Infrared Spectroscopic Analysis of Sub-Monolayer Perfluoropolyether Films Based on the $-(\text{CF}_2)_n\text{O}-$ Monomer Unit for $n = 2, 3$ and 4

Robert J. Waltman

HGST/Western Digital Company
5601 Great Oaks Parkway, San Jose, CA 95119-1003, USA

*Corresponding author: Robert.waltman@hgst.com

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Infrared specular reflection spectra of the TA-30, D-4OH and C4-4OH perfluoropolyether liquid films on gold substrates are simulated and studied experimentally. The simulated spectra were obtained using a classical dispersion analysis coupled with solutions of Maxwell's equations for transmission and reflection of electromagnetic radiation. The simulated spectra, which are based on a randomly oriented sample, provide excellent fits for the perfluoropolyethers over a wide film thickness range. Spectroscopic data are provided for TA-30, D-4OH and C4-4OH. The differences in the transverse and longitudinal optical IR spectra are discussed for off-normal reflection spectra in the thin film limit. Corrections to the IR reflection spectra for sub-monolayer coverage using effective medium theory are also discussed.

Keywords: perfluoropolyethers, infrared spectroscopy, specular reflection, boundary lubricants, dispersion analysis, ab initio computational chemistry

1. Introduction

Perfluoropolyether (PFPE) liquids are widely used in technology as vacuum pump fluids [1], hydrodynamic or elastohydrodynamic lubricants in space engineering devices [2], and as boundary lubricants in computer hard-disk drives (HDDs) [3]. In HDD technology, the PFPE is the critical boundary film that dissipates intermittent contact events between the low-flying slider and the rigid disk surface thereby providing tribological robustness [4]. The clearance between the slider read/write element and the disk surface in today's HDDs is a mere 1-2 nm. This exposes the slider/disk interface to large electrostatic and physicochemical forces that act on the boundary lubricant film itself [5]. PFPE designs that incorporate stiffer and shorter main chains can provide increased resistance to these effects [6-8]. For example, removing the $-(\text{CF}_2\text{O})-$ monomer unit in $-(\text{CF}_2\text{O})_p-(\text{CF}_2\text{CF}_2\text{O})_q-$ is one way in which chain flexibility can be reduced. Consequently, PFPEs derived from $-(\text{CF}_2\text{CF}_2\text{O})-$, or $-(\text{CF}_2\text{CF}_2\text{CF}_2\text{O})-$, or $-(\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O})-$ monomer units are increasingly being utilized [9,10].

As alluded to above, the large interfacial forces that act on the PFPE boundary lubricant can create lubricant thickness non-uniformity on the disk surface [11,12]. A local thickness reduction on the disk surface increases the surface energy and can cause increased contamination adsorption from outgassing materials in

the HDD environment [13,14]. Thus in order to assess or monitor the chemical integrity of the PFPE liquids on the rigid disk, suitable analytical tools which are capable of detecting minute physical interactions and chemical changes at interfaces are required. One such tool, infrared spectroscopy, in particular Fourier transform infrared (FTIR), is widely used [15]. Thin film coatings applied on metal surfaces present additional problems for an analysis using infrared spectroscopy. Due to specular reflection from the metal surface complicated optical interference effects render this analysis significantly less straightforward than one utilizing transmission spectroscopy. The interference depends on the film thickness, angle of incidence, polarization of the incoming electric field and the absorption characteristics of the metal substrate and overlaying films. In general, when the film is very thin specular reflection tends to simplify; however, one should not interpret this as a cardinal rule. For example, longitudinal optical (LO) excitations while IR-inactive in the bulk become observable as a result of finite film thickness effects [16].

Specular reflection in the infrared spectral region is completely simulated once the optical constants are known for the metal substrate and coated films. With the optical constants specular reflection spectra may be easily calculated from solutions to Maxwell's equations. Thus, a computer can be used to provide complex

refractive indices over the infrared, and in turn calculate reflection spectra for any film thickness, angle of incidence, or polarization of the incident electric field. In the computer disk industry, specular reflectance infrared spectroscopy is well-utilized to monitor changes in the composition of the disk surface. In order to understand the changes in the reflection spectrum of the disk surface due to contaminants that adsorb onto the disk surface or chemical and physical changes induced in the PFPE boundary lubricant film itself as a result of slider-disk interactions, one must first fully understand the reflection characteristics of the PFPE itself. In order to facilitate the interpretation of such spectra, we investigate herein the infrared spectroscopy of new PFPE lubricants based on the $-\text{[(CF}_2\text{)}_n\text{O]}-$ monomer unit for $n = 2, 3$ and 4, and report their optical constants and oscillator parameters. Thus PFPEs based on the “C2”, “C3” and “C4” monomer units, $-(\text{CF}_2\text{CF}_2\text{O})-$, $-(\text{CF}_2\text{CF}_2\text{CF}_2\text{O})-$ and $-(\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O})-$, respectively, are investigated.

