

Orientation of ethoxy, mono-, di-, and tri-fluoroethoxy on Cu(1 1 1): a DFT study

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Abstract

We have used plane wave density functional theory (DFT) to determine the structure and relative binding energies of ethoxy, mono-, di-, and tri-fluoroethoxy adsorbed on Cu(1 1 1). The FCC site is found to be the most stable binding site for all four adsorbed species. The orientations of ethoxy and tri-fluoroethoxy on the surface are found to be in good agreement with quantitative predictions based on previous FT-IRAS experiments. The orientations of mono- and di-fluoroethoxy on Cu(1 1 1) are also presented.

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1. Introduction

Understanding the characteristics of transition states for surface catalyzed reactions is one of the fundamental issues to be tackled in developing general concepts that account for the sensitivity (or insensitivity) of such reactions to surface structure and composition [1]. The study of sets of reactive species in which a non-reactive portion of the molecule is systematically varied has provided one useful avenue to experimental investigation of the characteristics of surface transition states [2]. One class of reaction that has been studied by use of these substituent effects is the β -hydride elimination of fluorinated alkoxy groups on metal surfaces [2]. β -hydride elimination is the dominant reaction path for a broad range of alkoxy and alkyl groups on metal surfaces [3].

A prerequisite for achieving a detailed understanding of the kinetics of any surface catalyzed process is a description of the geometry of the reactive species. A number of experimental studies have examined the geometries of ethoxy and its fluorinated derivatives on Cu surfaces. Crapper et al. used NEXAFS to examine ethoxy on Cu(1 1 0) and showed that that the C–O bond angle in this species is tilted at $35 \pm 15^\circ$

with respect to the surface normal [4]. Camplin and McCash examined ethoxy on Cu(1 0 0) using RAIRS and were able to rule out several possible surface structures but not definitively describe the geometry of the adsorbed species [5]. Street and Gellman used FT-IRAS to probe the orientation of ethoxy and 2,2,2-trifluoroethoxy on Cu(1 1 1) [6,7], providing precise measurements of the angle between the C–C and C–O bonds and the surface normal. They showed that the planes of both ethoxy species are tilted with respect to the surface and that the C–C bonds are tilted slightly away from parallel to the surface.

Several theoretical studies have also probed the geometry of alkoxy species on surfaces. Anderson and Uvdal recently used density functional theory (DFT) calculations using cluster approximations to examine methoxy and ethoxy adsorption on Cu(1 0 0) [8]. Both species were found to favor the four-fold hollow sites on the surface as binding sites. The binding of methoxy on Cu(1 1 1) has been studied using cluster-based DFT calculations by Gomes and Gomes [9] and plane-wave DFT by Greeley and Mavrikakis [10]. Both studies indicate that methoxy binds in the three-fold sites on Cu(1 1 1). In addition to the geometry of the adsorbed species, Greeley and Mavrikakis used DFT to estimate the activation energy for β -hydride elimination of methoxy on Cu(1 1 1) [10]. The effect of fluorination on adsorbate geometry

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has been examined by Natal Santiago and Dumesic, who used DFT to describe the adsorption on ethoxy and 2,2,2-trifluoroethoxy on silica [11]. The geometry of these two adsorbed alkoxy species was found to be very similar.

None of the theoretical studies mentioned above have examined the same species that have been used in the experiments of Gellman et al. to probe substituent effects on the β -hydride elimination of fluorinated alkoxy groups on Cu surfaces [1,12,13]. As an initial step towards a unified experimental and theoretical description of these reactions, we describe in this paper a series of plane wave density functional theory calculations that examine the geometry of adsorbed ethoxy, mono-, di- and tri-fluoroethoxy on Cu(111). In Section 2, we describe our calculation methods. In Section 3, we discuss the geometries and energies of the relevant surface structures of ethoxy and tri-fluoroethoxy on Cu(111) and compare these results with the available experimental data. Our results indicate that the FCC site is the most favorable binding site, and provide a detailed description of the structure of adsorbed species. Our DFT calculation results are in good agreement with the available data from FT-IRAS experiments [14]. The surface structures of mono- and di-fluoroethoxy, for which geometric information is not available from experimental data, are presented in Section 4. Section 5 summarizes our findings.

