

LETTERS

Adsorption of Perfluoroalkanes on Pt(111): Thermal Desorption and Infrared Reflection–Absorption Spectroscopic Results

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First results for the adsorption of perfluorohexane and perfluoroheptane adsorbed at 100 K on Pt(111) are presented. Thermal desorption spectra (TDS) of both perfluoroalkanes are similar and show two distinct desorption peaks due to monolayer species in addition to the expected overlayer peak attributed to multilayer formation. The higher-temperature desorption peaks (α_1) exhibit simple first-order desorption kinetics and increase in binding energy with increasing number of CF_2 groups (consistent with established desorption models). The second desorption peak (α_2) was not expected and is hypothesized to be due to adsorption of the perfluoroalkane in a tilted or puckered configuration in which the interaction with the surface is reduced by at least one CF_2 unit from α_1 . Preliminary infrared reflection–absorption spectroscopy (IRRAS) spectra show a shift in the antisymmetric CF_2 stretch for the adsorbed species toward higher wavenumber.

Introduction

For nearly 30 years the computer industry has used polyperfluoroethers (PPFPO) as the lubricant of choice for the interface between magnetic hard disks and heads. For this application, the bonding of the lubricant is important, and several workers have studied the surface chemistry of ether and carbonyl functionality of fluorocarbons and their hydrocarbon analogs on single-crystal metal surfaces.^{1–5}

Besides the ether linkages and the various end anchoring groups, a good deal of the PPFPO polymer molecule is composed of perfluoromethylene (CF_2) groups. To what extent does this portion of the polymer play a role in the surface chemistry of PPFPO lubricants? We chose to approach the surface chemistry of the perfluoromethylene segments of these PPFPO polymers by studying small model compounds. In this paper we describe thermal desorption spectra (TDS) and preliminary infrared

reflection–absorption spectra (IRRAS) of perfluorohexane and perfluoroheptane adsorbed on Pt(111) under ultrahigh-vacuum conditions.

Experimental Section

Experimental data were obtained in a stainless steel ultrahigh-vacuum (UHV) system pumped with a 300 L/s ion pump. The base pressure obtained for these experiments was 7.0×10^{-10} to 2.0×10^{-9} Torr. A system schematic is shown in Figure 1. A 1-cm² platinum crystal was obtained from the Department of Materials Science at Cornell University and was cut and polished to within 1° of the 111 face on both sides. The Pt(111) crystal was cleaned by well-established oxidation–anneal cycles and argon ion bombardment.⁶ Surface cleanliness was monitored with an Auger electron spectrometer. The sample surface was exposed to gases via a stainless steel tube “doser” aimed directly at the surface. Vacuum and sample gas composition were monitored using a UTI-100C quadrupole mass spectrometer. Since flu-

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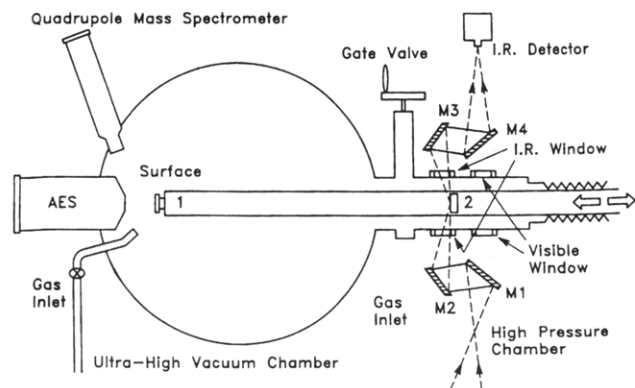


Figure 1. Schematic diagram of the ultrahigh-vacuum apparatus showing the relative positions of the Auger electron spectrometer (AES), quadrupole mass spectrometer, and FTIR sample beam. The FTIR itself is not shown. The sample is moved between position 1 and 2 with a stepper motor driven shaft enclosed in a stainless steel bellows.

