Orientation of Physisorbed Fluoropropenes on Cu(111)

Shane C. Street†

Department of Chemistry, University of Illinois, Urbana, Illinois 61801

Andrew J. Gellman*

Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

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Fourier transform infrared reflection absorption spectra (FT-IRAS) have been obtained for adsorbed monolayers of propene and a set of fluorinated propenes ($CFH_2CH{=}CH_2$, $CF_3CH{=}CH_2$, and $CF_3CF{=}CF_2$) on the Cu-(111) surface. These species interact weakly with the copper surface. The FT-IRAS spectra indicate that the molecules lie flat with the plane of the molecule defined by the C−C=C atoms essentially parallel to the surface regardless of the degree of fluorination. Quantitative analysis of the orientation of hexafluoropropene determines the tilt of the molecular plane with respect to the surface to be 11°. The results for propene indicate a molecular tilt of 20°. Where the ν(C=C) mode can be identified in the spectra of the adsorbed molecules, there is no perturbation of its frequency, which indicates that there is little backdonation between the metal and the π^* orbital of the propene.

1. Introduction

Fluorine substitution into molecular species on metal surfaces has been observed to have marked effects on surface chemistry.[1−4] These effects have provided an avenue for the understanding of surface reactivity and also the orientation of adsorbates. As part of a larger program aimed at understanding these effects and applying them to a variety of reactions, we have focused one investigation on the influence of fluorine on the bonding olefins, in this case propenes, to the Cu(111) surface.[1] These molecules adsorb weakly to the Cu(111) surface, and fluorine might be expected to have some influence on the backbonding between the double bond and the metal. Fluorination may also influence the orientation of these molecules on the surface. The goal of this particular work is to use Fourier transform infrared reflection absorption spectroscopy (FT-IRAS) to address these problems.

Backbonding between adsorbates and surfaces has been observed and has manifested itself in adsorbate vibrational spectra. Examples include molecules such as carbon monoxide (CO) and acetone ($O{=}C(CH_3)_2$). In the backbonding scheme, the adsorbate donates electron density to the empty d orbitals of the metal while the metal backdonates electron density to the empty antibonding π^* orbital of the molecule. The result is an increase in the bond strength between the adsorbate and the surface but a weakening of the double bond. This is accompanied by a decrease in the vibrational frequency of the mode involved (C=O in the examples given above).[5−8]

The adsorption of propene on Pt(111)[9−13] and Rh(111)[10,14,15] has been studied using a number of techniques. The studies conclude that at low temperatures propene on both surfaces forms a di-σ complex bonded to two metal atoms that dehydrogenates to form propylidyne at roughly room temperature. Temperature-programmed desorption (TPD) and ultraviolet photoelectron spectroscopy (UPS) of propene and trifluoropropene on oxidized Mo(100)[16−18] indicated that backbonding contributes to the chemisorption of the trifluoropropene but not the propene. The desorption energy of trifluoropropene was ∼3 kcal/mol higher than that of propene. It has been proposed that fluorinating the methyl group in propene lowers the energy of the π^* orbital, making backbonding more favorable.[18,19]

On the Cu(111) surface the adsorption of propene and a set of selectively fluorinated propenes have been investigated using TPD and high-resolution electron energy loss spectroscopy (HREELS).[1] The propenes adsorb reversibly, desorbing upon heating at temperatures between 120 and 140 K. Fluorinating the methyl group (to trifluoropropene) increased the barrier to desorption over that found for propene and monofluoropropene, but further fluorination of the molecule did not increase the activation energy for desorption. The limited resolution of the HREELS spectra did not identify any shift in the ν(C=C) mode that would indicate significant backbonding, and the overall TPD results indicated that the propenes bind only weakly to the Cu-(111) surface.

The FT-IRAS spectra presented in this paper allow the determination of the orientation of the physisorbed propenes and a higher-resolution picture of the effect of bonding on the ν(C=C) mode. The structural analysis is derived from the strict surface selection rule for IRAS, which states that only those modes that have a projection of their transition dipole moment vector along the surface normal will give rise to absorptions in the spectrum. The determined orientations indicate that the C=C bond in all the propenes is roughly parallel to the surface, but where it can be identified the mode is not significantly shifted from its gas phase value. All the molecules exhibit a characteristic loss of intensity in the in-plane modes upon formation of a monolayer, indicating that the plane of the molecule is roughly parallel to the surface regardless of the degree of fluorination. The methyl group appears to be tilted slightly away from the surface.

2. Experimental Section

The experiments were performed in a stainless-steel ultrahigh vacuum chamber equipped for IRAS, Auger electron spectroscopy (AES), temperature-programmed desorption (TPD), and argon ion sputtering, which is fully described elsewhere.[20] A base pressure of $<1.0 \times 10^{-10}$ Torr was achieved by a

† Present address: Department of Chemistry, Texas A&M University, College Station, TX 77843-3255.

* Author to whom correspondence should be addressed.

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cryopump and titanium sublimation pump. The chamber has a capillary array gas doser for line-of-sight exposure ("direct" dosing). Monolayer and multilayer coverages were determined by TPD (not shown), which agreed with previous results.[1] All the spectra obtained in this work were for saturated monolayers on the Cu(111) surface. Here, we have defined the monolayer as the coverage at which one observes onset of the multilayer desorption feature in the TPD spectra. The absolute coverages of the saturated monolayers have not been determined. The multilayers used in this work to obtain condensed phase spectra of the propenes represent ~20 monolayers (ML) of the adsorbate.