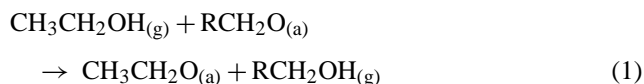
2. Computational methods

We performed plane wave density functional theory calculations using the Vienna ab initio Simulation Package (VASP) [15,16] with the ultrasoft pseudo-potentials available in this package [17,18]. We present below results from calculations with the generalized gradient approximation (GGA) using the Perdew-Wang 91 [19,20] functional. A plane wave expansion with a cutoff of 29.2 Ry was used in studying ethanol and ethoxy, while a cutoff of 31.3 Ry was used to examine fluorinated species. Total energy calculations were done using the residual minimization method for electronic relaxation, accelerated using Methfessel Paxton Fermi-level smearing with a width of 0.2 eV. Geometries were relaxed using the conjugate gradient algorithm until the forces on all unconstrained atoms were less than 0.03 eV/Å. The results below are from calculations with a $5 \times 5 \times 1$ k -point mesh. The Cu(111) surface was represented by a slab five layers thick and a vacuum spacing of 23.4 Å. All calculations placed a single adsorbed molecule in a 3×3 unit cell. Dipole corrections were applied to determine the total energy of the final structures determined in our geometry optimizations, although this correction made only negligible contributions to the total energy.

All calculations used supercells defined using the DFT-GGA optimized lattice constant for Cu, which is 3.64 Å, in good agreement with the experiment value of 3.62 Å [21]. All the results reported below are from calculations in which the surface atoms were held fixed. The impact of including

surface relaxation on the geometry and energy of adsorbed ethoxy is discussed below.

To characterize the relative energies of the adsorbed species on the surface, we computed the energy change, ΔE , associated with the overall reaction:



for $\text{R} = \text{CFH}_2$, CF_2H , and CF_3 . This energy change has been measured experimentally for $\text{R} = \text{CFH}_2$ and CF_3 to be $\Delta E = 0.03$ and 0.09 eV, respectively. To compare the relative binding energies, E_b , of a single species at different adsorption sites on the surface, we used the energy difference between the ethoxide adsorbed on the surface and the same ethoxide in the gas phase. That is, we computed:

$$E_b = E_{\text{adsorbate}/\text{Cu}(111)} - [E_{\text{adsorbate}} + E_{\text{Cu}(111)}], \quad (2)$$

where the three terms on the right hand side of this expression are the total energy of the supercell containing that molecule adsorbed on the surface, the energy of ethoxide in the gas phase, and the energy of the bare surface, respectively.

3. Ethoxy and trifluoroethoxy adsorption on Cu(111)

We first used DFT to calculate the geometry of ethanol in the gas phase, using the same size supercell as our subsequent surface adsorption calculations. The staggered conformer was found to be more stable than the eclipsed conformer. The resulting geometry is summarized and compared with experimental data in Table 1. As should be expected, the calculated results are in good agreement with the experimental data. After removing the H atom of the hydroxyl group, this structure was used as an initial approximation for adsorbed ethoxy. To explore the possible adsorption geometries of ethoxy on Cu(111), initial configurations were created with the O atom above a high symmetry surface site. For each such surface site, configurations were examined with the O–C bond initially oriented along several directions relative to the surface normal with these directions chosen in a manner to span the full range of possible orientation

Table 1
DFT and experimental data for the geometry of gas phase ethanol

Distance or angle	DFT	Experiment [26]
$d(\text{O}-\text{H})$	0.97	0.97
$d(\text{O}-\text{C}_1)$	1.44	1.43
$d(\text{C}_1-\text{C}_2)$	1.50	1.51
$d(\text{C}_1-\text{H})$	1.09	1.10
$d(\text{C}_2-\text{H})$	1.09	1.09
$\theta(\text{H}-\text{O}-\text{C}_1)$	108	105
$\theta(\text{O}-\text{C}_1-\text{C}_2)$	109	108
$\theta(\text{H}-\text{C}_1-\text{H})$	108	N/A
$\theta(\text{H}-\text{C}_2-\text{H})$	109	N/A

Distances are in Å and angles are in degrees.