2. Experimental Section

A sample of the C2 lubricant was kindly provided by Asahi Glass Co (Japan) under the tradename TA-30 ($M_n = 3000$). A C3 lubricant was purchased from Moresco (Japan) under the tradename D-4OH ($M_n = 2100$). A C4 sample was kindly provided by Moresco (Japan) under the tradename C4-4OH ($M_n = 2000$). The chemical structures are shown below.

The PFPE samples were applied to gold or sodium chloride substrates by spin coating the liquids from a hydrofluoroether solvent. Sample thicknesses were measured by relating the infrared integrated absorbance of a characteristic absorption band to film thickness. For

refractive index of the PFPE based on the perfluoropropyleneoxide monomer unit, $-[CF(CF_3)CF_2O]-$, has been reported [18]. Therefore, only those details pertinent for this report will be given. In essence, the method treats the polymer as consisting of a collection of Lorentzian oscillators whose band centers, widths and strengths are obtained from a transmission infrared absorption spectrum. The oscillator parameters are then used to compute the complex dielectric function, which in turn is equated to the complex refractive index. These, along with the refractive index of the metal (gold substrate) are combined with the solutions of Maxwell's equations for transmission and reflection of electromagnetic radiation at interfaces.

As an orientation for the optical parameters describing the specular reflection, consider the three layer system as the air-perfluoropolyether-gold system shown in Fig. 2. Hence, the three refractive indices are: $n_1 = 1.0$, for air; for polyperfluoroether,

$$\tilde{n}_2 = n_2 + i\kappa_2 \quad (1)$$

for the gold substrate,

$$\tilde{n}_3 = n_3 + i\kappa_3 \quad (2)$$

In Eqs. 1 and 2, n_2 and n_3 are the real parts of the refractive indices for the polyperfluoroether and gold, respectively, while κ_2 and κ_3 are the imaginary parts, respectively. In the calculations that follow the angle of incidence for the infrared light is maintained at 71° from normal and h is defined as the perfluoropolyether (PFPE) film thickness.

The optical constants for the PFPE were individually related to wavenumber through a dispersion analysis. Since the dispersion analysis is only performed on the PFPE, the subscript 2 will be dropped in the following discussion for the sake of brevity. The refractive index for the PFPE is cast in the form of the dielectric constant as

$$\varepsilon = (\tilde{n}_2)^2 = \varepsilon_r + i\varepsilon_i \quad (3)$$

Fig. 2 Illustration of the three layer system, air-PFPE-gold, used for the dispersion analysis and reflectance calculations

where

$$\varepsilon_r = n^2 - \kappa^2 \quad (4)$$

and

$$\varepsilon_i = 2n\kappa \quad (5)$$

Using Equations (4) and (5), the following expressions for n and κ are obtained.

$$n^2 = \frac{1}{2}(\sqrt{\varepsilon_r^2 + \varepsilon_i^2} + \varepsilon_r) \quad (6)$$

$$\kappa^2 = \frac{1}{2}(\sqrt{\varepsilon_r^2 + \varepsilon_i^2} - \varepsilon_r) \quad (7)$$

The real and imaginary part of the dielectric constant, ε_r and ε_i , were determined using the classical dispersion analysis reported by Spitzer and Kleinman [19] and Schatz and Maeda [20] as given below:

$$\varepsilon_r = \varepsilon_o + \sum_{j=1}^{j=N} 4\pi\rho_j v_j^2 \frac{v_j^2 - v^2}{(v_j^2 - v^2)^2 + \gamma_j^2 v_j^2 v^2} \quad (8)$$

and

$$\varepsilon_i = \sum_{j=1}^{j=N} 4\pi\rho_j v_j^2 \frac{\gamma_j v_j v}{(v_j^2 - v^2)^2 + \gamma_j^2 v_j^2 v^2} \quad (9)$$

where the summation is over the N oscillators in the system; ε_o is the short wavelength dielectric constant; v is the frequency; v_j is the frequency of the j^{th} oscillator; the damping constant, γ_j , is related to the band width at half-height by

$$\gamma_j = \frac{\Delta v_{j(1/2)}}{v_j} \quad (10)$$

and ρ_j is related to the oscillator strength by:

$$\rho_j = \frac{(\tilde{n} A_j)}{4\pi^3 v_j^2} \quad (11)$$

where

$$A_j = \frac{1}{h} \int \ln\left(\frac{T_o}{T}\right) dv \quad (12)$$

$\tilde{n}$ is the mean refractive index, and T_o/T is the inverse of the transmittance. To obtain n and κ it is necessary to have the short wavelength contribution to the dielectric constant, i.e., in this case the electronic contribution, the number of oscillators, their frequency, width and strength.