The FT-IRAS experiments were performed with a Mattson RS-1 spectrometer. The optical system is fully described elsewhere.[20] Briefly, IR radiation from the spectrometer was focused on the crystal inside the IR cell of the chamber at an incident angle of 85 ± 4° after passing through a wire grid polarizer oriented parallel to the surface normal. The reflected light was recollimated and focused on the narrow-band, liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. The spectra were collected in the form of double-sided interferograms using a forward/reverse mirror speed of 3.2 cm/s (50 kHz) and 4 cm^{-1} resolution. The interferograms were zero-filled and apodized by triangular apodization. The data acquisition time for a single beam spectrum was ~12 min (2500 scans). Peak-to-peak noise levels below 2×10^{-5} absorbance units at 2000 cm^{-1} were routinely achieved. Once the desired molecule had been adsorbed, data acquisition on the surface involved positioning the crystal in the IR cell and maximizing the centerburst signal. Single beam spectra of the adsorbate were acquired with the crystal at 100 K. Clean surface background spectra were acquired after annealing the crystal to 300 K to desorb the adsorbate and quickly cooling to 100 K. The gas phase spectrum of propene was obtained by filling the purge box of the system with some pressure of the gas and ratioing the reflectance spectra as the space was subsequently purged.

The crystal surface was judged to be clean if no impurities were detected by AES. The surface was cleaned by cycles of annealing to 1000 K during Ar^+ ion sputtering and also by high (~100 L) exposure to molecular oxygen at 800 K to remove carbon.

The gas samples of propene, monofluoropropene, and trifluoropropene were obtained from Aldrich. Hexafluoropropene was obtained from PCR, Inc. The purity of all samples was checked by mass spectrometry.

3. Results

3.1. FT-IRAS of Propene on Cu(111). Figure 1 shows the FT-IRAS spectrum of a monolayer of propene ($CH_3CH{=}CH_2$) adsorbed on the Cu(111) surface. Propene would not form a multilayer film even at the lowest crystal temperature (~95 K).[1] A gas phase spectrum of propene was obtained to determine the relative intensity changes upon formation of the monolayer, and there are assignments in the literature that give qualitative descriptions of the relative intensities of the modes in the liquid (e.g., very strong, strong, medium weak).[21] The assignments given in Table 1 are made for a molecule with C_s point group symmetry, which allows identification of the modes as either in-plane (A′) or out-of-plane (A″).[21−24] The in-plane modes for all four propenes are marked with dashed lines in Figures 1−4, while the out-of-plane modes are marked with solid lines.

What is apparent in the spectrum of the propene monolayer is the absence of any strong intensity from in-plane (A′) modes. The most intense modes are out-of-plane (A″), including ω-(CH_2) at 912 cm^{-1}, ρ(C═CH_2) (twist) at 990 cm^{-1}, the out-of-plane $\delta_a(CH_3)$ at 1436 cm^{-1}, and the $\nu_a(CH_3)$ mode at 2940 cm^{-1}. Even in-plane modes that are very strong in the gas and liquid phases are much less intense in the monolayer. Specifically, the ν(C═C) mode intensity is below the noise level in the monolayer spectrum but is very strong in the gas phase at 1651 cm^{-1} and very strong in the liquid phase (see Figure 1 and Table 1). The in-plane $\delta_a(CH_3)$ mode at 1453 cm^{-1} is less intense in the monolayer than its out-of-plane counterpart (1436 cm^{-1}), even though in the liquid phase it is significantly more intense.[21] However, a number of in-plane modes do give rise to absorptions in the monolayer spectrum of propene, in particular the C−H stretching modes and modes associated with

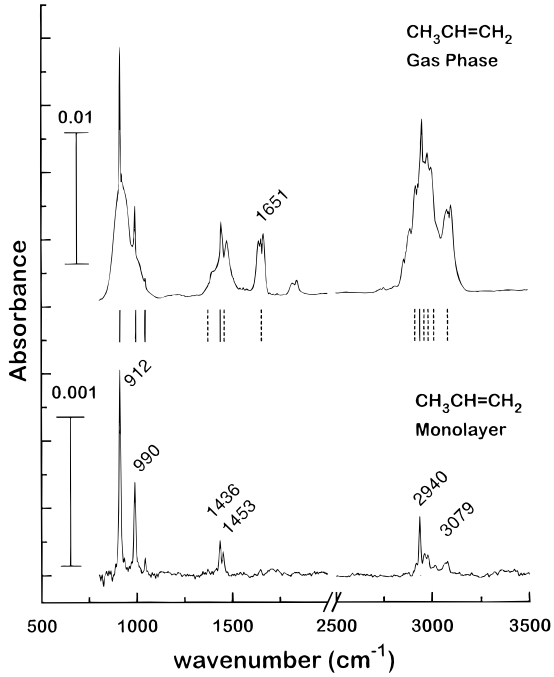

Figure 1. FT-IRAS of gas phase propene at 300 K (top) and a propene monolayer adsorbed on the Cu(111) surface at 100 K (bottom). Vibrational assignments are given in Table 1. Dashed lines indicate the positions of in-plane (A′) modes and solid lines the positions of out-of-plane (A″) modes.

