

Photochemical Attachment of Fluorobutyl Moieties on a Diamond (110)-Oriented Surface: A Multiple Internal Reflection Infrared Spectroscopic (MIRIRS) Investigation

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The chemistry of perfluorobutyl iodide (C_4F_9I) on H-free and H-terminated diamond (110)-oriented surfaces was investigated using multiple internal reflection infrared spectroscopy (MIRIRS). C_4F_9I physisorbed to form multilayers at 90 K for both surface terminations. The physisorbed C_4F_9I desorbed from the surface when heated above 200 K and the starting surface was regenerated. The electronic structure and vibrational spectra of the perfluorobutyl group were calculated for perfluorobutyl chloride and perfluorobutyl bromide and the MIRIRS of the physisorbed multilayer agreed well with calculated infrared spectra. After exposing the C_4F_9I multilayer at 90 K to UV radiation for 30 min and subsequently heating the surface above 200 K, characteristic vibrational features of the perfluorobutyl group were observed between 1138 and 1355 cm^{-1} . In a series of annealing experiments, these modes persisted on the surface up to 600 K and completely disappeared by 700 K. The same results were observed on both the H-free and H-terminated surfaces.

1. Introduction

The surface termination of diamond has a major role in determining its chemical,^{1,2} electrical,^{1,3} and tribological⁴ properties. Therefore, to manipulate these properties, selective control of the surface termination is desirable. Because diamond is a robust, chemically inert material, especially at low temperatures, the development of low-temperature methods for selective chemical modification of the surface would be invaluable. Methods for chemically modifying the diamond surface include ion implantation,⁵ oxidation,^{6–8} halogenation of the surface using atomic and molecular chlorine and fluorine,^{9,10} and selective metallization of the surface.¹ Recently, X-ray photolysis of C_4F_9I and CF_3I on C(100) was shown to be an efficient, mild means for attaching fluorine to the diamond surface.¹¹

In this work, we investigate the low-temperature photochemical attachment of the perfluorobutyl group on a (110)-oriented single-crystal diamond surface using ultraviolet (UV) irradiation. We employ multiple internal reflection infrared spectroscopy (MIRIRS) as a nondestructive probe to identify the perfluorobutyl surface species and to monitor the thermal stability of the adsorbate. We also employ density functional calculations to assist in the interpretation of the spectral data.

2. Experimental Details

2.1. Apparatus. An ultrahigh vacuum (UHV) system with a base pressure of $\sim 1.5 \times 10^{-10}$ Torr and a working pressure of $(3–5) \times 10^{-10}$ Torr was used in this investigation.^{3,12} The stainless steel UHV system included a cylindrical mirror analyzer for Auger electron spectroscopy (AES), a quadrupole mass spectrometer for residual gas analysis, two differentially pumped KBr windows for transmission of infrared (IR) light, and a quartz window for UV light transmission. Pinhole-dosers and tungsten filaments heated to 1900 K were used to dose the

diamond surface with perfluorobutyl iodide and hydrogen atoms, respectively.

A trapezoid-shaped, type IIA, natural-diamond ($15.2 \times 5.2 \times 0.71$ mm³) was used as an internal reflection element (IRE). The single-crystal IRE was mounted on a molybdenum (Mo) block in such a way that both large faces of the crystal were exposed. The Mo block was attached to a liquid-N₂-cooled manipulator. The temperature of the diamond IRE could be raised by a combination of radiative heating from a tantalum (Ta) filament located inside the Mo block and electron bombardment of the Mo block when the block was biased at +650 V. When performing annealing experiments with the fluorocarbon adsorbates, the sample was heated only by radiative heating to avoid the impingement of accelerated stray electrons on the surface that caused complete desorption of the adsorbates. The temperature of the diamond IRE was measured with a chromel–alumel thermocouple wedged in a laser-drilled hole in the diamond. A type-C thermocouple was inserted into a small well on the Mo block to monitor the discrepancies in the temperature of the sample and the heating block itself. Typically there is a difference of about 100° at the maximum temperature (1473 K).¹³

Infrared light from a Fourier transform infrared (FTIR) spectrometer was focused through a KBr window onto one beveled edge of the diamond IRE. After 35 internal reflections (incident angle = 30°) from the two large-area (110)-oriented faces, the light exited the opposite end of the IRE and passed through a slit before leaving the chamber through a second KBr window. Then the light was focused on a liquid-N₂-cooled wideband $Hg_xCd_{1-x}Te$ detector. The optical path length in the IRE was about 30 mm, and the diamond prism was opaque in the second and third phonon absorption regions (1750–2600 and 3200–3600 cm^{-1} , respectively) of the infrared (IR) spectrum.¹² The single-crystal IRE was oriented such that the light propagated along the [001] crystal lattice direction, while the electric field of the p- and s-polarized light lay in the [110] and $[1\bar{1}0]$ directions, respectively. Infrared spectra were collected at s- and p-polarization with 4 cm^{-1} resolution. The

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TABLE 1: Transmittance Range of UV–Vis Optical Filters Used for Photodissociation Experiments

filters ^a	wavelength (λ , nm)	energy (E , eV)
UG-5	$275 < \lambda < 375$; $\lambda > 700$	$3.30 < E < 4.50$; $E < 1.77$
WG-305	$\lambda > 305$	$E < 4.06$
WG-320	$\lambda > 320$	$E < 3.87$
WG-345	$\lambda > 345$	$E < 3.59$

^a Schott Glass Technologies Inc.

signal was averaged over 1000–5000 scans, and each spectrum was ratioed against a background spectrum to give $\delta R/R$. All spectra were taken at 90 K.

