Vibrational Shifts Induced by ^{13}C Isotopic Substitutions in a Surface Adsorbate Determined by Infrared Spectroscopy and *Ab Initio* Calculations

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Vibrational shifts of three carbon skeleton modes induced by ^{13}C substitutions were determined in $^{13}CH_3CH_2O$-, $CH_3{}^{13}CH_2O$-, and $^{13}CH_3{}^{13}CH_2O$- adsorbed on W(110) using surface infrared absorption spectroscopy. The experimentally determined frequency shifts of the three different modes are, on average, determined within 1.1 cm^{-1} using *ab initio* electronic structure calculations. These results indicate the validity of *ab initio* methods for the interpretation of vibrational spectra of adsorbed species. [S0031-9007(98)08133-2]

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On well-defined surfaces, vibrational spectroscopy remains our most powerful spectroscopic probe for all but the most simple adsorbates. However, the richness of the experimental data often makes the interpretation of vibrational spectra difficult and complex. The interpretation and assignment of vibrational spectra of adsorbed polyatomic molecules are, therefore, generally based on comparison with vibrational spectra of the corresponding free molecules. This so-called "fingerprint" technique has been successfully used to chemically identify adsorbed molecules [1] and surface reaction intermediates [2]. There are obvious limitations to this approach. For all but the most simple molecules, the quality of the available data for free molecules is often quite poor and the assignments ambiguous. Furthermore, an important motivation for investigating adsorbed molecules is to determine the modifications that the surface induces in the electronic structure of the molecule upon adsorption (modifications that, for instance, allow for new reaction pathways, not available in the gas phase, to be made accessible). In addition, there are many surface intermediates that do not have an analogous free molecule and therefore are difficult to identify by vibrational spectroscopy. However, the development of modern *ab initio* calculations allows for the quantitative determination of vibrational spectra not only for free molecules but also for species coordinated to metal surfaces [3–5] and on semiconductor surfaces [6,7]. For both systems, it has been shown that a good agreement between calculated and measured frequencies can be obtained, along with a qualitative understanding of observed intensities. Such information greatly enhances the applicability of vibrational spectroscopy as a tool for the understanding of species adsorbed on the surface.

In the following, we will demonstrate that even small vibrational shifts in the carbon skeleton of a metal-ethoxy complex induced by ^{13}C isotopic substitutions can be determined, almost within experimental error, by *ab initio* electronic structure calculations. The systems used in the present paper are CH_3CH_2O-, $^{13}CH_3CH_2O$-, $CH_3{}^{13}CH_2O$-, and $^{13}CH_3{}^{13}CH_2O$- adsorbed on a W(110) single crystal. In contrast, corresponding *ab initio* calculations for the analogous free molecule, ethanol ^{12}C and ^{13}C isotopomers, fail to correctly determine the vibrational shifts. The modes related to the C-H stretches and bends are not considered in this paper as they are coupled to other modes in ways that we cannot account for in our theoretical model. The C-H stretches are often strongly influenced by Fermi resonances [8], making an analysis of the ^{13}C induced shifts of these modes rather complex. A detailed account of C-H stretches and the Fermi resonances in ethoxy [9] adsorbed on W(110) will be given elsewhere [10]. The C-H bend modes in alkoxides are frequently influenced by coupling to the C-O stretch mode [11] and are therefore influenced by dipole-dipole coupling (see below). As we cannot account for dipole-dipole coupling in our model, the C-H bend modes are not considered further.

Experiments were performed in a new UHV chamber (base pressure 7×10^{-11} torr) equipped with a Bruker 66v/S Fourier transform infrared spectrometer. The W(110) single crystal was cleaned by standard techniques [12] until no contaminants could be detected by the retarding field LEED/Auger optics. The long term stability and cleanness of the crystal have also been confirmed by highly reproducible vibrational spectra over a period spanning several months. Spectroscopic grade ethanol, 99.5%, was used without any further purifications. The different ^{13}C isotopes were used as delivered from Cambridge Isotope Laboratories, Inc. The ethanol was stored over 3 Å baked molecular sieves and admitted into the chamber after several freeze-pump-thaw cycles.

Ab initio calculations were performed with version 94 of the GAUSSIAN program [13], and analysis of the potential energy distributions (PED) was performed with MOLVIB [14]. In the calculations the surface was represented by a single metal atom only. It has previously been shown

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that adsorbate vibrations are less sensitive to cluster size than the electronic states which determine binding energies [15,16], providing a justification for our primitive representation of the surface. Calculations were performed by substituting Mo for W due the inaccessibilities of basis sets for the latter. The Los Alamos effective core potentials were used for Mo with a double-zeta basis set on all other atoms at the Hartree-Fock level [17,18]. Geometry optimizations were performed to default tolerances, and frequencies were determined via numerical differentiation of the forces at the optimized geometries. A general scaling factor of 0.9 was applied to the vibrational frequencies, as previously performed [4]. Internal coordinates for the (PED) determinations were defined according to Pulay *et al.* [19]. Potential energy distribution analysis of the isotopically substituted species used the force constant matrix from the unsubstituted compound with only the masses of the appropriate atoms altered.