TABLE 1: Vibrational Frequencies (cm^{-1}) and Assignments for Propene on Cu(111)

mode	sym[a]	IR obsd[a]	$CH_3CH{=}CH_2$ liquid, 120 K[b]	$CH_3CH{=}CH_2$/ Ru(0001), 110 K[c]	$CH_3CH{=}CH_2$/ Cu(111), 100 K
$\nu_a(CH_2)$	A′	3091			3079
ν(CH)	A′	3015			3016
$\nu_s(CH_2)$	A′	2991			2980
$\nu_a(CH_3)$	A′	2973			2962
$\nu_a(CH_3)$	A″	2952			2940
$\nu_s(CH_3)$	A′	2932			2918
ν(C═C)	A′	1653	1646 (vs)	1646	1648
$\delta_a(CH_3)$	A′	1459	1451 (vs)	1455	1453
$\delta_a(CH_3)$	A″	1443	1435 (m)	1438	1436
$\delta(CH_2)$	A′	1420	1413 (w)	1412	
$\delta_s(CH_3)$	A′	1378	1371 (w)	1374	1373
ν(C−C)	A′	1174	1172 (vw)		
$\rho(CH_3)$	A″	1045	1042 (w)	1042	1044
δ(CH)	A″	990	992 (s)	994	990
or tw-(C═CH_2)	A″				
$\rho(CH_2)$	A′	935	934 (w)	936	
$\omega(CH_2)$	A″	912	910 (vs)	911	912

[a] Symmetry assignment for a C_s point group molecule. A′ modes are in-plane, and A″ modes are out-of-plane.[21−23] These assignments also serve to identify the gas phase absorptions. [b] Transmission IR spectrum of liquid propene film condensed on a KBr plate.[21] [c] FT-IRAS spectrum of monolayer propene.[21]

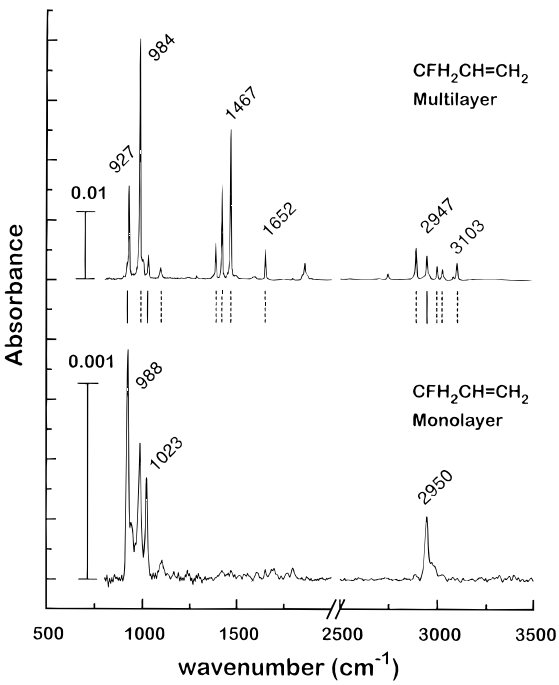

Figure 2. FT-IRAS of multilayer 3-fluoropropene (top) and a 3-fluoropropene monolayer (bottom) on the Cu(111) surface at 100 K. Vibrational assignments are given in Table 2. Dashed lines indicate the positions of in-plane (A′) modes and solid lines the positions of out-of-plane (A″) modes.

the methyl group such as $\delta_a(CH_3)$ (A′). This indicates that the plane of the molecule, defined by the C—C═C atoms, does not lie exactly parallel to the surface. It is not likely that adsorption to the surface changes the structure of the molecule from its gas phase configuration, given the similarity of the frequencies of their modes as listed in Table 1. Rather, it appears that the C═C bond axis is roughly parallel to the surface, but the methyl group (and hence, the plane of the molecule) is tilted slightly away from the surface plane.

The FT-IRAS spectrum of propene on the Cu(111) surface is similar to that of propene on Ru(0001) obtained by Ransley *et al.*[21] However, there are several important differences in the relative intensities of modes in the adsorbed species. For instance, no CH stretching bands were observed in the spectrum of propene on Ru(0001), whereas several bands appear in the spectrum of propene on Cu(111) (Table 1) and the out-of-plane (A″) $\nu_a(CH_3)$ mode intensity is strong. The in-plane (A′) δ_a-(CH_3) mode of propene on the Ru(0001) surface is stronger than the out-of-plane (A″) $\delta_a(CH_3)$ mode. The reverse is true in the spectrum of physisorbed propene on Cu(111) (Figure 1). Ransley *et al.* concluded that since vibrational modes both symmetric and antisymmetric with respect to the mirror plane passing through the carbon atoms were observed in their spectrum, there is no preferred orientation of the carbon skeleton, either parallel or perpendicular to the metal surface.[21] The characteristic loss of intensity of the in-plane modes of propene adsorbed on Cu(111) leads to the conclusion that the molecule prefers the side-on configuration of adsorption, with the molecular plane roughly parallel to the metal surface. This conclusion is supported by the results of a quantitative determination of the adsorbate orientation (see section 4).