2.2. Sample Preparation and C₄F₉I Dosing. Prior to insertion in the chamber, the diamond IRE was cleaned in a series of acid mixtures to remove any metals and amorphous carbon, followed by about 30 min of H-plasma treatment on both reflection surfaces. This procedure is quite effective for cleaning and smoothing the (100)-oriented surface.¹⁴ Recently it was found that the H-plasma treatment is also effective at fully hydrogenating the C(110)-oriented surface, but the (110) surface is comprised primarily of (111) microfacets that are enhanced by the H-plasma treatment.¹⁵ Therefore, we will refer to the IRE surfaces as the (110)-oriented surface rather than as the ideal bulk-terminated (110) surface. For experiments with the H-terminated surface, the crystal was heated to 673 K to remove any physisorbed organic impurities.¹⁶ To remove surface H, the crystal was heated to 1300–1400 K. High-resolution electron energy loss spectroscopy has shown that this method removes surface hydrogen.¹⁷ The diamond IRE surface was re-hydrogenated at room temperature by exposing both sides of the annealed prism to hydrogen atoms produced with a pair of tungsten filaments that were heated to 1900 K in the presence of 10^{-6} Torr H₂. The surface was fully hydrogenated after an H₂ exposure of ~ 3000 L. Before and after the surface treatments, the surface cleanliness was verified by AES, and no graphitic carbon or surface oxygen was detected.

Perfluorobutyl iodide (C₄F₉I, 98% purity) was obtained from Strem Chemicals Inc. Except for freeze–pump–thaw cycles to remove dissolved gases, the C₄F₉I was used without further purification. C₄F₉I was delivered to the IRE surface via two custom-made pinhole dosers, one located on each side of the prism. A pinhole (8 or 10 μ m diameter) was laser-drilled into the sealed end of a 1/8" stainless steel tube using a Nd:YAG laser system. The flux of gas through each pinhole into the UHV chamber was calibrated with H₂ by monitoring the pressure drop in the gas manifold as a function of time. To get an equal flux of C₄F₉I on the front and back faces of the prism, the doser-to-crystal geometry was adjusted for each pinhole doser.^{18,19} With 1 Torr of C₄F₉I in the gas manifold, the flux at the surface was 2.10×10^{14} molecules/(cm² s).

2.3. UV Light Source. A 200-Watt Hg arc lamp was employed as the UV source. The IRE was illuminated with the light from the lamp via a quartz window. The light was unfocused and directly illuminated one side of the IRE. During the UV irradiation, the sample temperature increased by about 5° due to light absorption by the mount. For most of the experiments the light from the Hg arc lamp was unfiltered. However, a series of spectra were collected using optical filters to identify the threshold for the photon energy which induced the chemistry (vide infra). The Schott glass part numbers for the filters and their transmission wavelengths and energies are listed in Table 1.

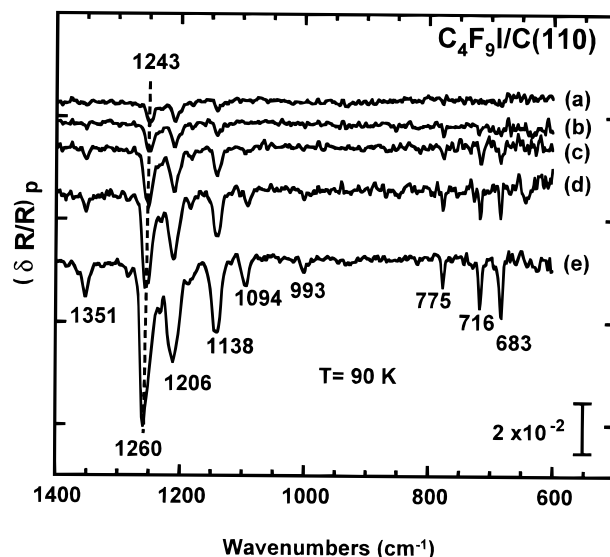


Figure 1. MIRIRS data for physisorbed C₄F₉I on a H-free C(110)-oriented surface at 90 K: (a) 0.21, (b) 0.42, (c) 1.05, (d) 2.01, and (e) 4.02×10^{15} molecules/cm² C₄F₉I dose.

2.4. Theoretical Methods. The electronic structure and vibrational spectra of the perfluorobutyl group were calculated for perfluorobutyl chloride and perfluorobutyl bromide. Calculations on perfluorobutyl iodide were not performed because of the large computational times required for all-electron calculations on heavy atoms. The electronic structure calculations used the B3LYP²⁰ hybrid density functional method and the 6-311G**^{21,22} basis set. Pure polarization functions were used. The basis set included a total of 260 and 278 functions for the perfluorobutyl chloride and perfluorobutyl bromide molecules, respectively. Geometries of the stationary points of the potential energy surface were determined by the Berny optimization method.²³ Harmonic vibrational frequencies at the stationary points were computed by analytic second-derivative methods. All calculations were performed with the Gaussian 94 program package.²⁴