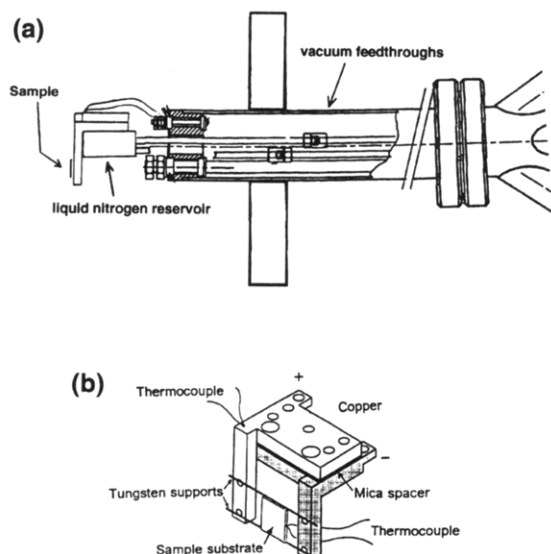


Figure 2. Detailed drawing of the sample holder: (a) side view and (b) oblique view. The sample is spot-welded to two 10-mil W support rods connected to copper dewar arrangement.

orinated adsorbates can be sensitive to electrons,^{7,8} a stainless steel screen was placed between the mass spectrometer's ionizer and the Pt surface. A 2000-V dc bias was applied to this screen during experiments to eliminate stray electron flux from the ionizer.

Figure 2 shows the sample heating and cooling arrangement, a design adapted from Thiel and Andregg.⁹ The Pt(111) crystal is spot-welded to two tungsten support wires. These support wires are attached to copper supports that are in thermal contact with a copper dewar. The Pt(111) sample is heated by thermal conduction when the tungsten wires are heated resistively. The sample can be cooled to 100 K by flowing liquid nitrogen through the copper dewar. Temperatures of the sample and the copper dewar are monitored with chromel–alumel thermocouples.

The mass spectrometer, oriented in line of sight with the sample, was used to monitor desorbed species. Preliminary TDS data showed no evidence for desorption of species other than perfluorohexane or perfluoroheptane. Since the cracking patterns for both perfluorohexane and perfluoroheptane were dominated by amu 69 (CF_3^+), detailed TDS were obtained by monitoring only mass 69 as a function of surface temperature. A stainless steel gas handling system (not shown) was used to supply the sample gas to the doser. Fluorocarbons were obtained from PCR, Inc., and used without further purification. The gases were passed through a liquid nitrogen trap before admission to the doser, and the purity of the resulting dosing gas was monitored by the mass

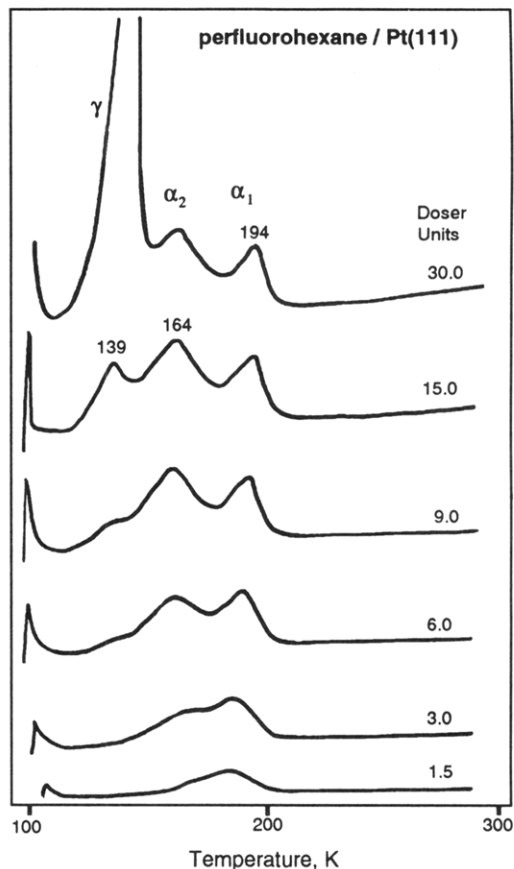


Figure 3. Thermal desorption spectra of perfluorohexane on Pt(111) as a function of increasing exposure, in doser units, at 100 K. Spectra were obtained by monitoring mass 69. Heating rates were ≈ 4.5 K/s. Doser units = dose pressure \times dose time.