3.2. FT-IRAS of Fluorinated Propenes on Cu(111). *$CFH_2CH{=}CH_2$.* The spectra of multilayer and monolayer 3-monofluoropropene on the Cu(111) surface are presented in Figure 2. As with all the multilayer spectra presented in this paper, the coverage nominally represents ∼20 ML, produced by exposure through a capillary array of 1 L of the gas to the crystal held at ∼100 K. Assignments are given in Table 2.

The *cis* conformer of 3-monofluoropropene is the most energetically favorable.[25] The spectrum of monolayer 3-monofluoropropene shows preferential loss of intensity of the in-plane modes (marked with dashed lines) with respect to the same modes in the multilayer. For instance, the ν(C═C) mode at 1652 cm^{-1} in the multilayer spectrum is not readily identified in the monolayer spectrum. The set of absorptions in the region 1300−1500 cm^{-1} in the multilayer spectrum are all in-plane modes, for a *cis* conformation of the molecule, and are all absent in the monolayer spectrum. The strong absorptions in the lower-frequency region of the monolayer spectrum are modes that, although highly coupled,[25] contain out-of-plane motions in their spectroscopic description, particularly contributions from ω-$(=CH_2)$ and $\rho(=CH_2)$ (twist) modes. The ν(CF) mode at 988 cm^{-1} is the only in-plane vibration with significant intensity in the monolayer, and its absorption is substantially reduced from its intensity in the multilayer. In the C−H stretch region, the strongest intensity comes from the out-of-plane $\nu_a(CH_2)$ (CFH_2 group) mode. These findings are consistent with a structure in which *cis*-3-fluoropropene is adsorbed with its molecular plane essentially parallel to the surface.

$CF_3CH{=}CH_2$. The spectra of multilayer and monolayer 3,3,3-trifluoropropene on the Cu(111) surface are presented in Figure 3. Assignments are given in Table 3 and are made with reference to the literature.[26] The C−H stretches are extremely weak in these spectra and are not shown in Figure 3. The pattern of intensity loss of the in-plane modes is again evident, although not quite as dramatic as in the cases of propene and 3-fluoropropene. The two out-of-plane modes are a $\nu(CF_3)$ vibration at (1145 cm^{-1}) and a mode at 977 cm^{-1}, which has been assigned to a combination of $tw(CH_2) + \omega(CH_2)$ in ref 26. Comparison of the monolayer and multilayer spectra indicates that the intensity of these modes with respect to the out-of-plane modes is greater for the monolayer. The ν(C═C) mode is weak in the multilayer spectrum (1678 cm^{-1}) and not present in the monolayer spectrum. In-plane modes such as the $\delta(CH_2)$ scissors mode (1435 cm^{-1}) and δ(CCH) skeletal deformations (1314 cm^{-1}) are easily observed in the multilayer spectrum but are much weaker in the monolayer spectrum. The in-plane modes that do give rise to absorptions in the monolayer spectrum of 3,3,3-trifluoropropene have contributions from modes of vibrations associated with bonds that determine the orientation of the trifluoromethyl group, such as the feature at 1430 cm^{-1} (ν(CC) contribution) and the $\nu(CF_3)$ feature at 1289 cm^{-1}. Once again, this interpretation of the spectra indicates an adsorption geometry in which the molecules lie with their molecular planes roughly parallel to the surface. The fact that the intensities of the in-plane modes do not decrease to the extent that they do in the other propene spectra suggests that the $C-CF_3$ bond is tilted further away from the surface than in the other propenes.

$CF_3CF{=}CF_2$. Figure 4 shows the spectra of multilayer and monolayer hexafluoropropene on the Cu(111) surface. The assignments are again made for a molecule with C_s point group symmetry as identified in the literature[26] (Table 4). The ν-(C═C) mode is coupled to the $\nu(CF_2)$ mode (1808 cm^{-1} in the multilayer spectrum) and is not significantly perturbed in frequency in the monolayer (1792 cm^{-1}). All the modes in the observable frequency range are in-plane according to the normal coordinate analysis,[26] except for an out-of-plane $\nu(CF_3)$ mode, which gives rise to the strongest absorbance in the monolayer spectrum (at 1186 cm^{-1}). The qualitative interpretation of these spectra indicates that, as with all the propenes, the hexafluo-

TABLE 2: Vibrational Frequencies (cm^{-1}) and Assignments for 3-Fluoropropene on Cu(111)

mode	sym[a]	IR obsd[b]	calcd[b]	$CFH_2CH{=}CH_2$/Cu(111) multilayer	$CFH_2CH{=}CH_2$/Cu(111) monolayer
$\nu_a(=CH_2)$	A′	3114 (g)	3114	3103	
$\nu(=CH)$	A′	3026	3032	3027	(3024)
$\nu_s(=CH_2)$	A′	2998	2998	3000	
$\nu_a(CH_2)$	A″	2959	2990		2950
$\nu_s(CH_2)$	A′	2945	2926	2947	
?		2890	NI	2892	2893
$2 \times \delta(=CH_2)$		2788 Raman	NI	2746	
$2 \times \nu$?, $\nu + \nu$?				1860	
$\nu(C{=}C)$	A′	1649	1653	1652	
$\delta(CH_2)$	A′	1468 (g)	1467	1467	
$\delta(=CH_2)$	A′	1416	1417	1421	
$\omega(CH_2)$	A′	1385	1388	1388	
$\omega(=CH_2) + \delta(CH)^{ip}$	A′	1109	1108	1094	
$tw(=CH_2) + \delta(CH)^{op} + r(=CH_2)$	A″	1032	1091	1030	1023
$\nu(CF) + \omega(=CH_2)$	A′	976	974	984	988
$\rho(CH_2) + tw(=CH_2)$	A″	928	872	927	923