3. Results

3.1. Physisorbed Molecular C₄F₉I. Initially, we examined the coverage dependence of the MIRIR spectrum for C₄F₉I on the H-free surface. Figure 1 shows a series of p-polarized spectra obtained for various C₄F₉I doses to the diamond surface held at 90 K. At this temperature, C₄F₉I is molecularly physisorbed on the sample surface and can form a condensed multilayer.¹¹ Assuming the sticking coefficient for C₄F₉I at $T_{\text{surf}} = 90$ K is unity, a multilayer coverage of C₄F₉I would be expected for exposures $> 6.9 \times 10^{14}$ molecules/cm² (the closest packing density of C₄F₉I when the iodine atom is down and the molecular axis is normal to the surface). At the lowest exposure shown (spectrum 1a), three absorption bands are observed at 1243, 1206, and 1138 cm⁻¹. As the coverage increases, these peaks show steady growth in intensity and a fourth feature appears at 1350 cm⁻¹ (spectrum 1c). When the exposure reaches 2.01×10^{15} molecules/cm² (spectrum 1d), features at 1094 and 993 cm⁻¹, and a group of sharp features at 775, 716, and 683 cm⁻¹ appear and become more intense at higher coverages. For the C₄F₉I exposures $> 4.02 \times 10^{15}$ molecules/cm² (spectrum 1e), all the spectral features show continuous growth in their intensities. Throughout the data series in Figure 1, all the spectral frequencies remain fixed except for the mode at 1243 cm⁻¹. This mode shows a blue

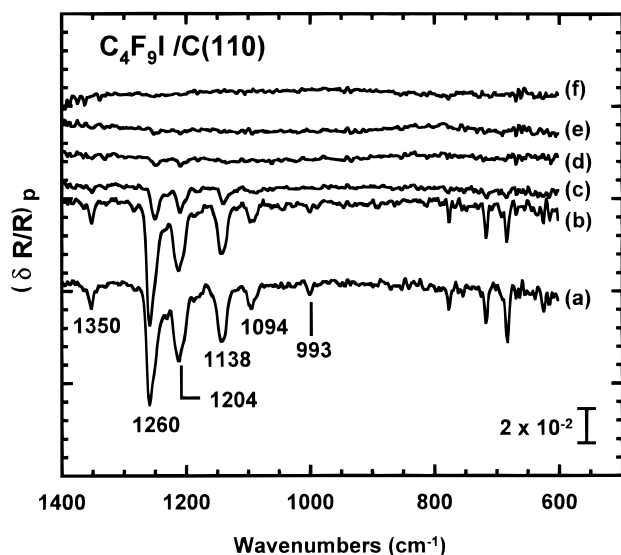


Figure 2. MIRIRS data for C_4F_9I on a H-free C(110)-oriented surface annealed to (a) 90 K, (b) 156 K, (c) 201 K, (d) 228 K, (e) 280 K, and (f) 300 K.

shift as the coverage is increased, indicating that the lateral interactions within the layer affect the energy of the mode.

In Figure 2, the dependence of the IR spectrum on the annealing temperature is shown for C_4F_9I (4.02×10^{15} molecules/ cm^2 adsorbed at 90 K) on the H-free C(110)-oriented surface. Spectra 2a–f correspond to the features obtained after annealing at 90, 156, 201, 228, 280, and 300 K, respectively. Most of the C_4F_9I desorbs by 228 K. There is no evidence of surface species following heating to 300 K. Therefore, C_4F_9I does not react with the H-free diamond (110)-oriented surface.

The absorption bands observed in the 1100–1360 and 520–830 cm^{-1} regions generally are related to the C–F stretching and deformation vibrations, respectively.²⁵ However, C–F stretching modes in fluorocarbon compounds lie in a region where skeletal modes (C–C vibrations) occur, and the coupling in those internal modes results in a series of bands in the 1100–1360 cm^{-1} region. Thus it is difficult to ascribe observed frequencies to particular functional groups in these molecules. Consequently, we calculated the IR spectra of the lowest energy conformations of perfluorobutyl bromide and perfluorobutyl chloride with Gaussian 94 using density functional theory as described in Section 2.4. To facilitate direct comparison with the measured spectra, the computed vibrational frequencies and IR intensities were used to generate simulated spectra using a Gaussian profile. Although a detailed analysis of the vibrational spectra of the C_4F_9X ($X = Cl, Br, \text{ or } I$) molecule is beyond the scope of this paper (a more detailed paper on this subject is forthcoming²⁶), we present some relevant results of those calculations to assist in the interpretation of the data in this manuscript.

Density functional theory (DFT) calculations show that the observed, condensed C_4F_9I spectrum (in Figures 1, 2, and 3) is consistent with the unreacted physisorbed molecule. A comparison is made in Figure 3 between the observed C_4F_9I spectrum and the calculated spectra of C_4F_9Cl and C_4F_9Br . The data in Figure 3 are tabulated in Table 2. All corresponding modes in each spectrum in Figure 3 are close in vibrational energy and nearly identical in relative intensity. DFT calculations on C_4F_9I were not performed because of the large computational times required for all-electron calculations on heavy atoms. Because there is little change in the modes associated with the perfluorobutyl functional group in the DFT