The short wavelength contribution to the dielectric was taken as the value measured at the $0.6328 \mu\text{m}$ line of a He/Ne laser [21]. The real part of the refractive index for TA-30, D-4OH and C4-4OH at this wavelength were all of them 1.300 ± 0.002 . The refractive index for gold was taken from a Drude model fit [21] using a damping frequency (v_r) of 216 cm^{-1} and a plasma frequency (v_p) of $7.25 \times 10^4 \text{ cm}^{-1}$. Both n_3 and κ_3 were calculated using the following expressions:

$$n_3^2 = \frac{1}{2}(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1) \quad (13)$$

$$\kappa_3^2 = \frac{1}{2}(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1) \quad (14)$$

where

$$\varepsilon_1 = \varepsilon_\infty - \frac{v_p^2}{v^2 + v_r^2} \quad (15)$$

$$\varepsilon_2 = \frac{\nu_p^2 \nu_\tau}{\nu^3 + \nu \nu_\tau^2} \quad (16)$$

$\varepsilon_\infty = 1.0$, and ν is the frequency at which a particular value for the dielectric constant is required.

The process of obtaining a dispersion analysis is, in essence, an iterative process where the integrated absorbance, A_j , the band width at half-height, and the oscillator frequency are obtained using transmission spectra. Subsequently, the spectra are fit to Eqs. 6 and 7. The reflectance in the infrared was calculated following the formalism given by Born and Wolfe [23]. The equations for the reflection coefficients for the components of the electric field parallel and perpendicular to the plane of incidence at interfaces 12 and 23 are well known and can be found in a previous publication [18]. Using these equations, the reflectance spectra may be calculated for any PFPE film thickness and angle of incidence. The experimental reflection IR spectra reported herein are obtained using p-polarized light, and so the calculated reflectance spectra are also p-polarized.

Fig. 3 (a) The experimental reflection infrared spectrum for a 34 Å TA-30 film on Au for p-polarized light with $\theta = 71^\circ$. (b) The experimental transmission infrared spectrum for a 0.060 mm TA-30 film on a NaCl substrate. (c), (d) The B3LYP/6-31G(d) and HF/6-31G(d) computed IR spectra for C2 (the TA-30 model structure $C_{10}F_{22}O_4$) at the half-height bandwidth of 16 cm^{-1} . (e) The corresponding “stick spectrum” of (d). All of the computed IR spectra are uniformly scaled in wavenumber (cm^{-1}) by 0.94 and 0.87 for (c) and (d), respectively, to match the transmission experimental spectrum at 1220 cm^{-1} .

4. Results and Discussion

The experimental transmission and reflection IR spectra for TA-30, D-4OH and C4-4OH are shown in Figs. 3, 4 and 5, respectively. We will first focus on the transmission IR spectra, Figs. 3b, 4b and 5b, since the oscillator parameters used to simulate both the transmission and reflection spectra are derived from these spectra. The corresponding reflectance spectra, Figs. 3a, 4a and 5a, are shown directly above the transmission spectra to highlight their significantly different spectral characteristics compared to the transmission IR spectra. The origin for these differences is discussed later. Referring now to the transmission spectra, the various IR absorption bands from the $-(CF_2)_nO-$ main chain, where $n = 2, 3$ and 4 for TA-30, D-4OH and C4-4OH, respectively, are shown in the $1500\text{--}800 \text{ cm}^{-1}$ “fingerprint” region for the PFPEs. In general the spectra consist of bands for stretching frequencies attributed to C-C, C-F and C-O. The spectra are generally broad, due to the large number of coupled oscillators per PFPE molecule. Since the oscillator parameters derived from the transmission spectrum will be used as the basis for the reflectivity calculations to be shown later, we first provide some qualitative understanding

Fig. 4 (a) The experimental reflection infrared spectrum for a 29 Å D-4OH film on Au for p-polarized light with $\theta = 71^\circ$. (b) The experimental transmission infrared spectrum for a 0.037 mm D-4OH film on a NaCl substrate. (c), (d) The B3LYP/6-31G(d) and HF/6-31G(d) computed IR spectra for C3 (the D-4OH model structure $C_9F_{20}O_2$) at the half-height bandwidth of 16 cm^{-1} . (e) The corresponding “stick spectrum” of (d). All of the computed IR spectra are uniformly scaled in wavenumber (cm^{-1}) by 0.94 and 0.87 for (c) and (d), respectively, to match the transmission experimental spectrum at 1210 cm^{-1} .