Table 2
Calculated geometry of ethoxy adsorbed on Cu(1 1 1) in surface fcc and hcp sites, with binding energy in eV, angles in degrees, and distances in Å

	fcc site	hcp site
Binding energy	−1.91	−1.85
$\theta(\text{C—O—normal})$	11 ± 1	13 ± 4
$\theta(\text{C—C—normal})$	72 ± 5	70 ± 1
$d(\text{O—Cu})$	2.02	2.02
$d(\text{O—C}_1)$	1.44	1.44
$d(\text{C}_1\text{—C}_2)$	1.51	1.51
$d(\text{C}_1\text{—H})$	1.10	1.10
$d(\text{C}_2\text{—H})$	1.09	1.09
$\theta(\text{O—C}_1\text{—C}_2)$	112	108
$\theta(\text{H—C}_1\text{—H})$	108	108
$\theta(\text{H—C}_2\text{—H})$	108	108

$d(\text{O—Cu})$ is the distance between the O atom and the nearest Cu atom in the surface. $d(\text{C—H})$ is the average value of the relevant C—H bond lengths, and $\theta(\text{H—C}_2\text{—H})$ is the average value of the angles between C_2 and H.

angles for this bond. Each configuration was then optimized using energy minimization as described in Section 2, which allowed all degrees of freedom in the adsorbate to vary. This procedure was used to separately examine adsorption of ethoxy in three-fold, bridge, and on-top sites.

Our calculations indicate that the three-fold sites are the stable binding sites for ethoxy on Cu(1 1 1). On-top and bridge sites are not stable minima for ethoxy adsorption; configurations that began at on-top or bridge sites ultimately converged to geometries with the O atom in a three-fold site. The fact that ethoxy binds in a site that maximizes the coordination between the chemisorbed O atom and the surface is consistent with previous DFT calculations of methoxy binding on Cu(1 1 1) and Cu(1 0 0) [8–10] and ethoxy on Cu(1 0 0) [8,22]. The energy of ethoxy (as defined using Eq. (2)) in the three-fold fcc and hcp sites as determined in our calculations are summarized in Table 2. There is a small energetic preference for ethoxy to bind in fcc sites relative to hcp sites. This energy difference, 0.06 eV, is very similar to the energy difference computed by Greeley and Mavrikakis for the difference in the binding of methoxy in the fcc and hcp sites on this surface [10]. Two views of ethoxy bound in the favored fcc site on Cu(1 1 1) are shown in Fig. 1. It can be seen from this figure that in the plane of the surface, the C—C bond

is aligned approximately from the three-fold site towards a bridge site.

Table 2 also summarizes the geometry of ethoxy bound to the fcc and hcp three-fold sites. The molecule favors an antiplanar conformer. When minimizing the energy of the adsorbed molecule from several different initial structures, our calculations yielded a small range of bond angles relative to the surface normal. The uncertainties given in Table 2 represent the full range of observed angles. The uncertainties calculated in a similar way for the other bond angles (bond lengths) in Table 2 were smaller than 1° (0.01 Å). It can be seen from Table 2 that the geometry of ethoxy is very similar for the fcc site and hcp sites. Our results for the angle between the surface normal and the C—O and C—C bonds are in good agreement with the FT-IRAS data of Street and Gellman [7]. These angles are illustrated in Fig. 2. With ethoxy in the fcc site, the inclination of the C—O bond to the surface normal is found to be $11 \pm 1^\circ$ in our calculation, compared to $17 \pm 2^\circ$ in experiment. For the C—C bond, the DFT prediction is $72 \pm 5^\circ$ and the experimental result is $71 \pm 2^\circ$. The C—C—O bond angle in the adsorbed molecule is 112° , while in gas phase ethanol it is 109° .