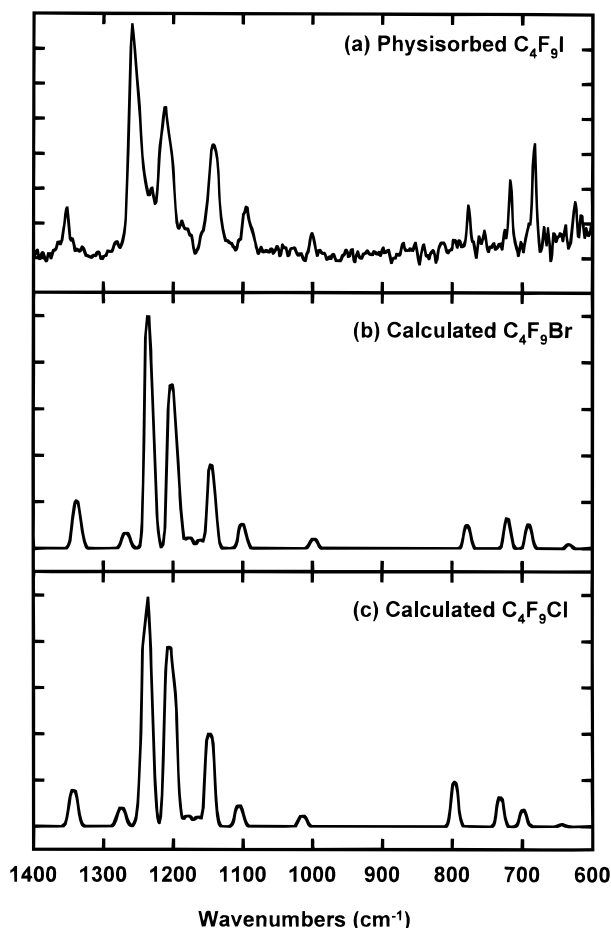


Figure 3. Comparison of the calculated IR spectra of C_4F_9Cl and C_4F_9Br with the measured MIRIR spectrum of C_4F_9I [coverage = 4.02×10^{15} molecules/ cm^2 (multilayer) on H-free C(110)].

calculations as the X is changed from Cl to Br and the calculated spectra reasonably match the measured spectra for $X = I$, we conclude that the C_4F_9Cl and C_4F_9Br calculations serve as reasonable models for the vibrational motions of the perfluorobutyl group.

Consistent with the comments of Socrates,²⁵ our calculations show that there is considerable coupling of the C–F and C–C stretches in each of the modes of the spectrum. This coupling makes it difficult to associate any one of the observed modes to characteristic group frequencies of the molecule (such as the symmetric CF_3 stretch). It is for this reason that we list an approximate description of the *dominant motion* of the vibration for a given absorption band in Table 2.

3.2. Photolysis of C_4F_9I : Formation of a Chemisorbed Fluorocarbon Species. Figure 4 shows the results of an experimental series in which the photochemical attachment of a functional group to the diamond surface was investigated. The surface treatment in Figure 4 was similar to that in Figure 2, except the C_4F_9I multilayer on the 90 K H-free diamond surface was exposed to UV irradiation from an Hg arc lamp for 30 min. Spectra 4a–e correspond to anneal temperatures of 90, 155, 198, 237, and 300 K, respectively.

Comparison of the 90 K spectra (Figures 2a and 4a) reveals subtle differences in the spectrum of the irradiated multilayer; they are, (1) a mode appears to have grown in at about 1228 cm^{-1} after UV exposure, and (2) the mode at 1260 cm^{-1} is shifted down to 1247 cm^{-1} . At temperatures >200 K, however, there is a significant difference between the two experiments. Spectral features in the 1100–1400 cm^{-1} region are present

TABLE 2: Infrared-Active Vibrational Modes of C_4F_9Cl , C_4F_9Br , and $C_4F_9I^a$

approximate mode descriptions	C_4F_9Cl , calculated ^b	C_4F_9Br , calculated ^b	C_4F_9I , condensed ^b
C—C sym str + CF ₃ , CF ₂ sym str	1343	1340	1351 m
C—C asym str + CF ₃ , CF ₂ asym str	1275	1271	1280 vw
CF ₃ asym str + CF ₂ (β,γ) asym str + C—C—C bend (out-of-plane)	1236	1235	1260–1247 ^c vs
CF ₃ asym str + CF ₂ (α,β,γ) asym str + C—C—C bend (out-of-plane)	1206	1205	1206 m
CF ₂ asym str + CF ₃ sym str	1147	1147	1138 m
CF ₃ , CF ₂ sym str + C—C bend (in-plane)	1105	1102	1094 w
C—C str + C—C—C bend (in-plane) + CF ₃ , CF ₂ sym str	1015	1000	993 w
CF ₃ sym bend + CF ₂ bend	797	780	775 w
C—C—C bend (in-plane) + CF ₂ bend	731	723	716 w
C—C—C bend (in-plane) + CF ₂ bend	699	692	683 w

^a All frequencies are in cm^{-1} : s, strong; m, medium; w, weak; v, very; str, stretching; sym, symmetric; asym, asymmetric. ^b Data in Figure 2. ^c Vibrational frequency influenced by the surface coverage.

