-OMo	12	800	829	625	νC-O 43	νO-Mo 29	ρ_sCD$_3$ 20	
		13	980	956	335	ρ_sCD$_3$ 52	νC-O 22	δCCO 18	
d_8	(CD$_3$)$_2$(D)C-OD	11	~800	852	74	νC-O 33	δCOD 30	ρ_sCD$_3$ 28	
		13	nr	951	5	ρ_sCD 52	ρ_sCD$_3$ 18	νC-O 16	
d_7	(CD$_3$)$_2$(D)C-OMo	12	800	813	365	νC-O 25	ρ_sCD$_3$ 24	ρ_sCD 18	νO-Mo 17
		14	935	915	533	νC-O 43	ρ_sCD 14	ρ_sCD$_3$ 14	νO-Mo 10

O) modes of adsorbed 2-propoxide-d_0 are best described as two ν_s(C-C) modes, in phase at 800 cm^{-1}, and out of phase at 910 cm^{-1}, with the ν(C-O) mode (Table I). The vibrational spectra for (CD$_3$)$_2$(H)C-O and (CD$_3$)$_2$(D)C-O appear to be qualitatively similar to 2-propoxide-d_0 in that two intense modes are observed upon propoxide formation [Figs. 2(c) and 2(a) and Table I]. However, in these cases the C-O stretch is coupled to the ρ_s(CD$_3$) and ρ_s(CD) but not to the C-C stretch. The differences in the coupling are due to shifts in the vibrational energies of the pure modes upon deuteration.

The coupling of the C-O and the C-C stretches is reduced in 2-propoxide-2,2,2-d_3 by virtue of the reduction in the symmetry to C$_1$ compared to C$_s$ for the other alkoxide isotopomers due to the loss of the mirror plane. As a consequence, the intramolecular coupling is reduced for this isotopomer, since only modes having the same symmetry couple strongly. In agreement, our calculations indicate that the mode at 880 cm^{-1} has 40% ν(C-O) character and 19% ν_s(C-C), and that no other modes have a large (> 12%) component of the ν(C-O).

The most obvious exception to the excellent agreement between experiment and theory is the mode with the most ν(Mo-O) character, and it is certainly an indication of the limitations of the one-atom model. The calculated values are 514 and 481 cm^{-1} for 2-propoxide-d_0 and -d_3, respectively, compared to experimental data values of 570 and 560 cm^{-1}, respectively. These discrepancies are probably due to the use of a single Mo atom as the surface; i.e., no consideration is given to the nature of the coordination site or influence of metal-metal bonding.

The calculations indicate that the C-O bond is the bond most strongly influenced by the adsorption. There is a 2% increase in the C-O bond length, whereas the C-C bonds show a contraction of ~1%. The C-H bonds are essentially unaffected, as shown by the close correspon-

dence in their vibrational frequencies for condensed 2-propanol and 2-propoxide. Hence the dynamic dipole moment of the C-O stretch is increased and the ν(C-O) energy is down-shifted upon coordination of 2-propoxide to Mo. In turn, these changes alter the degree of coupling of ν(C-O) to other modes.

Our work firmly establishes that the vibrational spectrum of a polyatomic molecule adsorbed on a metal surface can be determined, with a high degree of accuracy, using *ab initio* electronic-structure calculations. The present model accounts for all major experimentally observed effects. This investigation demonstrates that the vibrational spectrum of a molecule adsorbed on a metal surface may be strongly perturbed upon adsorption due to changes in the intramolecular vibrational coupling. Our work underscores the need for theoretical modeling in order to make accurate vibrational assignments and, thus, determine structure and changes in bonding. Such theoretical approaches may yield a level of understanding concerning structural and chemical changes of adsorbed species not previously obtained due to a high degree of uncertainty in the assignment of experimental vibrational spectra. Further theoretical work based on more detailed models of the solid would allow for variation in site geometry and possible associated changes in the coupling to be analyzed.

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