We used the structure of ethoxy bounded in an fcc site as a means to probe the effect of surface relaxation in our results. Taking the structure described above as a starting point, energy minimization was performed while allowing the top two layers of the five layer Cu slab to relax. After this minimization, the binding energy of ethoxy increased by 0.09 eV, the angle of the C—O bond relative to the surface normal changed from 11° to 9° , and the C—C angle with the surface normal changed from 72° to 77° . This calculation suggests that changes in these bond angles due to surface relaxation are within the range of values observed in our calculations that did not incorporate surface relaxation. For clarity, we reiterate that the results in Table 1 and in the tables discussed below are from calculations in which the Cu surface was held rigid.

Calculations similar to those described above were used to explore the geometry of 2,2,2-trifluoroethoxy on Cu(1 1 1). The initial structure of the gas phase molecule was generated by replacing the H atoms in the CH_3 group in ethanol with

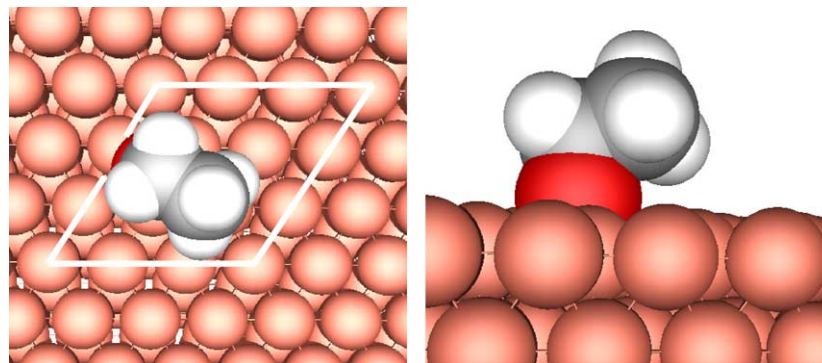


Fig. 1. The optimal geometry of adsorbed ethoxy molecule in a (3 × 3) unit cell on Cu(1 1 1), top and side views.

Table 3
The same as Table 2, but for trifluoroethoxy adsorbed on Cu(1 1 1)

	FCC site	HCP site
Binding energy	−1.92	−1.83
$\theta(\text{C—O-normal})$	20 ± 3	23 ± 2
$\theta(\text{C—C-normal})$	58 ± 1	57 ± 1
$d(\text{O—Cu})$	2.01	2.01
$d(\text{O—C}_1)$	1.41	1.41
$d(\text{C}_1\text{—C}_2)$	1.52	1.51
$d(\text{C}_1\text{—H})$	1.10	1.10
$d(\text{C}_2\text{—F})$	1.36	1.36
$\theta(\text{O—C}_1\text{—C}_2)$	114	113
$\theta(\text{H—C}_1\text{—H})$	109	108
$\theta(\text{F—C}_2\text{—F})$	107	107

F atoms with C–F bonds 1.35 Å in length. As with ethoxy, only the three-fold adsorption sites were found to be stable minima for the chemisorbed 2,2,2-trifluoroethoxy. The calculated energies and geometries of 2,2,2-trifluoroethoxy in the fcc and hcp sites of Cu(1 1 1) are summarized in Table 3. The calculated energy difference between the favored fcc site and the hcp site is found to be slightly greater for the fluorinated species than for ethoxy. The energy difference defined by Eq. (1) for the relative energy of ethoxy and 2,2,2-trifluoroethoxy on the surface was calculated to be $\Delta E = 0.06$ eV, in good agreement with the experimental result of 0.09 eV [12].