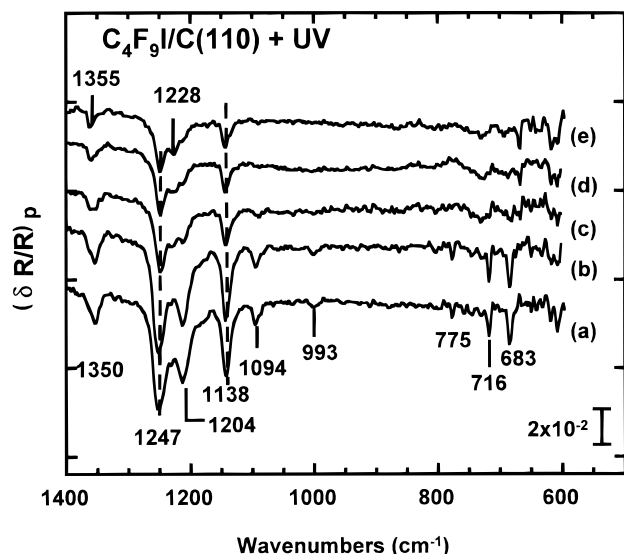


Figure 4. MIRIRS data for C_4F_9I on a H-free C(110)-oriented surface. The surface was annealed after exposure to UV light. Annealing temperatures are (a) 90 K, (b) 155 K, (c) 198 K, (d) 237 K, and (e) 300 K.

for the UV-irradiated C_4F_9I layer, whereas nothing is seen in that region for the layer that has not been exposed to UV radiation. This result indicates that (1) photolysis of C_4F_9I by UV radiation yields *chemisorbed species* that are stable at room temperature when photolyzed by UV radiation and (2) spectra a–c in Figure 4 can be attributed to the mixture of physisorbed C_4F_9I and the chemisorbed fluorocarbon species.

To determine whether the coverage of the chemisorbed species was saturated under our experimental conditions (90 K, 4.02×10^{15} C_4F_9I molecules/ cm^2 , 30 min UV exposure), a series of experiments was performed in which 4.02×10^{15} molecules/ cm^2 of freshly dosed C_4F_9I was exposed to UV

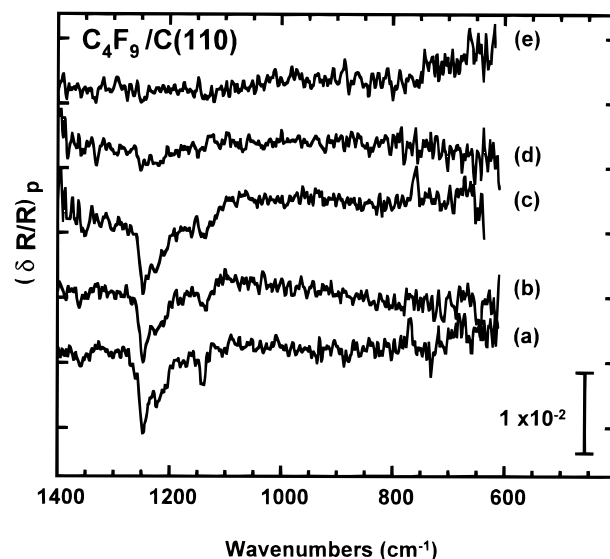


Figure 5. MIRIRS data for the experiment using a series of color filters. (a) Unfiltered arc lamp light exposure. The remaining spectra were collected after passing light at wavelengths of (b) 275 to 375 nm, (c) >305 nm, (d) >320 nm, and (e) >340 nm during exposure to the Hg arc lamp.

radiation for times that varied between 15 and 180 min. All resulting spectra were identical to the data in Figure 4 in spectral features, intensity, and thermal profile. We also conducted experiments for lower coverages of physisorbed C_4F_9I while keeping the UV exposure time fixed at 30 min and found that the spectral intensity for the chemisorbed species was reduced. In addition, the chemisorbed layer after annealing to 300 K was subjected to a subsequent dose of 4.02×10^{15} C_4F_9I molecules/ cm^2 , 30 min of UV radiation, and a 300 K anneal. After the subsequent treatment, no change was observed in the spectral intensity of the chemisorbed species; that is, the coverage of the chemisorbed species did not increase with additional cycles of C_4F_9I and UV dosing. Thus, we conclude that a 30-min exposure of condensed 4.02×10^{15} C_4F_9I molecules/ cm^2 to UV radiation yields a saturation coverage of the chemisorbed moiety.

To characterize the threshold photon energy that induces the photoattachment of the fluorocarbon moiety on the diamond surface, we performed experiments using a series of UV–Vis optical filters. For each IR spectrum in Figure 5, the H-free diamond surface was dosed with 4.02×10^{15} C_4F_9I molecules/ cm^2 at 90 K followed by a 30-min exposure to the UV source and a 300 K anneal. Spectra 5b–e were obtained after using optical filters that transmit light at wavelengths between 275 and 375 nm (spectrum b) and above 305, 320, and 340 nm (spectra c, d, and e, respectively) during the UV exposure. Spectrum 5a was obtained after using the unfiltered light from the UV source and was added to the figure for comparison of the intensities of the spectral features with spectra 5b–e. As shown in Figure 5, when the filters that pass light at wavelengths >320 and >340 nm were used, the chemisorbed species was not observed. However, the filters that transmit light with wavelengths >305 and >275 nm yielded spectra with intensities comparable to spectrum a. These results indicate that the UV light at wavelengths $\lesssim 305$ nm ($E > 4.06$ eV) is responsible for the observed photochemistry.