spectrometer. Since the doser is a simple stainless steel tube with an inner diameter approximately 3 mm (not a capillary type), dose amounts, were estimated from total chamber pressure, as measured by a Bayard-Alpert ionization gauge (BAG), and exposure time. Because of concerns about fluorocarbon sensitivity to stray electrons, dosing times and rate for our Grainville-Phillips leak valve were calibrated against the BAG gauge readings so that the BAG gauge could be turned off during the actual sample dosing. Adsorption of both perfluorohexane and perfluoroheptane was done with the surface at 100 K. Heats of desorption were determined using Readhead's method,¹⁰ using $\nu = 10^{13}$ /s and applying the Walczak et al. correction.¹

IRRAS spectra were obtained with a Bomem DA3 FTIR arranged as shown in Figure 1. Two wavenumber resolution sample and reference spectra of the surface were taken at grazing incidence with a fixed polarizer oriented parallel to the plane of reflection. The method has been described elsewhere.^{11–13} Sample and reference files consisted of 500 coadded scans each and were subject to severe instrumental drift. The spectra were recovered with base-line correction techniques and are only reported here as preliminary. TDS experiments performed with the sample in the IRRAS analysis position showed delays in the desorption peak positions due to indirect sampling by the mass spectrometer but were otherwise unchanged.

Results

Perfluorohexane. Figure 3 shows the TDS spectra after adsorption of perfluorohexane at 100 K on Pt(111). The spectra are obtained by monitoring mass 69 as a function of temperature for increasing exposures. At low exposures a state at 194 K, denoted α_1 , increases in intensity but does not saturate before a second state, α_2 , begins to grow at 164 K. Both states continue

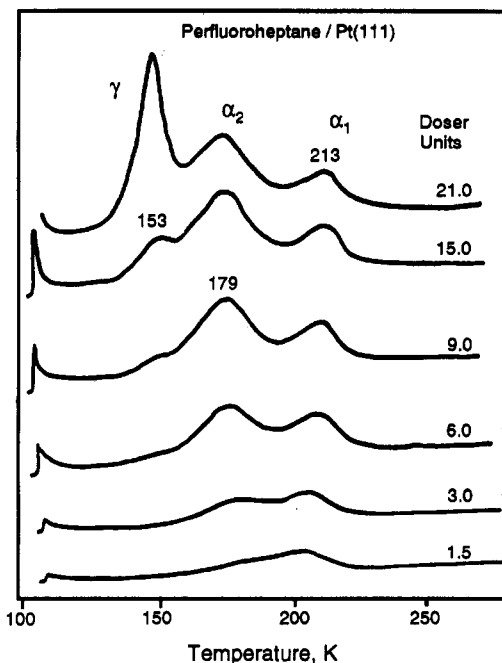


Figure 4. Thermal desorption spectra of perfluoroheptane on Pt(111) as a function of increasing exposure, in doser units, at 100 K. Spectra were obtained by monitoring mass 69. Heating rates were ≈ 4.5 K/s. Doser units = dose pressure \times dose time.

to grow but then saturate as the final state, γ , fills in at 139 K. The γ state does not saturate with increasing exposure, indicating that the state is due to multilayer condensation.