Calculations of the ethoxy-metal complex were performed using a $+1$ charged complex which we have previously used to successfully determine vibrational spectra of various deuterated methoxies [5], ethoxies [3], and isopropoxies [4] adsorbed on Mo(110). The motivation for choosing this, in principle, unphysical complex has been discussed in detail [4]. Briefly, the open shell calculations required for a zero charged complex could not be performed, but the $+1$ charge complex (in contrast to -1 charge) was shown, through a Mulliken charge population analysis, to best model the charge distribution of a zero charge complex.

The geometry optimization results in a 180° Mo-O-C bond angle and a C_s symmetric complex. Experimental results for both ethoxy and methoxy adsorbed on W(110) support this geometric structure. We do not observed any asymmetric (A'') modes in the vibrational spectra of ethoxy on W(110) showing that the mirror plane of the complex, determined by the calculations, is preserved for the adsorbed species as well. Preliminary results show that methoxy is oriented with the C-O axis normal to the W(110) surface. Based on these observations, we conclude that ethoxy will adsorb in a geometry on W(110) which is in accordance with the calculations. A necessary shortcoming of the present model is that the influence of different coordination numbers and the symmetry of the adsorption site cannot be investigated. However, it has been experimentally verified, by isotopic decoupling of the symmetric C-H stretch mode, that an adsorbed methoxy species may exhibit C_{3v} symmetry on the Mo(110) surface [8] and therefore does not probe the C_{2v} symmetry of this surface. There may be two reasons for this: the coordination number is actually one, or the adsorbate experiences the surface as very weakly corrugated. In both cases, the one metal atom representation of the surface will exhibit the correct site symmetry. The physical and chemical similarities between Mo(110) and W(110) surface should make these results applicable to the W(110) surface as well.

Spectra were recorded with 1.0 cm^{-1} resolution. In order to confirm the reproducibility of the frequencies, each spectrum in Fig. 1 consists of three co-added spectra corresponding to three separate preparations of the adsorbate layer. The co-added spectrum resulted in no further line broadening demonstrating the high reproducibility of the preparation of the ethoxy overlayer. It was necessary to make the preparation highly reproducible as the mode 1 and 2 frequencies are sensitive to the coverage. This was accomplished by careful thermal treatment. 1 l ethanol was dosed while the crystal was kept at 210 ± 1 K, a temperature at which ethoxy is formed upon adsorption. The crystal was thereafter directly heated to 300 K to desorb possible excess ethanol. Both spectra and background were collected below 90 K, the background after a flash to 1100 K.

The vibrational spectra of the 800–1200 cm^{-1} region of the four different adsorbed isotopes, CH_3CH_2O-, $^{13}CH_3CH_2O$-, $CH_3{}^{13}CH_2O$-, and $^{13}CH_3{}^{13}CH_2O$- are shown in Fig. 1. Included in Fig. 1 as vertical lines are the calculated vibrational shifts. The frequencies are normalized with respect to the CH_3CH_2O- species. It is immediately clear that the calculations reproduce the ^{13}C

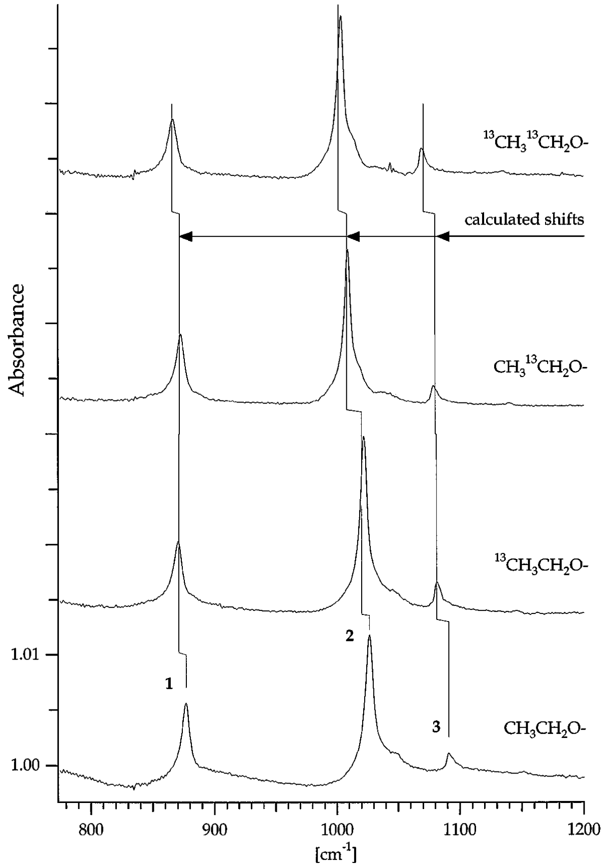

FIG. 1. Infrared absorption spectra of CH_3CH_2O-, $^{13}CH_3CH_2O$-, $CH_3{}^{13}CH_2O$-, and $^{13}CH_3{}^{13}CH_2O$-, adsorbed on W(110). Vertical lines correspond to the calculated shifts. The calculated values are normalized with respect to the ^{12}C species.