The optimal geometry of 2,2,2-trifluoroethoxy on Cu(1 1 1) is shown in Fig. 3. As with the non-fluorinated species, the C–C bond points approximately along the direction from the surface three-fold site to a bridge site in the plane of the surface. The computed geometries are in good agreement with FT-IRAS experiments [7]. The calculations give the angles of the C–O and C–C bonds relative to the surface normal of $20 \pm 3^\circ$ and $58 \pm 1^\circ$, respectively, while the experimental results are $30 \pm 7^\circ$ and $50 \pm 5^\circ$ [7]. The calculations and experiments both indicate that fluorination causes the C–O (C–C) bond to be slightly more (less) tilted away from the surface normal than in ethoxy. The C–C–O bond angle in adsorbed 2,2,2-trifluoroethoxy is 113° , slightly

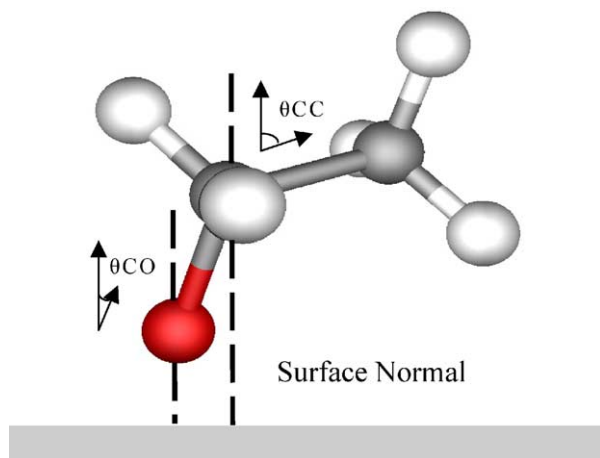


Fig. 2. A schematic view of the orientations of ethoxy on Cu(1 1 1). $\theta(\text{CO})$ is the angle between the C–O bond axis and the surface normal, while $\theta(\text{CC})$ is the angle between the C₁–C₂ bond axis and the surface normal.

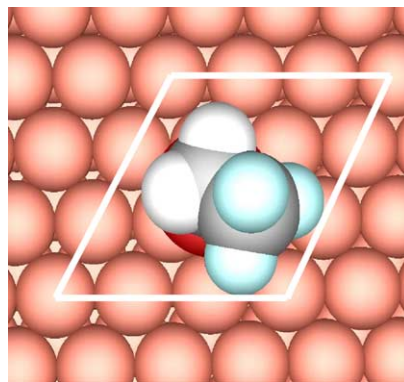


Fig. 3. Similar to the top view in Fig. 1, but for 2,2,2-trifluoroethoxy adsorbed on Cu(1 1 1).

larger than the angle of 109° observed in gas phase 2,2,2-trifluoroethanol.

4. Mono- and di-fluoroethoxy adsorption on Cu(1 1 1)

In order to provide a complete description of the influence of fluorination on the geometry of adsorbed ethoxides on Cu(1 1 1), we extended our calculations to 2-monofluoroethoxy and 2,2-difluoroethoxy. In these calculations, we only considered adsorption in the fcc site on the surface.

We first examined 2-monofluoroethanol in the gas phase, by removing one H in the CH₃ group of the ethanol geometry described above and replacing it with an F atom with a C–F bond length of 1.35 Å. Exploring the conformations available to this molecule showed that there is an energy barrier of ~ 0.27 eV to rotate the CFH₂ group from the staggered conformer to the eclipsed conformer. The gauche conformation of 2-monofluoroethanol was found to be the most stable of the conformations available via rotation of the CFH₂ group, a conclusion consistent with previous studies of this molecule [23–25]. The gauche configuration was used as an initial structure for the adsorbed species.

The energy and geometry of the optimized structure of 2-monofluoroethoxy in the fcc site on Cu(1 1 1) are summarized in Table 4. The relative energies associated with Eq. (1) give $\Delta E = 0.01$ eV when comparing 2-monofluoroethoxy with ethoxy. This is in excellent agreement with the experimental value of 0.03 eV [12]. The orientation of the fluorinated species is very similar to that of ethoxy, with the C–O and C–C bonds tilted relative to the surface normal by approximately 10° and 70° , respectively. To determine the orientation of the C–F bond relative to the surface, we optimized several initial configurations with varying C–F bond orientations. The preferred orientation is shown schematically in Fig. 4. We find that the C–F bond is oriented essentially parallel to the surface, forming an angle of $91 \pm 3^\circ$ with the surface normal. This is consistent with the prediction from FT-IRAS by Street and Gellman that this bond is parallel to the surface [7].