[a] Symmetry assignment for a C_s point group molecule. A′ modes are in-plane, and A″ modes are out-of-plane. NI = not investigated in ref 25. [b] Observed infrared bands are for the solid unless noted (g) for gas phase. The calculations were carried out for the stable *cis* conformation with C_s symmetry.

TABLE 3: Vibrational Frequencies (cm^{-1}) and Assignments for 3,3,3-Trifluoropropene on Cu(111)

mode	sym[a]	IR obsd[b]	calcd[b]	$CF_3CH{=}CH_2$/Cu(111) multilayer	$CF_3CH{=}CH_2$/Cu(111) monolayer
$\nu_a(CH_2)$	A′	3120	3120		
$\nu(CH)$	A′	3066	3066	3067[c]	
$\nu_s(CH_2)$	A′	3023	3023	3022[c]	
$\nu(C{=}C)$	A′	1670	1670	1678/1663	
$\delta(CH_2) + \delta(CCH) + \nu(CC)$	A′	1431	1435	1435	1430
$\delta(CCH) + \delta(CCH_2)$	A′	1311	1313	1314	
$\nu(CF_3) + \nu(C{=}C) + \delta(CCH_2)$	A′	1284	1285	1287	1289
$\nu(CF_3)$	A′	1185	1175	1191/1186	1180
$\nu(CF_3)$	A″	1165	1173	1145	1145
$\omega(CH_2) + tw(CH_2)$	A″	1020	1022	1030/1017	1017
$\rho(CH_2)$	A′	978	978	981/972	977
$tw(CH_2) + \omega(CH_2)$	A″	963	961	981/972	977

[a] Symmetry assignment for a C_s point group molecule. A′ modes are in-plane, and A″ modes are out-of-plane.[26] [b] Reference 26. [c] These modes are very weak in the multilayer spectrum (not shown).

ropropene physisorbs to the Cu(111) surface with its molecular plane roughly parallel to the surface.

4. Discussion

The straightforward assignment of modes to either in-plane or out-of-plane symmetry in the four propenes makes possible a qualitative description of the orientation of the molecules on the Cu(111) surface. In all cases the in-plane modes, which are fairly intense in the randomly oriented multilayer phase, lose intensity with respect to the out-of-plane modes when a single monolayer of the propene is adsorbed on the surface. The implication of this is that all four molecules lie with their planes roughly parallel to the surface and that the transition moments of the in-plane modes have only small projections onto the surface normal. The in-plane modes experience the least decrease in intensity for 3,3,3-trifluoropropene, which might be expected to have the greatest tilt with respect to the surface as a result of the size of the CF_3 group. One of the implications of this self-consistent set of observations is that the C_s symmetry of the molecules in the gas or multilayer phases is only weakly broken as a result of physisorption to the surface.

A quantitative method for determination of orientation has been described elsewhere[20] and is used here to estimate the tilt of the molecular planes of hexafluoropropene and propene with respect to the surface. The method is based on the fact that the

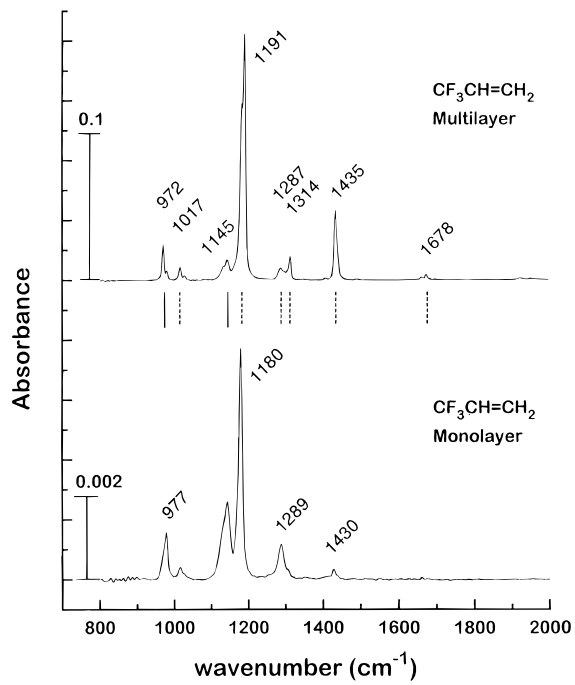

Figure 3. FT-IRAS of multilayer 3,3,3-trifluoropropene (top) and a 3,3,3-trifluoropropene monolayer (bottom) on the Cu(111) surface at 100 K. Vibrational assignments are given in Table 3. Dashed lines indicate the positions of in-plane (A′) modes and solid lines the positions of out-of-plane (A″) modes.

intensity of a given vibrational mode is given by

$$I \propto \mu^2 \cos^2 \theta_{\hat{n}\vec{\mu}} \tag{1}$$

The quantity $\theta_{\hat{n}\vec{\mu}}$ is the angle between the surface normal ($\hat{n}$) and the transition moment vector ($\vec{\mu}$) of the vibrational mode. In other words, the intensity is proportional to the square of the projection of the transition dipole moment onto the surface normal ($I \propto \mu_{\hat{n}}^2$). The magnitude of the transition moment (μ) can be obtained from the spectra of the randomly oriented gas or multilayer phase.