Both the α_1 and α_2 states appear to behave according to simple first-order kinetics.¹⁰ Assuming a preexponential factor, ν , of 10^{13} /s gives heats of desorption, E_d , of 11.68 and 9.82 kcal/mol for α_1 and α_2 , respectively.¹⁰

Perfluoroheptane. Figure 4 shows the TDS spectra after adsorption of perfluoroheptane at 100 K on Pt(111). The spectra obtained are qualitatively identical to those for perfluorohexane, the only difference being the temperatures for the desorption peak maxima. Using the same nomenclature and methods as above, the α_1 state at 213 K gives E_d of 12.86 kcal/mol, while α_2 at 179 K gives 10.75 kcal/mol for E_d .

IRRAS Spectra. Spectrum A in Figure 5 is the transmission spectrum of a thin film (neat) of perfluorohexane. The band at 1254 cm^{-1} is assigned to ν_2 (antisymmetric CF_2 stretch, CF_2 rock, CC stretch, CCC bend).¹⁴ Spectrum B in Figure 5 is the IRRAS spectrum of the perfluorohexane adlayer on Pt(111) resulting from a 30 doser unit exposure at 100 K. Spectrum C is the IRRAS spectrum taken after the γ state was removed by heating the Pt(111) surface to 150 K and the sample recooled to 100 K. By comparison with the transmission spectrum A, the absorbance shoulder at ca. 1254 cm^{-1} in spectrum B is attributed to ν_2 of the γ multilayer state while the shoulder at 1276 cm^{-1} in spectrum C is attributed to ν_2 of the surface monolayer states.

Discussion

α_1 State. It is well-known that fluorination of alkyl chains weakens the alkyl-metal interaction, partly because of fluorine-metal repulsion. Nonetheless, the intrinsic Lewis acidity of the Pt(111) surface can promote very weak acceptance of nonbonding electron pairs from the fluorine atom into empty acceptor states near the Fermi level of the surface.⁵ Thiel and co-workers¹⁻⁴ point out that alkyl-metal interactions of methylene groups are complex, with several opposing contributions.¹⁶ The net interaction, while positive, is less for CF_2 groups than for CH_2 groups. For perfluorohexane and perfluoroheptane, the additive effect of the CF_2 groups is enough to produce adsorbed species at these surface temperatures.

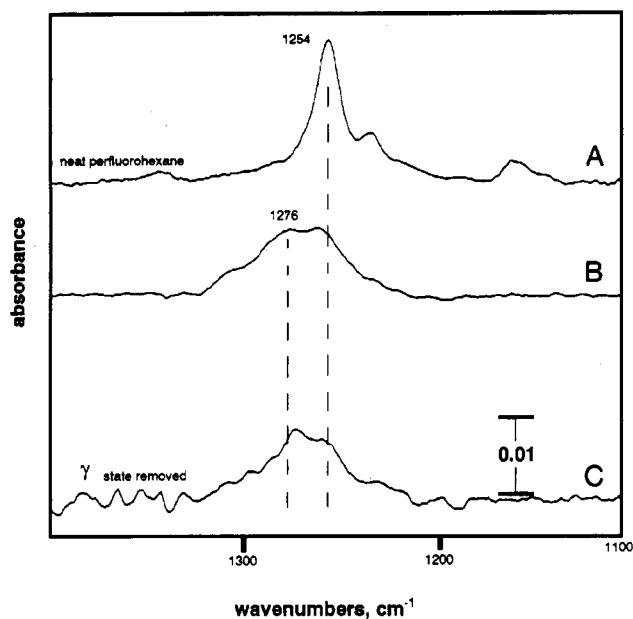


Figure 5. FTIR spectra: (A) transmission infrared spectrum of neat perfluorohexane; (B) IRRAS spectrum of perfluorohexane adsorbed on Pt(111) at 100 K and dose 30 langmuirs; (C) IRRAS spectrum of perfluorohexane as in (B) but after sample was heated to remove the γ condensed layer. (Absorbance calibration is for IRRAS spectra only.)