3.3. Orientation and Thermal Stability of the Chemisorbed Species. The orientation of the chemisorbed species was investigated using s- and p-polarized light (Figure 6). The two spectra in Figure 6 are nearly identical except that the intensity of the p-polarized spectrum is $\sim 30\%$ more intense and

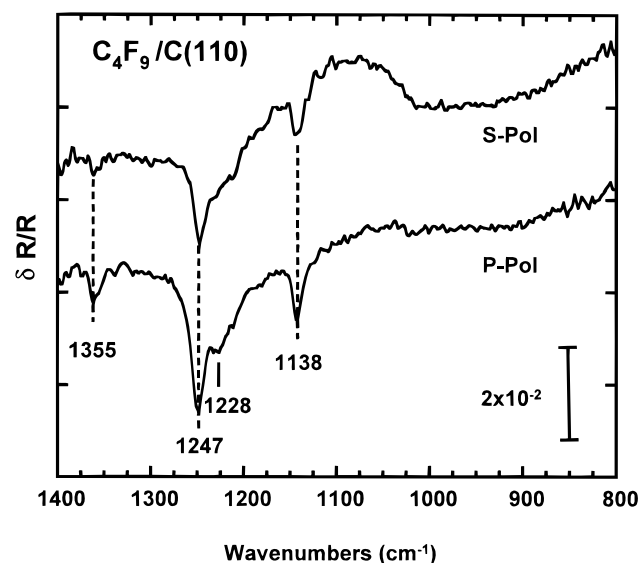


Figure 6. MIRIRS data for chemisorbed C_4F_9 using s- and p-polarized light. For each spectrum, the H-free diamond surface is dosed with 4.02×10^{15} molecules/cm² C_4F_9I at 90 K followed by a 30-min exposure to the UV source and annealing to 300 K.

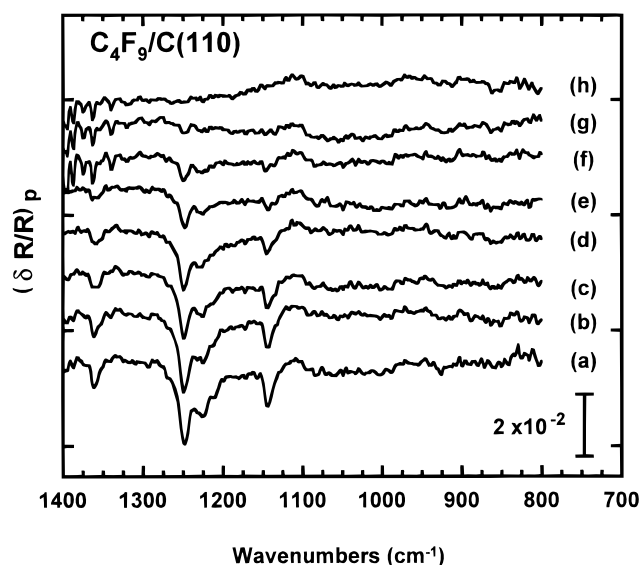


Figure 7. MIRIRS data for chemisorbed C_4F_9 annealed to (a) 300 K, (b) 430 K, (c) 496 K, (d) 533 K, (e) 611 K, (f) 633 K, (g) 688 K, and (h) 737 K.

there is a bump at 1100 cm^{-1} in the s-polarized spectrum due to a background miscancellation. Because the s- and p-polarized spectra are very similar, it appears that the C–F stretching modes and the chemisorbed species are oriented randomly. However, considering that the C(110)-oriented surface is rough and comprised predominantly of (111) microfacets,¹⁵ the interpretation of the orientation from the s- and p-polarized measurements may be much more complicated.

We already established that the chemisorbed species is stable on the surface at 300 K. The thermal stability of the chemisorbed species above room temperature was examined by collecting spectra at 90 K after annealing at temperatures from 300 to 740 K (spectra a–h in Figure 7). The H-free diamond surface was (1) exposed to 4.02×10^{15} molecules/cm² C_4F_9I , (2) exposed to UV radiation for 30 min, and (3) annealed to the specified temperatures. Unfortunately, the IRE moved slightly when the sample holder was heated. The movement caused a miscancellation of the $600\text{--}800\text{ cm}^{-1}$ region when

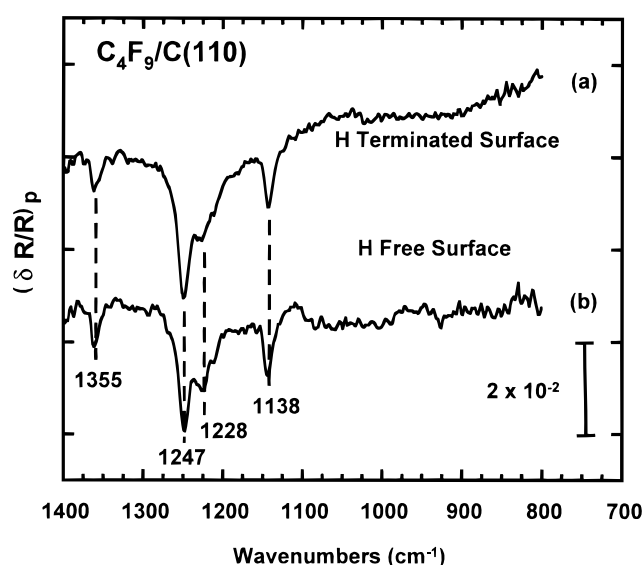


Figure 8. MIRIRS data for the chemisorbed C_4F_9 on (a) H-terminated and (b) H-free C(110)-oriented surfaces.

the annealed spectra were compared with the reference spectrum. A similar spectral response (miscancellation) was observed when an annealing control experiment was done with an adsorbate-free surface. Consequently, this portion of the spectrum is of little value in this series of data. In contrast, the C–F stretching region ($1100\text{--}1400\text{ cm}^{-1}$) was not significantly affected by the slight movement of the IRE. In the annealing experiment (Figure 7), the vibrational modes associated with the C–F stretches exhibited little change up to 533 K. The C–F stretching modes began to show significant decreases in intensity after the 611 and 633 K anneals, and completely disappeared by 700 K. The mode energies were unchanged, and the mode intensities were reduced evenly as the surface was heated. Also, no new vibrational features appeared during the annealing series. (Sharp features in the region between 1300 and 1400 cm^{-1} are absorption bands due to water in the detector that condensed on the detector window when the liquid-nitrogen reservoir was refilled.) The data suggest that the chemisorbed species remained intact on the C(110)-oriented surface until it desorbed.

