

## First-Principle Calculations of the Experimental Vibrational Spectrum of a Surface Adsorbate: Anharmonic Resonance Coupling between Fundamental and Binary Modes

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(Received 6 September 2002; published 19 February 2003)

By including relevant physical properties in our modeling of a surface adsorbate system we can, from first principles, correctly calculate all experimentally observed features in the vibrational spectrum of  $\text{CH}_3\text{CH}_2\text{O}$ - and  $\text{CD}_3\text{CH}_2\text{O}$ - adsorbed on  $\text{Cu}(100)$ . That is, we reproduce the number of observed modes, the vibrational frequencies, and intensities of the modes including the presence/absence of binary overtone and combination modes. No scaling was performed. Our calculations show that the anharmonic terms of the potential energy surface of free ethanol are transferrable to the corresponding surface adsorbate, ethoxy, while the harmonic terms are not.

DOI: 10.1103/PhysRevLett.90.076103

PACS numbers: 68.35.Ja, 78.30.-j, 68.43.-h

For investigations of all but the smallest surfaces adsorbates, vibrational spectroscopy remains the most powerful spectroscopic probe for well-characterized surfaces. It is also the only spectroscopic technique which allows for chemical identification of single molecules at surfaces [1]. From the vibrational spectra, a variety of properties can be obtained, e.g., chemical identity and geometric structures. The richness and complexity, however, of the vibrational spectrum generally makes assignment and interpretation difficult and ambiguous. It is therefore often assumed that a molecule or a group in a molecule has characteristic frequencies and intensities and that these are transferrable between molecules and groups. These characteristics are often referred to as the fingerprint. Much of the power of surface adsorbate vibrational spectroscopy relies on this principle. That is, assignments made for the free molecule are transferrable to the molecule adsorbed on the surface.

For a more detailed analysis, however, the surface induces changes in the electronic structure which in general cannot be traced back to the free molecule. Indeed, one of the most important reasons for studies of surface adsorbates is the alteration in electronic structure induced by the surface. Efforts have therefore been made to expand surface vibrational spectroscopy beyond the fingerprint technique by *ab initio* and density functional electronic structure calculations of small model systems to calculate the vibrational properties of surface adsorbates. We have previously shown that it is possible to obtain a quantitative description of isotopic induced shifts of many fundamental modes of surface adsorbates, e.g., ethoxy [2,3], methoxy [4], and pyridine [5]. Vibrational frequencies of different adsorbates and reaction intermediates have also been successfully calculated by density functional cluster calculations for some different silicon surfaces [6–8]. In all these studies, the calculated frequencies were scaled. That is, correlated electron motion (for the Hartree-Fock method) and anharmonicity are treated in a rather unsophisticated manner. In these

treatments, only the harmonic coupling between different modes was included. When vibrations are near degenerate, the anharmonic or Fermi resonance coupling between fundamental and combination or overtone vibrations may, however, have a profound influence on the intensity distribution and the vibrational frequencies also for surface adsorbates [9–13]. Anharmonic resonances are particularly important for organic molecules because of the energy match between binary modes of the fundamental C-H deformation modes [ $2 \times (1400\text{--}1500 \text{ cm}^{-1})$ ] and the fundamental C-H stretch modes ( $2800\text{--}3000 \text{ cm}^{-1}$ ). As a result, the number of lines observed in the C-H stretch region frequently constitutes a large fraction of the total spectral information. In the vibrational spectrum of ethoxy adsorbed on  $\text{Cu}(100)$ , 17 lines are observed, Figs. 1 and 2, of which 10 are observed in the C-H stretch region.

In the present Letter, we will demonstrate that the frequencies and the intensities of all experimentally observed absorption lines of a polyatomic surface adsorbate can be reproduced from first-principle calculations. The harmonic frequencies of the normal modes of the adsorbate are calculated using a  $\text{Cu}_{17}$  cluster representing the  $\text{Cu}(100)$  surface, whereas the anharmonic constants are calculated from ethanol. That is, we make the assumption that the anharmonic properties of the adsorbate are transferrable from the free molecule, whereas the harmonic properties are not. The anharmonicities,  $x_{ij}$ , are calculated from standard expressions for energy third derivatives and semidiagonal fourth derivatives via second order perturbation theory [14] and are added to the harmonic wave numbers  $\omega$  via a term expression (see, e.g., [14,15]) to yield the fundamental frequencies.