In order to define the orientation, a molecular coordinate system (x, y, z) is assigned to the molecule with the C=C bond of the propene defining the x-axis; the plane of the molecule is the xz-plane and the y-axis is perpendicular to the molecular plane. A coordinate system (x'', y'', z'') is also assigned to the surface with the y''-axis lying along the surface normal. The

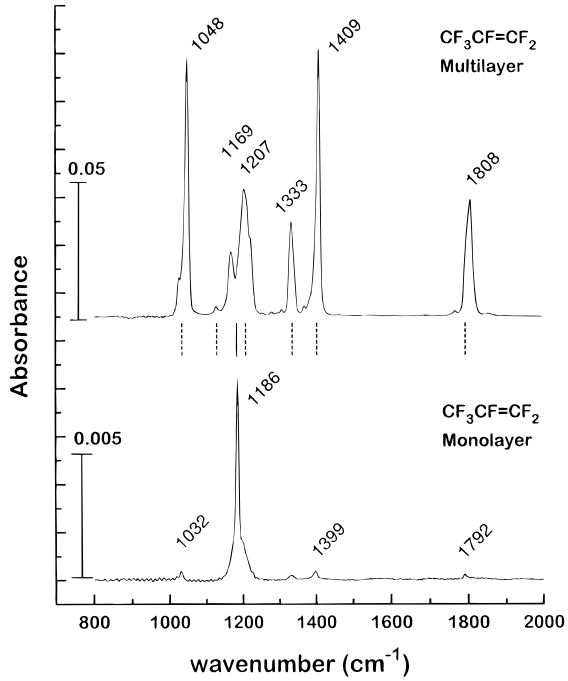

Figure 4. FT-IRAS of multilayer hexafluoropropene (top) and a hexafluoropropene monolayer (bottom) on the Cu(111) surface at 100 K. Vibrational assignments are given in Table 4. Dashed lines indicate the positions of in-plane (A′) modes and solid lines the positions of out-of-plane (A″) modes.

TABLE 4: Vibrational Frequencies (cm^{-1}) and Assignments for Hexafluoropropene on Cu(111)

mode	sym[a]	IR obsd[b]	calcd[b]	$CF_3CF{=}CF_2$/Cu(111) multilayer	$CF_3CF{=}CF_2$/Cu(111) multilayer
$\nu(C{=}C) + \nu(CF_2)$	A′	1796	1782	1808	1792
$\nu_a(CF_2)$	A′	1398	1412	1409	1399
$\nu(CF) + \nu(CC)$	A′	1334	1332	1333	1333
$\nu(CF_3)$	A′	1212	1210	1207	sh
$\nu(CF_3)$	A″	1178	1179	1169	1186
$\nu(CF_3) + \nu(CC) + \nu(CF_2)$	A′	1117	1144	1129w	
$\nu_s(CF_2) + \nu(CF_3)$	A′	1036	1009	1048	1032

[a] Symmetry assignment for a C_s point group molecule. A′ modes are in-plane, and A″ modes are out-of-plane.[26] [b] Reference 26.

orientation of the molecule can be described in terms of a rotation by an angle θ about the x''-axis followed by a rotation by an angle φ about the z''-axis needed to align the molecular coordinate system with the surface coordinate system.

The rotation angles can be determined from the intensities of the vibrational modes observed in the FT-IRAS experiment. The projection of a transition dipole moment vector in the molecular coordinate system ($\vec{\mu} = (\mu_x, \mu_y, \mu_z)$) along the surface normal is given by

$$\mu_{\hat{n}} = -\mu_x \sin\theta \cos\varphi + \mu_y \cos\theta \cos\varphi + \mu_z \sin\varphi \quad (2)$$

Provided that the directions of the transition dipole moment vectors are known in the molecular coordinate system (x, y, z), one can calculate their projections onto the surface normal in terms of the rotation angles θ and φ. For two modes (ν_1, ν_2) one can define a function

$$R(\theta, \varphi) = \frac{(\mu_{\hat{n}1}/\mu_{\hat{n}2})^2}{(\mu_1/\mu_2)^2} \quad (3)$$

which should be equal to the experimentally determined quantity

$$R_{exp} = \frac{(I_1^s/I_2^s)}{(I_1^g/I_2^g)} \quad (4)$$

I_ν is the measured intensity of a mode, the superscript 's' indicates a surface species, and the superscript 'g' indicates a species in the randomly oriented multilayer phase. Equating any two values of R_{exp} with the corresponding expressions for $R(\theta, \varphi)$ allows a unique determination of the orientation angles θ and φ. It should be pointed out that one of the assumptions that is implicit in this analysis is that the intrinsic magnitudes of the transition dipole moment vectors μ_ν are the same in the multilayer and the monolayer. It should also be pointed out that the angles that result from this analysis give an average orientation of the adsorbate. The method cannot distinguish between a system in which all molecules have an identical orientation and cases where there is in fact a distribution of two or more adsorbate orientations.