Fig. 5 (a) The experimental reflection infrared spectrum for a 22 Å C4-4OH film on Au for p-polarized light with $\theta = 71^\circ$. (b) The experimental transmission infrared spectrum for a 0.42 mm C4-4OH film on a NaCl substrate. (c), (d) The B3LYP/6-31G(d) and HF/6-31G(d) computed IR spectra for C4 (the C4-4OH model structure $C_{12}F_{26}O_2$) at the half-height bandwidth of 16 cm^{-1} . (e) The corresponding “stick spectrum” of (d). All of the computed IR spectra are uniformly scaled in wavenumber (cm^{-1}) by 0.94 and 0.87 for (c) and (d), respectively, to match the transmission experimental spectrum at 1210 cm^{-1} .

of the relationship between the observed transmission IR spectrum and the oscillators that produce the absorption bands. We use the power of ab initio calculations [24] to provide insight into the transmission IR spectrum. The C2, C3 and C4 model structures used to calculate the (transmission) IR spectra are summarized in Fig. 6. The corresponding stoichiometries are $C_{10}F_{22}O_4$, $C_9F_{20}O_2$ and $C_{12}F_{26}O_2$. The model structures contain at least 9 carbon atoms based on balancing computational tractability and reproducibility of the computed to the experimental IR spectrum. The model structures are fully optimized geometries with no computed imaginary frequencies. The characterization data for each model structure is summarized in Table 1. The computed IR spectra for the C2, C3 and C4 model structures are shown in Fig. 3c-e, Fig. 4c-e and Fig. 5c-e, respectively, below each experimental IR spectrum. The bottom-most “stick spectra” highlight all of the computed normal modes in this wavenumber regime for each model structure. Otherwise the ab initio computed IR spectra are presented as a series of Lorentzian oscillators whose band widths at half-height are set equal to 16 cm^{-1} . This appears to reproduce the basic features of each IR spectrum and thus allows credible assignments for the PFPE IR bands. The computed potential energy distributions for these “bands” are summarized in Table 2. The modes with the highest frequencies are due to the symmetric and asymmetric C-C stretching vibrations. While they occur at the higher frequencies, the C-C

Fig. 6 The HF/6-31G(d) optimized geometries for the C2, C3 and C4 model structures

Table 1 Characterization data for the optimized geometries of C2, C3 and C4 PFPE model structures (Fig. 6). NIMAG equals the number of computed imaginary frequencies

Structure (Fig. 6)	Total Energy (Hartree) HF/6-31G(d)	Total Energy (Hartree) B3LYP/6-31G(d)	NIMAG HF, B3LYP
C2 (C ₁₀ F ₂₂ O ₄)	-2865.841672	-2878.426799	0, 0
C3 (C ₉ F ₂₀ O ₂)	-2479.333946	-2490.178037	0, 0
C4 (C ₁₂ F ₂₆ O ₂)	-3189.554741	-3203.514381	0, 0

motions inherently have weak intensities. These peaks are labeled 1 and 2 in Figs. 4 and 5. For TA-30 the C-C motions are coupled to C-F and C-O stretches and are identified as the bands labeled 3 and 4 in Fig. 3. At lower frequencies, the majority of the bands between ~ 1250 and 1000 cm⁻¹ are attributed to C-F and C-O stretching vibrations which are in most cases highly coupled. C2, having the -(CF₂CF₂O)_n monomer unit, shows a strong C-O stretch at 1130 cm⁻¹ (band 5, Fig. 3) In C3 and C4 the intensity of the C-O stretch is weakened due to the larger C/O ratio in the monomer unit (band 6, Fig. 4) and occur more coupled with the C-F stretches (bands 3, 4, and 6, Fig. 4; bands 4, 6, and 7, Fig. 5).