In the case of near degeneracy, the perturbation expansion breaks down and the resonant parts are removed from the  $x_{ij}$ :s (see, e.g., [14,15]). A Hamiltonian matrix is formed in which the fundamentals and binary combinations are placed on the diagonal. The resonant terms removed from the  $x_{ij}$ :s are included explicitly as

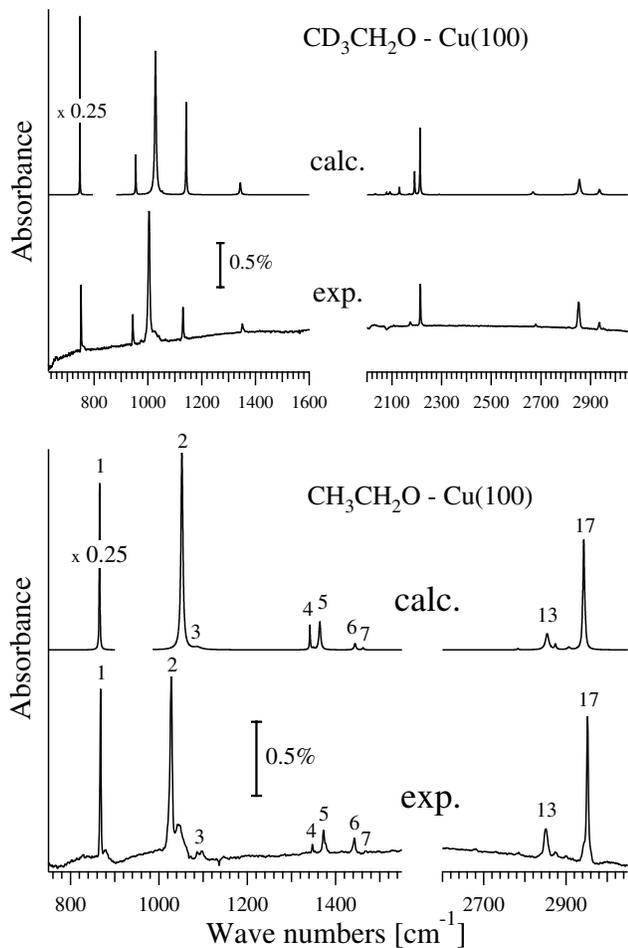


FIG. 1. Comparison between experimental and calculated vibrational spectra of  $\text{CH}_3\text{CH}_2\text{O}^-$  (bottom) and  $\text{CD}_3\text{CH}_2\text{O}^-$  (top) adsorbed on  $\text{Cu}(100)$ . The numbers 1–17 in the  $\text{CH}_3\text{CH}_2\text{O}^-$  spectra refer to the modes in Table I.

off-diagonal elements coupling the near-degenerate states in the Hamiltonian matrix. Through diagonalization, all new states are then expressed in terms of the original ones, e.g., as a mix of fundamental and binary vibrations. As mentioned, near degeneracy between different vibrations results in state mixing and intensity transfer, anharmonic resonances. In this manner, the resonances are included in the theory. It is, however, still a matter of choice, which energy separation,  $\varepsilon$ , should be considered as near degeneracy. In our treatment we have used two different  $\varepsilon$  to reproduce experimental data for ethoxy and a single  $\varepsilon$  for deuterated ethoxy.