induced experimental shifts almost within experimental error (±0.6 cm^{-1}) [20]. The calculated ethoxy-Mo complex and measured adsorbed ethoxy frequencies are summarized and compared in the upper part of Table I together with mode assignments. A few results are notable. The absolute frequencies of the two, predominantly ν(C-O) stretch modes, 1 and 2, are underestimated in the calculations as the dipole-dipole coupling in the adsorbate layer is not accounted for. In contrast to, for example, methoxy [21] and diatomic molecules [22], the presence of two coupled modes exhibiting large dynamic dipole moments makes it a nontrivial task to experimentally determine the dipole induced shift of the two modes (e.g., via isotopic dilution, thereby separating it from possible coverage-dependent chemical shifts). The emphasis is, therefore, on the isotopic shifts rather than absolute values, as the dipole coupling should have only a marginal effect on these shifts since they are small. A reduction of the coverage to a fraction of 0.45 ± 0.05 (as determined from the intensity of mode 3) results in shifts of 3 cm^{-1} of mode 1, 10 cm^{-1} of mode 2, and only 1 cm^{-1} of mode 3. That is, the shifts are clearly related to the intensity and the dynamic dipole moment of the modes, consistent with dipole-dipole coupling induced shifts of mode 1 and 2. As expected, the frequency of mode 3 is correctly reproduced since the dynamic dipole moment of this mode is much smaller than for 1 and 2. The calculated value of mode 3 is 1089 cm^{-1} versus a measured value of 1091 cm^{-1}. In the bottom part of Table I the calculated frequencies of the corresponding ethanol isotopes are shown. Even though the direction of all of the shifts is correctly reproduced by both ethanol and the ethoxy-Mo complex, it is clear that the metal complex is a more accurate model of the adsorbate/surface system. This is summarized in Fig. 2, where a comparison on how well the experimental data is reproduced is made between ethanol and the ethoxy-Mo complex. The average deviation from experimental data

	Calculated mode frequency [cm^{-1}]	Measured mode frequency [cm^{-1}]	Calculated shift [cm^{-1}]	Measured shift	Difference	Modes and potential energy distribution (%)							
	ω*	ω	Δω*	Δω	Δω*−Δω								
CH_3CH_2O-Mo													
1	869.5	877.0				ν(O-C)	42	ν(C-C)	25	ρ(CH_3)	16	ν_s(Mo-O)	14
2	1004.3	1026.5				ν(C-C)	47	ν(O-C)	40				
3	1089.7	1091.0				ρ(CH_3)	57	ν(C-C)	23	sc(OCC)	14		
$^{13}CH_3CH_2O$-Mo													
1	863.5	870.5	-6.0	-6.5	0.5	ν(O-C)	38	ν(C-C)	28	ρ(CH_3)	17	ν_s(Mo-O)	13
2	998.0	1022.0	-6.3	-4.5	-1.8	ν(C-C)	46	ν(O-C)	43				
3	1079.9	1081.5	-9.8	-9.5	-0.3	ρ(CH_3)	59	ν(C-C)	21	sc(OCC)	14		
$CH_3{}^{13}CH_2O$-Mo													
1	864.2	872.5	-5.3	-4.5	-0.8	ν(O-C)	43	ν(C-C)	25	ν_s(Mo-O)	15	ρ(CH_3)	13
2	986.0	1009.0	-18.3	-17.5	-0.8	ν(C-C)	52	ν(O-C)	37				
3	1079.0	1079.0	-10.7	-12.0	1.3	ρ(CH_3)	61	ν(C-C)	19	sc(OCC)	14		
$^{13}CH_3{}^{13}CH_2O$-Mo													
1	858.2	866.5	-11.3	-10.5	-0.8	ν(O-C)	39	ν(C-C)	29	ν_s(Mo-O)	14	ρ(CH_3)	14
2	979.2	1003.5	-25.1	-23	-2.1	ν(C-C)	50	ν(O-C)	41				
3	1069.5	1069.0	-20.2	-22	1.8	ρ(CH_3)	63	ν(C-C)	17	sc(OCC)	13		
CH_3CH_2OH													
1	867.5					ν(O-C)	45	ν(C-C)	33	ρ(CH_3)	21		
2	1013.0					ν(C-C)	47	δ(HOC)	23	ν(O-C)	14	ρ(CH_3)	13
3	1068.2					ν(O-C)	42	ρ(CH_3)	30	δ(HOC)	10		
$^{13}CH_3CH_2OH$													
1	859.7		-7.8	-6.5	-1.3	ν(O-C)	42	ν(C-C)	36	ρ(CH_3)	21		
2	1004.9		-8.1	-4.5	-3.6	ν(C-C)	45	δ(HOC)	22	ν(O-C)	16	ρ(CH_3)	15
3	1065.2		-3.0	-9.5	6.5	ν(O-C)	43	ρ(CH_3)	30				
$CH_3{}^{13}CH_2OH$													
1	860.6		-6.9	-4.5	-2.4	ν(O-C)	47	ν(C-C)	34	ρ(CH_3)	18		
2	1001.7		-11.3	-17.5	6.2	ν(C-C)	51	ν(O-C)	21	δ(HOC)	18		
3	1057.1		-11.1	-12.0	0.9	ρ(CH_3)	38	ν(O-C)	33	δ(HOC)	13		
$^{13}CH_3{}^{13}CH_2OH$													
1	852.8		-14.7	-10.5	-4.2	ν(O-C)	43	ν(C-C)	37	ρ(CH_3)	18		
2	993.6		-19.4	-23	3.6	ν(C-C)	49	ν(O-C)	23	δ(HOC)	16	ρ(CH_3)	11
3	1053.7		-14.5	-22	7.5	ρ(CH_3)	38	ν(O-C)	35	δ(HOC)	12		