This analysis has been used to estimate the orientations of propene and hexafluoropropene on the Cu(111) surface. Unfortunately, in the cases of fluoropropene and 3,3,3-trifluoropropene it is not possible to identify enough modes for which the intensities are measurable in both the monolayer and multilayer phases and for which the orientation of the transition moment in the framework of the molecule can be determined.

$CF_3CF{=}CF_2$. In order to estimate the orientation of hexafluoropropene, three orthogonal pairs of modes have been chosen from the vibrational spectra. Since there is only one available out-of-plane mode, $\nu(CF_3)$ (A″), it has been used as one of the two modes in all three pairs. This introduces the possibility of a systematic error in the solution, but it is unavoidable. The three in-plane modes (A′) have transition dipole moments with different orientations in the molecular coordinate system. Thus, there are three algebraically different expressions $R(\theta, \varphi)$ used to solve for two unknowns, the rotation angles θ and φ. The orthogonal pairs of modes, the expressions $R(\theta, \varphi)$, and values of R_{exp} are given in Table 5.

The angles θ and φ have been found by minimizing a squared error expression of the form

$$SSE(\theta, \varphi) = \sum_\nu [R_{exp} - R(\theta, \varphi)]^2/R_{exp}^2 \quad (5)$$

summing over all three pairs of modes "ν". The errors are weighted by R_{exp}^{-1} so that the relative error in each contributes equally. The SSE is minimized for values of $\theta = 5°$ and $\varphi = 10°$. Given these angles, one can calculate other orientation parameters. For a unit vector ($\hat{\mu}$) described in the molecular coordinate system ($\hat{\mu}_x$, $\hat{\mu}_y$, $\hat{\mu}_z$) the angle (α) between $\hat{\mu}$ and the surface normal ($\hat{n}$) is given by

$$\cos\alpha = -\hat{\mu}_x \sin\theta \cos\varphi + \hat{\mu}_y \cos\theta \cos\varphi + \hat{\mu}_z \sin\varphi \quad (6)$$

The vector associated with the C−C single bond has an angle of $\alpha_{CC} = 79°$ with respect to the surface normal, and the plane of the molecule is tilted 11° away from the surface. The C=C bond is tilted by 5° from the surface. A simple analysis of the dichroic ratio of the in-plane and out-of-plane $\nu(CF_3)$ modes, normalized using the ratio of intensities of the same modes in the randomly oriented multilayer, indicates that the C_{3v} axis of the $\nu(CF_3)$ (A′) mode (and hence, the coincident C−C bond) is tilted 77° from the surface normal. This agrees well with the tilt angle (α_{CC}) found from considering both θ and φ. A pictorial image of the molecule on the surface is given in Figure 5.

TABLE 5: Hexafluoropropene. $R(\theta, \varphi)$ and R_{exp} for Select Mode Pairs and Errors, $\Delta(\theta, \varphi)$, at the Optimum Solution for the Angles θ and φ

modal group (A″)/(A′)	R_{exp}	$R(\theta, \varphi)$	$\Delta(\theta, \varphi) = \lvert R_{exp} - R(\theta, \varphi)\rvert/R_{exp}$
$\nu(CF_3)/\nu(CF_3)$	20	$\dfrac{(\cos\theta\cos\varphi)^2}{[(0.866)\sin\varphi + (0.5)\sin\theta\cos\varphi]^2}$	0.23
$\nu(CF_3)/\nu(C{=}C) + \nu_s(CF_2)$	130	$\dfrac{(\cos\theta\cos\varphi)^2}{(\sin\theta\cos\varphi)^2}$	0.07
$\nu(CF_3)/\nu_a(CF_2)$	86	$\dfrac{(\cos\theta\cos\varphi)^2}{(\sin\varphi)^2}$	0.65
minimum sum of errors, $\Delta(\theta, \varphi)$ at $\theta = 5°$, $\varphi = 10°$			=0.95
average error			=0.32

TABLE 6: Propene. $R(\theta, \varphi)$ and R_{exp} for Select Mode Pairs and Errors, $\Delta(\theta, \varphi)$, at the Optimum Solution for the Angles θ and φ

modal group (A″)/(A′)	R_{exp}	$R(\theta, \varphi)$	$\Delta(\theta, \varphi) = \lvert R_{exp} - R(\theta, \varphi)\rvert/R_{exp}$
$\omega(CH_2)/\nu_a(CH_2)$	9.8	$\dfrac{(\cos\theta)^2}{(\sin\varphi)^2}$	0.063
$\nu_a(CH_3)/\nu_s(CH_3)$	4.5	$\dfrac{(\cos\theta\cos\varphi)^2}{[(0.866)\sin\varphi + (0.5)\sin\theta\cos\varphi]^2}$	0.003
$\nu_a(CH_3)/\nu_a(CH_2)$	3.9	$\dfrac{(\cos\theta\cos\varphi)^2}{(\sin\varphi)^2}$	0.045
minimum sum of errors, $\Delta(\theta, \varphi)$ at $\theta = 3°$, $\varphi = 20°$			=0.111
average error			=0.037