Table 4
Structural and energetic properties of mono- and di-fluoroethoxy adsorbed in a Cu(1 1 1) FCC site

	Mono-fluoroethoxy	Di-fluoroethoxy
E_b	-1.99	-1.99
$\theta(\text{C}_1\text{—O-normal})$	9.0 ± 2	14.0 ± 2
$\theta(\text{C}_1\text{—C}_2\text{-normal})$	69 ± 3	60 ± 1
$\theta(\text{C}_2\text{—F-normal})$	91 ± 3	—
$d(\text{O—Cu})$	2.02	2.02
$d(\text{O—C}_1)$	1.43	1.41
$d(\text{C}_1\text{—C}_2)$	1.50	1.51
$d(\text{C}_1\text{—H})$	1.10	1.10
$d(\text{C}_2\text{—H})$	1.10	1.10
$d(\text{C}_2\text{—F})$	1.41	1.39
$\theta(\text{O—C}_1\text{—C}_2)$	113	114
$\theta(\text{H—C}_1\text{—H})$	108	108
$\theta(\text{H—C}_2\text{—H})$	110	—
$\theta(\text{H—C}_2\text{—F})$	107	108
$\theta(\text{F—C}_2\text{—F})$	—	106

The notation is similar to Tables 2 and 3.

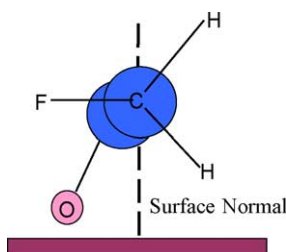


Fig. 4. Schematic view of the geometry of 2-fluoroethoxy on Cu(1 1 1).

Similar methods were used to examine the adsorption of 2,2-difluoroethoxy in the fcc site on Cu(1 1 1). The relative energies of 2,2-difluoroethoxy and ethoxy defined by Eq. (1) were found to be $\Delta E = 0.02$ eV. This value is intermediate between the relative energies described above for the mono- and tri-fluorinated species. No experimental data for the binding energy of 2,2-difluoroethoxy on Cu(1 1 1) are available. The geometry can be described as intermediate between that observed for ethoxy and 2,2,2-trifluoroethoxy. The C—O (C—C) bond angle of 2,2-difluoroethoxy was found to be tilted by $14 \pm 2^\circ$ ($60 \pm 1^\circ$) relative to the surface normal compared to $11 \pm 1^\circ$ ($72 \pm 5^\circ$) and $20 \pm 3^\circ$ ($58 \pm 1^\circ$) for ethoxy and 2,2,2-trifluoroethoxy, respectively. It can be seen from Fig. 5

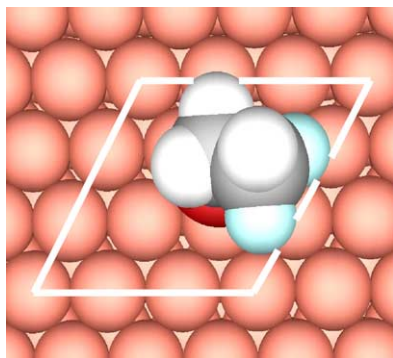


Fig. 5. Similar to the top view in Fig. 1, but for 2,2-difluoroethoxy adsorbed on Cu(1 1 1).

that the two F atoms in the terminal group of the adsorbate point down towards the surface. Similar to ethoxy and 2,2,2-trifluoroethoxy, the C—C—O bond angle in the mono- and difluorinated species on their surface are several degrees larger than in the gas phase alcohols.