For the calculations, we used the GAUSSIAN 98 package and the hybrid density functional method LG1LYP, by Adamo and Barone [16]. It consists of the Lacks-Gordon exchange functional [17] and the correlation functional by Lee, Yang, and Parr [18]. Ethoxy is placed in a fourfold hollow site [19] with the mirror plane along the (001) direction. The  $\text{Cu}_{17}$  cluster was frozen throughout the optimization at nearest neighbor distances of bulk copper,

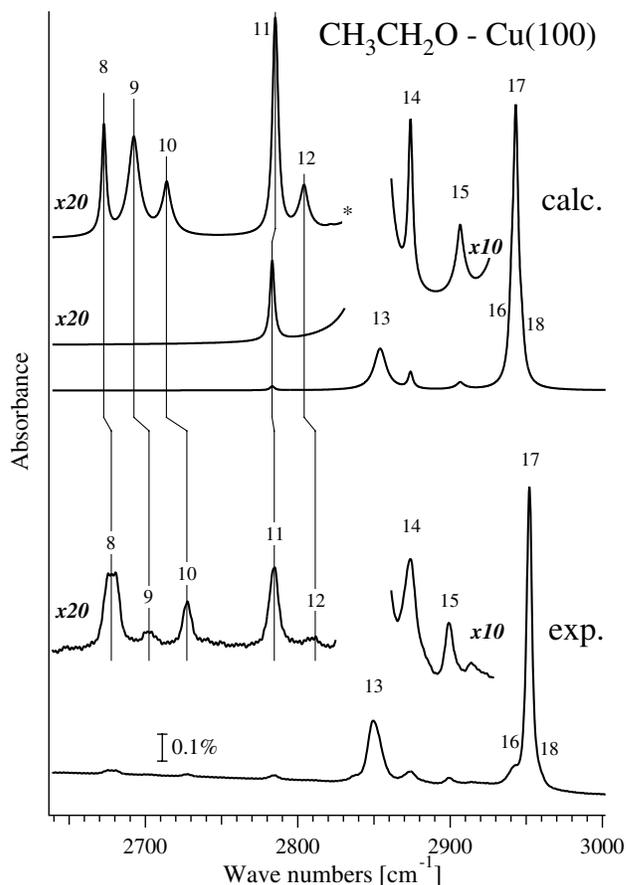


FIG. 2. Comparison between experimental and calculated vibrational spectra of  $\text{CH}_3\text{CH}_2\text{O}^-$  in the C-H stretch region,  $2640\text{--}3000\text{ cm}^{-1}$ . The weak spectral features are magnified for both experimental and calculated spectra. All calculated spectra have an energy separation  $\varepsilon = 50\text{ cm}^{-1}$  with the exception of the spectrum marked with “\*” where  $\varepsilon = 250\text{ cm}^{-1}$  was used.

$2.556\text{ \AA}$ . There are no imaginary frustrated adsorbate motions, showing that the adsorbate geometry is at a minimum. The basis set 6-311 +  $G(d, p)$  used for the adsorbate was checked for convergence (with respect to diffuse functions and polarized basis sets) for the corresponding free molecule, ethanol. For the substrate, the basis set LANL2DZ was used for the five metal atoms in contact with the adsorbate, whereas for all other Cu atoms the basis set by Bagus *et al.* [20] was used. Energy third and fourth derivatives were calculated for the free ethanol molecule optimized with tight convergence criteria. The fourth derivatives were calculated using a finite difference method [21]. All frustrated motions are excluded in our treatment.

The convergence of the intramolecular modes with respect to the basis sets of the copper cluster was ensured. The limited basis set by Bagus *et al.* [20] was replaced by the LANL2MB basis set on the outer copper atoms, and alternatively the LANL2DZ basis set was replaced by the

CEP-31G basis set on the inner copper atoms. In both investigations, the same copper cluster was used while ethoxy was replaced by methoxy. In both cases, the modification of the intramolecular frequencies was smaller than the accuracy of our ethoxy calculations. As for the cluster size, two recent studies of methoxy, on Al(100) [22] and Cu(111) [23], showed that no significant change of the vibrational frequencies was induced by increasing the cluster size. It is also known [20] that the vibrational frequencies converge much more rapidly than, e.g., the adsorption energy with respect to cluster size.