3.4. Influence of Surface H. To explore the effect of surface H on the reactivity of the fluorobutyl radicals, experiments were conducted on the H-terminated diamond (110)-oriented surface. The H-terminated surface was generated either by H-atom dosing (3000 L H_2) in the UHV system¹⁷ or ex situ H-plasma treatment.¹⁵ In Figure 8, spectra of chemisorbed perfluorobutyl are shown for the H-terminated and H-free surface starting conditions. Both surfaces were (1) dosed with 4.02×10^{15} C_4F_9I molecules/cm² at 90 K, (2) exposed to UV light for 30 min, and (3) heated to 300 K. The resulting IR spectra were identical for both surfaces (Figure 8) and the chemisorbate exhibited similar thermal behavior on each surface (not shown).

4. Discussion

Molecular C_4F_9I physisorbed on the H-terminated and the H-free C(110)-oriented surfaces at 90 K. It desorbed from the surface without reacting when heated to 200 K (Figure 2). In contrast, dosing the C_4F_9I multilayer with UV radiation resulted in the production of a chemisorbed species that was stable on the surface to a threshold desorption temperature of about 620 K (Figures 4 and 7).

The wavelength-dependent photolysis study (Figure 5) revealed that photon energies $>4.06\text{ eV}$ (wavelengths $<305\text{ nm}$)

were required to induce chemisorption. This threshold energy is consistent with several studies of the UV photochemistry of gas-phase alkyl iodide compounds.^{27–30} The absorption band in the UV spectrum of alkyl iodide compounds is broad, extending from 210 to 350 nm.³⁰ This band is attributed to the excitation of the nonbonding electrons of iodine to the sigma antibonding orbital of the C–I bond. An exposure of alkyl iodide to this energy range, therefore, causes the breakage of the bond and generates alkyl radicals and I atoms.²⁹ Because it is known that the absorption is highly localized to the C–I bond,³⁰ similar attribution can be made for fluorinated alkyl iodide compounds. Therefore, we conclude that the chemisorbed species is formed via the photolysis of the C–I bond of C₄F₉I and the interaction of the resulting perfluorobutyl radical with the diamond surface.

To identify the species formed from the photolysis of condensed C₄F₉I, the MIRIR spectrum of the chemisorbed species at 300 K (Figure 4, spectrum e) is compared with the spectra of physisorbed molecular C₄F₉I (Figures 1 and 2). Because most of the vibrational modes of the chemisorbed species are, in fact, similar to those of the physisorbed molecule at low coverage (Figure 1a–c), we suggest that there is not a gross change in the molecular structure as the photolyzed radicals react with the diamond surface. However, there are differences in the spectra of the physisorbed and chemisorbed species. The chemisorbed species has unique modes at 1228 and 1247 cm^{−1}, whereas physisorbed molecular C₄F₉I has unique modes at 1206 and 1260 cm^{−1}. The 1260 cm^{−1} mode of the physisorbed molecule is coverage dependent, shifting to 1243 cm^{−1} as the coverage decreases (see Figure 1), indicating the influence of strong intermolecular interactions. We suggest that the 1260 cm^{−1} mode shifts to 1247 cm^{−1} after UV irradiation due to a change in the intermolecular interaction of the adsorbed species.

After the physisorbed multilayer is exposed to UV radiation (see Figure 4a), a mode at 1228 cm^{−1} is observed that becomes distinct when the physisorbed molecular layer desorbs. Based on our calculations (Figure 3), the majority of the motion in the 1206 cm^{−1} mode of the molecule is associated with coupling between the out-of-plane skeletal C–C bending and CF₂ asymmetric stretching motions of the molecule. If the perfluorobutyl group chemisorbed on the diamond surface, this mode would be influenced (stiffened) by attachment to the rigid diamond surface. Consequently, we assign the 1228 cm^{−1} band to the out-of-plane bending/asymmetric CF₂ stretching vibrations of the fluorinated butyl moiety, a shift in frequency from 1206 cm^{−1} in the molecular species.

There are other slight changes in the vibrational spectrum of the chemisorbed species in the region between 1200 and 1400 cm^{−1}. The mode at 1350 cm^{−1} for the physisorbed layer shifts to 1355 cm^{−1} for the chemisorbed species. The 1350 cm^{−1} vibration is primarily characteristic of the C–C stretch of the CF₃–CF₂ functional group, and will only be slightly influenced by chemisorption of the perfluorobutyl group.²⁵ The mode at 1138 cm^{−1} primarily results from CF₂ symmetric stretches and only slightly shifts to 1142 cm^{−1} for the chemisorbed butyl group.