5. Discussion

We have used DFT to assess the structure and relative stability of ethoxy and several fluoroethoxides adsorbed on Cu(1 1 1). The fcc site is found to be the most stable site for these species. This result is consistent with the binding site that has been observed for methoxy and ethoxy on Cu(1 0 0) and Cu(1 1 1) in previous theoretical studies [10,22,26]. The adsorbate geometries are in good agreement with the data available from FT-IRAS experiments by Street and Gellman [6,7]. Our results imply that $\text{CF}_2\text{HCH}_2\text{O}_{(\text{ad})}$ has an orientation closer to that of $\text{CF}_3\text{CH}_2\text{O}_{(\text{ad})}$ than $\text{CH}_3\text{CH}_2\text{O}_{(\text{ad})}$, while $\text{CFH}_2\text{CH}_2\text{O}_{(\text{ad})}$ has an orientation closer to that of $\text{CH}_3\text{CH}_2\text{O}_{(\text{ad})}$. Our results are consistent with the experimental conclusion that the binding energies of the fluorinated ethoxy species that we have examined are very similar [12]. The similarities in binding energy and adsorption geometry in the adsorbates, we have studied and provide strong support for the idea that observing the overall reaction kinetics associated with this set of adsorbates can be used to consistently study substituent effects associated with the elementary β -hydride elimination reaction available to these species.

The results of this work have a number of implications for prior investigations of the structure and reactivity of ethoxy groups on metal surfaces. The aforementioned experimental determination of the structures of ethoxy and 2,2,2-trifluoroethoxy on the Cu(1 1 1) surface made use of infrared absorption intensities measured using single reflection at glancing incidence. The absorption intensity of a given vibrational mode is given by:

$$I \propto (\hat{n} \cdot \vec{\mu})^2 \quad (3)$$

where \hat{n} is the surface normal and $\vec{\mu}$ is the dynamic dipole moment of the absorbing species. The structure determination was made by measuring the relative absorption intensities of several pairs of ν_{CH} , ν_{CD} , and ν_{CF} modes in a set of partially deuterated ethoxy groups and 2,2,2-trifluoroethoxy groups. Doing so required that the relative magnitudes of the dynamic dipole moments, $|\vec{\mu}|$, be known and that their relative orientations within the framework of the molecules be known. One assumption made in that work was that the relative magnitudes of the dipole moments could be obtained from infrared absorption measurements of the alcohols in the gas phase where the dipoles are randomly oriented. This was a reasonable assumption given that none of the C—H, C—D or C—F bonds were directly involved in bonding to the surface. The second assumption was that the relative orientations of the dipole moments within the molecular framework could be deduced from their symmetry. For example, the dynamic

dipole moment of the symmetric $\nu_{\text{CF}_3}^{\text{s}}$ mode was assumed to lie parallel to the C–C bond and the dynamic dipole moments of the asymmetric $\nu_{\text{CF}_3}^{\text{a}}$ modes were assumed to lie perpendicular to the C–C bond. Again these are reasonable but unverifiable assumptions. The fact that ethoxy structures predicted on the basis of the DFT calculations presented in this work agree with those predicted on the basis of FTIR absorption measurements indicates that assumptions that went into the analysis of the FTIR measurements are indeed valid. Furthermore, it suggests that the method used to analyze those FTIR spectra is a viable approach to the quantitative determination of adsorbate structures.

The second important contribution of this work is to our understanding of the effects of substituents on the energetics of β -hydride elimination. Prior work showed that the difference in the heats of formation of the ethoxy and 2,2,2-trifluoroethoxy groups on Cu(111) from their corresponding alcohols differed by < 0.1 eV. By comparison, fluorination induces a > 0.6 eV increase in the activation barrier to β -hydride elimination. The suggestion, based on those results is that the effect of fluorination can be attributed to its effect on the transition state energetics. The transition state is deemed to be anionic with respect to the initial state ethoxy group, $[\text{C}^{\delta+} \dots \text{H}^{\delta-}]$. The results of the DFT calculations reported in this work support the suggestion that the effect of fluorination is on the transition state energies rather than the initial states.

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