Adapting the work of Sexton and Hughes¹⁵ and Madey and Yates¹⁷ to this case, the shift to higher desorption energy (ΔH_{des}) with increase in number of CF_2 groups can be described by

$$\Delta H_{\text{des}} = \Delta H_0 + n\Delta H_{\text{CF}} \quad (1)$$

where ΔH_{CF} is the interaction due to n perfluoromethylene groups in the chain and ΔH_0 is the remainder. Taking the difference in ΔH_{des} for perfluoroheptane and perfluorohexane, we find $\Delta H_{\text{CF}} = 1.2$ kcal/mol. If we discount conformational effects, the ΔH_0 term can be ascribed to the methyl groups, and we get a binding energy per methyl group of 3.48 kcal/mol. (It should be noted, however, that more data are required before we feel comfortable with this assignment for ΔH_0 .)

The reported binding energies for CH_2 in ethers and alcohols adsorbed on Pt(111) are in the range 1.2–1.55 kcal/mol.¹⁵ The value we estimate here, 1.2 kcal/mol, is at the lower end of this range, consistent with expectations, but suggests that these perfluoromethylene-metal interactions are perhaps larger than expected.

α_2 State. The TDS data for α_2 show a diminished but still significant shift in desorption temperature for the perfluoroalkanes as a function of size. The ΔH_{des} are 9.82 and 10.75 kcal/mol for perfluorohexane and perfluoroheptane, respectively. This corresponds to a lowered interaction with the surface of approximately 1.5 CF_2 groups. It is not possible, from the present data, to determine the exact configuration of the α_2 state. But, this lower interaction of α_2 with the substrate must be due to a decrease in contact of the molecule with the surface, either through a methyl "heat-on" configuration, puckering of the alkane chain out of the plane of the surface, or tilting as a rigid rod at some angle relative to the normal. In addition to different binding geometries, perfluoroalkanes have two nearly isoenergetic conformations, the anti and twist-anti, which distinguish them from their hydrocarbon analogs.¹⁹ Thus, the α_1 and α_2 surface states could involve different conformers.

IRRAS Spectrum. The IRRAS spectrum in Figure 5C is, according to the surface selection rules,¹¹ evidence that components of perfluoromethylene dipole derivatives are oriented along the surface normal. The dipole derivatives of the antisymmetric CF_2 stretch are in the plane of the triangle formed by the CF_2 ,

indicating that the IRRAS spectrum is probably of the α_1 adlayer. The signal-to-noise ratio of this spectrum is insufficient to resolve features due to the α_2 state, although the width of the IRRAS absorption suggests that some perfluoromethylenes in α_2 may also have their dipole derivatives along the surface normal.

The interaction of hydrocarbons with metal surfaces is usually described in terms of C-H to metal hydrogen bonding, indicative of the early stages of C-H bond activation. The IRRAS absorption peak for the antisymmetric methylene stretch of hexane adsorbed on Pt(111) is approximately 18 wavenumbers lower than for the bulk sample.²⁰ C-F stretches are also highly sensitive to considerable frequency shifts because of interactions with neighboring groups and local environments.¹⁸ The shift in ν_2 to higher frequency for the surface species is not what one would normally expect for C-F bond activation but, rather, may reflect a constrained environment for the CF₂ oscillators. However, differences in coupling of the C-C and C-F motions for surface bonded species may also be sufficient to account for the observed shift.

Conclusion

We have used TDS to find that the adsorption of perfluoroheptane and perfluorohexane on Pt(III) is characterized by two distinct monolayer states, indicating that the behavior of these simple analogs to PPFPO type lubricants is more complicated than expected. In analyzing the TDS data for the state with the highest binding energy (α_1), we find that the interaction of the perfluoromethylene groups of these molecules with the Pt surface may be stronger than previously anticipated. In addition, the state that grows in at higher coverage (α_2) is probably not lying entirely in the plane of the surface but may be tilted or folded up and away from the surface. The shift to higher frequency in IRRAS spectra of ν_2 suggests that the monolayer molecular structure differs from the γ multilayer state. The infrared surface

selection rules and these IRRAS data may also imply that most of the carbon backbone of these molecules lies in the plane of the surface.

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