TABLE I. The calculated and measured frequencies for ethoxy-Mo complex and ethanol isotopes, both compared to measured ethoxy-W(110) isotope frequencies.

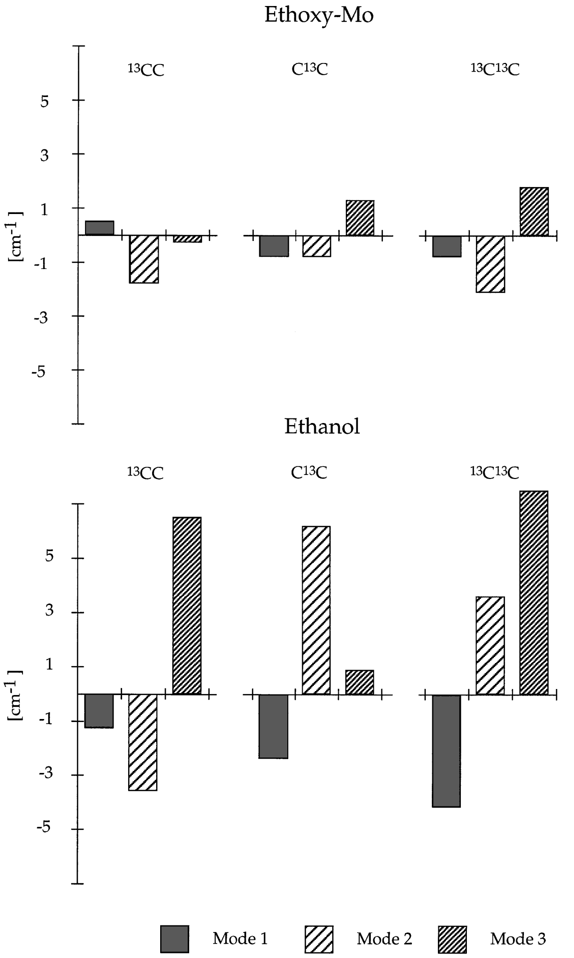

FIG. 2. Deviations from experimental ^{13}C induced frequency shifts compared to two different theoretical models: ethoxy-Mo complex and ethanol.

is only 1.1 cm^{-1} for the ethoxy-Mo complex, whereas for the ethanol it is 4.0 cm^{-1}. The former deviation is almost within the experimental error (approximately ± 0.6 cm^{-1}), whereas the latter deviation is significantly larger than the experimental error.

In conclusion, we have shown that even a primitive representation of the metal surface is adequate to theoretically determine small vibrational shifts induced by ^{13}C substitutions, involving carbon skeleton modes in adsorbed ethoxy. This is an important step in quantitative adsorbate vibrational spectroscopy as it demonstrates that such shifts can be theoretically modeled successfully using our approach. This ability will, for example, allow for detailed reaction mechanism studies involving ^{13}C labeling. The recent development of single-molecule vibrational spectroscopy [23] has opened up new avenues in the field and will, for instance, allow for studies of molecules in a more complex environment. It is essential that these advances are followed up by theory, and the present study is an important step towards a better understanding of the vibrational properties of adsorbed molecules.

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