The experiments were performed in an UHV chamber (base pressure  $7 \times 10^{-11}$  torr) equipped with a Fourier-transform infrared spectrometer, Bruker 66v/S. The setup and the Cu(100)/ethoxy system have been described elsewhere [3]. An InSb detector equipped with a Spectrogon LP3000 filter was used for the 2500–3000  $\text{cm}^{-1}$  region (resolution 0.5  $\text{cm}^{-1}$ ) and a MCT detector was used for the 760–3000  $\text{cm}^{-1}$  region (resolution 1  $\text{cm}^{-1}$ ).

The experimental and calculated vibrational spectra of both  $\text{CH}_3\text{CH}_2\text{O}^-$  and  $\text{CD}_3\text{CH}_2\text{O}^-$  are compared in Fig. 1. The number of observed modes, the vibrational frequencies, and the intensities are all reproduced for both isotopes. The results are also summarized, for  $\text{CH}_3\text{CH}_2\text{O}^-$ , in Table I along with the labeling of all observed adsorption lines. Only adsorbate modes of  $A'$  symmetry are included in the table. The calculated intensities have been normalized with respect to line 2 and modified according to the surface dipole selection rule. The linewidths of the calculated spectra have been adjusted to the

experimental linewidths of the fundamental vibrations using a Lorentzian line shape. Importantly, the relative intensities as well as the frequencies for the *entire spectral* region are reproduced by the calculations. The only exception is the intense narrow line 1 which is overestimated by a factor of 4. We attribute this to a deficiency of the limited copper cluster used. The shoulders observed on lines 1 and 2, and the splitting of line 3, are attributed to inhomogeneity.

The details of the anharmonic resonance coupling in the C-H stretch region of  $\text{CH}_3\text{CH}_2\text{O}^-$  is shown in Fig. 2. The intensity transfer from the fundamentals to the binary modes is also shown in Table I. Note that, since two different  $\varepsilon$  have been used, the total intensity from both  $\nu_s(\text{CH}_2)$  and  $\nu_s(\text{CH}_3)$  will add up to more than 100% [the sum of the entries without asterisks ( $\varepsilon = 50 \text{ cm}^{-1}$ ) do, however, add up to 100%]. The linewidths of the binary modes in the calculated spectrum are assumed to be the same as the fundamental mode from which the intensity is derived from. All ten vibrational features can be assigned from the calculations of this region. The line labeled 18 while not resolved at this coverage is observed at lower coverage. In the calculated spectrum shown as a solid black line, upper panel in Fig. 2, an energy separation  $\varepsilon$  of 50  $\text{cm}^{-1}$  was used which reproduces the experimental frequencies and intensities. In order to allow for coupling to the lower lying binary vibrations ( $> 50 \text{ cm}^{-1}$  from nearest fundamental), it was necessary to use a separation of 250  $\text{cm}^{-1}$  also. The results obtained with this energy separation are shown in the

TABLE I. Observed and calculated frequencies for  $\text{CH}_3\text{CH}_2\text{O}^-$ -Cu(100). All frequencies are in  $\text{cm}^{-1}$ . The modes marked with an asterisk have been calculated with  $\varepsilon = 250 \text{ cm}^{-1}$ . All other modes are calculated using  $\varepsilon = 50 \text{ cm}^{-1}$ .