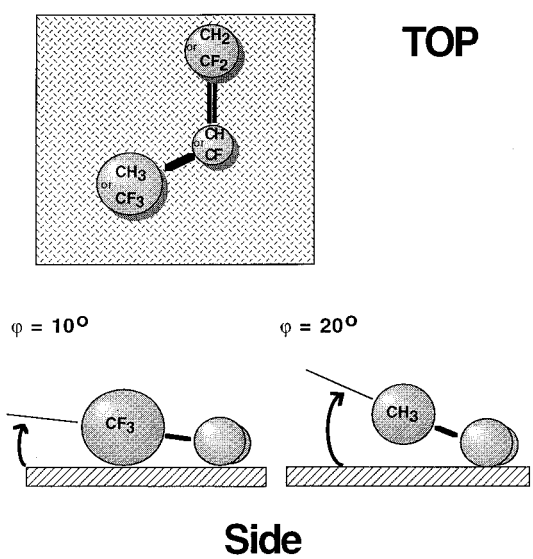

Figure 5. Qualitative depiction of the orientation of propene and the fluoropropenes on the Cu(111) surface implied by the vibrational spectra.

$CH_3CH{=}CH_2$. A similar calculation was carried out for the propene orientation using the gas phase spectrum to normalize for the intrinsic intensities. The expressions for $R(\theta, \varphi)$ and the values of R_{exp} are given in Table 6. The results give $\theta = 3°$ and $\varphi = 20°$. This translates into a C−C single bond tilt angle of $\alpha_{CC} = 71°$ with respect to the surface normal and a tilt of the molecular plane of 20° with respect to the surface. The C=C bond is tilted by 3° from the surface. The dichroic ratio calculation for the in-plane and out-of-plane $\nu(CH_3)$ modes yields an angle of 65° for the tilt of the C−C bond away from the surface normal. This is in reasonable agreement with the value obtained considering all three pairs of modes.

Error Analysis. The random propagation of errors into the solutions for the angles θ and φ have been determined from expressions of the form

$$\sigma_\theta^2 = \sum_\nu \left(\frac{d}{dR}\theta\right)^2 \sigma_R^2 \qquad (7)$$

The sum is over all three pairs of modes used to evaluate θ and φ. The quantity σ_R^2 is the variance in the values of R_{exp}, and the quantity $d\theta/dR$ has been evaluated numerically using the minimization of the SSE(θ, φ). By use of spectra obtained for ethoxides, our ability to reproduce the relative intensity of a vibrational mode has been estimated at ∼17%.[20] This translates into a reproducibility of R_{exp} of $\sigma_R/R \approx 0.24$. Note that the differences, or errors, between the observed values R_{exp} and the the predicted values of $R(\theta, \varphi)$ are listed in the right-hand column of Tables 5 and 6. The average value of the error for hexafluoropropene is 0.32, while for propene it is 0.037. These are less than or roughly equal to the errors introduced by our ability to reproduce R_{exp}. Using the value $\sigma_R/R = 0.24$ yields deviations in θ and φ of $\sigma_\theta = 1°$ and $\sigma_\varphi = 2°$ for both solutions (propene and hexafluoropropene) and reflects the *intrinsic* error introduced into the quantitative analysis by the experimental ability to reproduce the relative intensity ratio of a given pair of modes. The solutions presented above agree with the qualitative interpretation of the spectra and the simple analyses of the orientations of the methyl groups based on the dichroic ratio.

Molecular Orientation. Figure 5 shows a schematic view of our proposed structures for propene and 3,3,3-trifluoropropene on the Cu(111) surface. The molecular planes are tilted by 20° and 11°, respectively. Our analysis of the error in these angles introduced by random variance in our ability to reproduce relative intensities suggests that these numbers are significantly different. It is not immediately obvious how to rationalize this difference, and it is important to point out that there are potential sources of systematic error in our quantitative analysis of the orientation. Small couplings between in-plane modes result in small errors in our predictions of their orientations within the framework of the molecule. Certainly, the adsorption of the propenes onto the surface must break the C_s symmetry of the gas phase molecule used to assign modes to purely in-plane and out-of-plane representations. Our apparent success in assigning modes to these representations indicates that the symmetry breaking is weak but its magnitude is unknown. Nonetheless, our quantitative estimates of the orientation of propenes adsorbed on the Cu(111) surface are in clear agreement with the results of qualitative analysis of the vibrational mode intensities observed in Figures 1−4 and give some idea of the range of tilt angles to be expected.

5. Conclusion

The FT-IRAS spectra of propene and a set of fluorinated propenes on the Cu(111) surface indicate that the molecules lie with their molecular planes, defined by the C−C═C atoms, essentially parallel to the surface regardless of the degree of fluorination. The ν(C═C) modes of the propenes, where they can be identified in the monolayer spectra, do not show any significant perturbation in frequency, which indicates little contribution to the adsorbate−metal bond strength from π^* orbital backdonation from the metal. The quantitative analysis of the average orientation of hexafluoropropene finds that the molecular plane is tilted about 11° from the plane of the surface while that of propene is 20° from the plane of the surface.

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