Below 1100 cm^{−1}, the chemisorbed and physisorbed multilayer spectra show significant differences in that there are no detectable absorption bands for the chemisorbed species. The absence of the absorption bands in this region can be due to (1) a decrease in the number of absorbing species or (2) a change in the orientation of the dipoles. Because these modes do not change with polarization (Figure 6), we conclude that the

absence of these modes for the chemisorbed species is not related to the orientation of the chemisorbate. Consequently, the absence of the low frequency modes for the chemisorbed species probably is related to a lower surface coverage. Our coverage-dependent study of physisorbed C₄F₉I at 90 K (Figure 1) shows that the features below 1100 cm^{−1} are weak and that the intensity is significant only when the surface coverage is greater than a monolayer (Figure 1c). Hence, we conclude that the modes below 1100 cm^{−1} are too weak to be observed with our current signal-to-noise ratio.

We must address the lack of polarization dependence of the observed spectra for the chemisorbed species. We are left to conclude from the data in Figure 6 that the chemisorbed perfluorobutyl groups are randomly oriented on the surface. But, the absence of a polarization dependence also could result from other factors that include heterogeneity (roughness) of the C(110)-oriented surface,¹⁵ and the complexity of motion of the coupled vibrations of the perfluorobutyl group. In either case, extraction of detailed orientation information from the polarization data is not possible.

The UV photochemical dissociation of C₄F₉I at 90 K and subsequent chemisorption of the *fluorobutyl group* on the diamond (110) surface is consistent with the results obtained by Smentkowski and Yates on C(100) with XPS.¹¹ Despite the fact that the stretching mode of the C–I bond (200–600 cm^{−1})²⁵ falls well below our KBr window cutoff, the specificity of the photon energy that causes the chemisorption, the coupled C–F and C–C modes, and the thermal stability of the surface moiety confirm that the C–I bond dissociates and the fluorinated butyl radicals subsequently react with the surface. The role of iodine atoms produced by dissociation is not clear from our results, although Smentkowski and Yates¹¹ reported the desorption of DI from the deuterated C(100) surface upon X-ray photolysis of the physisorbed perfluorobutyl iodide. This result is consistent with our observation that H-termination of the surface did not inhibit photoinduced chemisorption of the perfluorobutyl group (Figure 8). Smentkowski and Yates concluded that the surface D (H) atoms were abstracted by the photolyzed I species.¹¹ Similar H abstraction reactions have been observed when the H-terminated surface was exposed to photolyzed chlorine species.³¹ We suggest that surface H *does not inhibit* the photochemical attachment of the perfluorobutyl species because of the abstraction of H by the iodine.

Smentkowski and Yates,¹¹ using X-ray photoelectron spectroscopy, observed thermal decomposition of the perfluorobutyl group on the C(100) surface between 300 and 700 K and the formation of chemisorbed atomic fluorine that is stable to 1500 K. In contrast, we do not see a change in the vibrational spectrum of the chemisorbed perfluorobutyl group until the species desorbs above 600 K. When we dissociated XeF₂ on the C(110) surface, a broad mode was observed at 1267 cm^{−1} for chemisorbed atomic F.³² The mode at 1267 cm^{−1} was not observed for the perfluorobutyl spectrum even upon annealing to high temperature. We cannot unequivocally dismiss the presence of any chemisorbed F with our data because the 1267 cm^{−1} mode may be obscured by the 1247 cm^{−1} mode of the perfluorobutyl group. However, we did not see any evidence for the chemisorbed atomic F after heating to >700 K.

There are two possibilities for the differences in the thermal stability of the perfluorobutyl moiety on the C(100) and C(110)-oriented surfaces: (1) the chemistry of the two surface orientations may be significantly different, and (2) the X-ray beam used for probing the chemisorbed layer on C(100) may have induced decomposition of the adsorbed perfluorobutyl group.

It is well-known that an X-ray beam can damage adsorbates as well as substrate surfaces.^{33,34} In this work, photolysis was possible only during the UV radiation exposure, and a nondestructive probe, IR spectroscopy, was used to characterize the chemisorbed species. Consequently, we believe that our results more accurately reflect the thermal stability of the perfluoroalkyl group on the diamond surface.

Finally, we attempted to determine the energetics for the loss of the perfluorobutyl group from the diamond surface by estimating the threshold desorption temperature from the MIRIRS data. Using Redhead³⁵ desorption kinetics analysis (assuming a first-order process, a preexponential factor of $1 \times 10^{13} \text{ s}^{-1}$, and a threshold desorption temperature of 600 K), we estimate the threshold activation energy for scission of the bond between the alkyl group and the surface carbon to be $40 \pm 1 \text{ kcal/mol}$. Although this may seem low for a C–C bond scission, we must remember that the energy gained by reconstructing the covalent diamond surface will assist in lowering this value.³⁶

5. Conclusion

In this study, we investigated the low-temperature photochemical attachment of a fluorinated butyl chain on H-free and H-terminated diamond (110)-oriented surfaces. For both surface terminations, exposure of the physisorbed $\text{C}_4\text{F}_9\text{I}$ to UV light at wavelengths $<305 \text{ nm}$ ($E > 4.06 \text{ eV}$) induced the chemical attachment of C_4F_9 . Spectral evidence was provided for the thermal stability of the chemisorbed species up to 600 K. No evidence was found for the thermal decomposition of the adsorbed species up to the desorption temperature. This work indicates that UV photolysis is a viable method for selective functionalization of a diamond surface. Successful attachment of an intact alkyl chain on the diamond surface may bear significance for further chemical functionalization of the surface and the development of effective means for selectively writing molecular patterns on diamond surfaces for various device applications.

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References and Notes

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