Mode No.	Experimental frequency	Calculated frequency	Deviation calc.-exp.	% unperturbed $\nu_s(\text{CH}_3)$	% unperturbed $\nu_s(\text{CH}_2)$	% unperturbed $\nu_{as}(\text{CH}_3)$	Mode description
1	867.8	865.6	-2.2				$\nu_s(\text{OCC})$
2	1027.6	1052.1	24.5				$\nu_{as}(\text{OCC})$
3	1087.3	1087.2	-0.1				$\rho(\text{CH}_3)$
4	1347.5	1342.0	-5.5				$w(\text{CH}_2)$
5	1372.9	1364.3	-8.6				$\delta_s(\text{CH}_3)$
6	1442.0	1444.0	2.0				$\delta_{as}(\text{CH}_3)$
7	1468.2	1462.3	-5.9				$sc(\text{CH}_2)$
8	2677.7	2672.0*	-5.7	2	6	0	$2 \times w(\text{CH}_2)$
9	2702.5	2690.9*	-11.6	10	1	0	$w(\text{CH}_2) + \delta_s(\text{CH}_3)$
10	2727.3	2712.0*	-15.3	4	1	0	$2 \times \delta_s(\text{CH}_3)$
11	2784.7	2783.4	-1.3	0	4	0	$2 \times \delta_s(\text{CH}_3)(A'')$
12	2811.5	2796.3*	-15.2	3	0	0	$\delta_s(\text{CH}_3) + \delta_{as}(\text{CH}_3)$
13	2850.3	2854.2	3.9	89	0	0	$\nu_s(\text{CH}_2)$
14	2873.2	2874.1	0.9	2	17	0	$2 \times \delta_{as}(\text{CH}_3)(A')$
15	2899.6	2906.8	7.2	9	3	0	$\delta_{as}(\text{CH}_3) + sc(\text{CH}_2)$
16	2940.5	2940.4	-0.1	0	52	3	$\nu_s(\text{CH}_3)$
17	2952.1	2943.2	-8.9	0	6	91	$\nu_{as}(\text{CH}_3)$
18	~2955	2947.1	-7.9	0	17	6	$2 \times sc(\text{CH}_2)$
Mean absolute deviation			7.1				

upper panel of Fig. 2. As seen, the frequencies are well reproduced while the intensities of the binary combination modes are somewhat overestimated. Most of the error of calculated frequencies of the binary modes can be derived from errors in the corresponding fundamental modes. In the corresponding C-H and C-D stretch regions in  $\text{CD}_3\text{CH}_2\text{O}^-$  (Fig. 1), a single value for  $\varepsilon$  ( $200\text{ cm}^{-1}$ ) was used as our focus is on the CH stretch region. This means that the intensities in the CD stretch region in  $\text{CD}_3\text{CH}_2\text{O}^-$  are slightly more qualitative than for  $\text{CH}_3\text{CH}_2\text{O}^-$  (Fig. 1). A complete account of several ethoxy isotopomers will be given elsewhere.

In spite of the quite substantial efforts [24] made in [3], we could not even assign all the fundamental  $A'$  modes in the C-H stretch region correctly. The weak feature 15 in Fig. 2 was incorrectly assigned to the  $\nu_s(\text{CH}_3)$  mode. The reason is seen in Table I; the intensity of the  $\nu_s(\text{CH}_3)$  mode is distributed over nine different modes. This example demonstrates that one cannot in general trust assignments, based on calculations at the harmonic level only, of modes involving Fermi resonance coupling.

In conclusion, the vibrational spectra of  $\text{CH}_3\text{CH}_2\text{O}^-$  and  $\text{CD}_3\text{CH}_2\text{O}^-$  adsorbed on Cu(100) have been calculated. By including the anharmonic coupling between binary and fundamentals modes, the calculations reproduce all the experimentally observed spectral features, with a mean absolute deviation of less than  $10\text{ cm}^{-1}$ . Our results show that the anharmonic terms of the potential energy surface are transferrable from a free molecule to a corresponding surface adsorbate, while the harmonic terms are not. Exceptions from this principle will show that this particular part of the potential energy surface is strongly perturbed by the adsorption.

The single most important physical reason why the anharmonic terms are transferrable is that the absolute value of the calculated unperturbed modes has to be within  $\sim 10\text{ cm}^{-1}$  in order to reproduce experimentally observed frequency shift and the intensity transfer induced by the Fermi resonance. That is, a larger relative inaccuracy can be accepted for the anharmonic terms which are  $\leq |140|\text{ cm}^{-1}$ . It is, however, necessary to use the calculated anharmonic terms rather than a general scaling factor as the variation of these terms is as large as  $40\text{ cm}^{-1}$  for, e.g., the C-H stretch modes.

The anharmonic coupling between different intramolecular modes [25] and between intramolecular modes and hindered rotations and translations of surfaces adsorbates [26,27] governs the energy dissipation and randomization of initially localized modes. As such, they are, e.g., a key to the realization of bond-selected chemistry. Our approach shows that the anharmonic coupling between vibrations in polyatomic surface adsorbates can be explored and understood in detail.

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- [1] B. C. Stipe, M. A. Rezaei, and W. Ho, *Science* **280**, 1732 (1998).
- [2] P. Uvdal, R. Ásmundsson, and A. D. MacKerell, Jr., *Phys. Rev. Lett.* **82**, 125 (1999).
- [3] R. Ásmundsson, P. Uvdal, and A. D. MacKerell, *J. Chem. Phys.* **113**, 1258 (2000).
- [4] M. P. Andersson, P. Uvdal, and A. D. MacKerell, *J. Phys. Chem. B* **106**, 5200 (2002).
- [5] M. P. Andersson and P. Uvdal, *J. Phys. Chem. B* **105**, 9458 (2000).
- [6] M. K. Weldon, B. B. Stefanov, K. Raghavachari, and Y. J. Chabal, *Phys. Rev. Lett.* **79**, 2851 (1997).
- [7] B. B. Stefanov, A. B. Gurevich, M. K. Weldon, K. Raghavachari, and Y. J. Chabal, *Phys. Rev. Lett.* **81**, 3908 (1998).
- [8] K. T. Queeney, Y. J. Chabal, and K. Raghavachari, *Phys. Rev. Lett.* **86**, 1046 (2001).
- [9] P. Uvdal, M. K. Weldon, and C. M. Friend, *Phys. Rev. B* **50**, 12258 (1994).
- [10] U. Engström and R. Ryberg, *Phys. Rev. Lett.* **78**, 1944 (1997).
- [11] P. Jakob, *Phys. Rev. Lett.* **79**, 2919 (1997).
- [12] P. Jakob, *J. Chem. Phys.* **108**, 5035 (1998).
- [13] R. Ásmundsson and P. Uvdal, *J. Chem. Phys.* **112**, 366 (2000).
- [14] I. M. Mills, *Molecular Spectroscopy: Modern Research* (Academic, New York, 1972), Vol. 1, p. 115.
- [15] D. A. Clabo, W. D. Allen, R. B. Remington, Y. Yamaguchi, and H. F. Schaefer, *Chem. Phys.* **123**, 187 (1988).
- [16] C. Adamo and V. Barone, *J. Comput. Chem.* **19**, 418 (1998).
- [17] D. J. Lacks and R. G. Gordon, *Phys. Rev. A* **47**, 4681 (1993).
- [18] C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- [19] The hollow site has been experimentally determined for methoxy on Cu(11); see, e.g., Ref. [3] for a detailed discussion.
- [20] P. S. Bagus, C. W. Bauschlicher, C. J. Nelin, B. C. Laskowski, and M. Seel, *J. Chem. Phys.* **81**, 3594 (1984).
- [21] W. Schneider and W. Thiel, *Chem. Phys.* **159**, 49 (1992).
- [22] L. T. Sein and S. A. Jansen, *J. Chem. Phys. B* **102**, 2415 (1998).
- [23] J. R. B. Gomes and J. A. N. F. Gomes, *J. Mol. Struct.-Theochem.* **503**, 189 (2000).
- [24] In Ref. [3], a combined experimental and HF calculational study of four  $^{12}\text{C}/^{13}\text{C}$  isotopomers was performed. The anharmonicity was treated through a general scaling factor. The Fermi resonance coupling was ignored in the calculations but was acknowledged as the phenomena behind some of the vibrational shifts and the high intensities of the observed binary modes.
- [25] E. W.-G. Diau, J. L. Herek, Z. H. Kim, and A. H. Zewail, *Science* **279**, 847 (1998).
- [26] B. C. Stipe, M. A. Rezaei, and W. Ho, *Phys. Rev. Lett.* **81**, 1263 (1998).
- [27] T. Komeda, Y. Kim, M. Kawai, B. N. J. Persson, and H. Ueba, *Science* **295**, 2055 (2002).