The use of correlated wavefunctions often improves the computed IR spectrum even at the modest 6-31G(d) basis set. This aspect was explored for the C2, C3 and

C4 model structures and the results are shown in Figs. 3c, 4c and 5c. While the correction factor of the normal mode frequencies is greatly reduced from the 0.87 used to correct the HF frequencies to 0.94 for the DFT (density functional theory) frequencies, the computed IR spectra are qualitatively similar after all. Thus the normal modes shown in Table II are assigned based on the HF/6-31G(d) calculations.

Guided by the computed infrared spectra, the film thickness, integrated intensities, band centers and widths were extracted from the experimental transmission spectra of TA-30, D-4OH and C4-4OH. These oscillator data are listed in Tables 3, 4 and 5 for TA-30, D-4OH and C4-4OH, respectively. These data were in turn used to generate the optical constants using the dispersion analysis described herein. The optical constants are shown in Fig. 7. The reflectance IR spectra are then

Table 2 Potential energy distribution (PED) of the major IR bands

Structure Fig. 6	Band # Figs. 3-5	PED
C2	1	C-F str (CF ₃)
	2	C-F str (CF ₃)
	3	C-F str; C-O str; C-C str
	4	C-F str; C-O str; C-C str (C-F str near CO bond)
	5	C-O str
	6	C-F str; C-O str
C3	1	C-C str
	2	C-C str
	3	C-F str (C-F str in CF ₃ + C-F str near CO bond)
	4	C-O str; C-F str (CF ₃)
	5	C-F str (C-F str near CO bond)
	6	C-O str
	7	C-F str; C-O str
	8	C-F str; C-O str; C-C str
	9	C-O str; C-F str
	10	C-O-C bend; C-C-O bend
C4	1	C-C str
	2	C-C str
	3	C-F str (CF ₃)
	4	C-O str; C-F str
	5	C-F str (C-F str near CO bond)
	6	C-O str; C-F str
	7	C-F str; C-O str
	8	C-O-C bend; C-C-O bend

Table 3 Oscillator parameters for a 0.060 μm film of TA-30 (C2)

ν_j Band Center (cm^{-1})	$A_j h$ Integrated Area (cm^{-1})	$\Delta\nu_{j(1/2)}$ Band Width (cm^{-1}) at half-height
1292.0	0.10	33.0
1200.7	6.51	47.0
1144.0	1.56	43.0
1117.0	1.60	41.0

Table 4 Oscillator parameters for a 0.037 μm film of D-4OH (C3)

ν_j Band Center (cm^{-1})	$A_j h$ Integrated Area (cm^{-1})	$\Delta\nu_{j(1/2)}$ Band Width (cm^{-1}) at half-height
1360.0	0.14	29.0
1316.0	0.19	27.0
1254.0	0.050	17.0
1224.0	0.35	24.0
1204.1	1.00	32.0
1151.0	0.88	36.0
1116.5	0.37	24.0
1027.9	0.053	15.0
1010.9	0.11	17.0
994.6	0.054	17.0
977.7	0.054	20.0

Table 5 Oscillator parameters for a 0.42 μm film of C4-4OH (C4)

ν_j Band Center (cm^{-1})	$A_j h$ Integrated Area (cm^{-1})	$\Delta\nu_{j(1/2)}$ Band Width (cm^{-1}) at half-height
1362.0	0.090	23.0
1342.0	0.34	23.0
1314.0	0.60	22.0
1286.0	1.92	30.0
1209.0	15.20	44.0
1191.0	5.20	35.0
1147.5	7.14	25.0
1119.0	2.16	20.6
1098.0	0.35	27.5
1054.0	0.43	28.0
954.0	0.48	28.0
934.0	0.070	18.0
914.0	0.14	18.0
889.0	0.98	28.0
813.0	0.090	20.0
743.5	0.63	55.0
713.0	0.25	13.8
694.0	0.15	18.0

Fig. 7 The real (n_2) and imaginary (k_2) parts of the refractive index for (a), (b) TA-30; (c), (d) D-4OH; and (e), (f) C4-4OH

calculated from the optical constants together with the polynomial fit to n_3 and κ_3 and the reflection formula of Born and Wolf [23]. The quality of the oscillator parameters listed in these tables to generate the optical constants was assessed by first computing the transmission IR spectra from which they were derived. These data are shown in Fig. 8 together with the experimental transmission spectrum at the identical film thickness. The side-by-side comparison indicates an excellent fit between the experimental and simulated transmission IR spectra and indicates that the oscillator parameters derived by this methodology are useful and the data in Tables 3-5 can be used in a general manner.

We now discuss the IR reflection spectra of TA-30, D-4OH and C4-4OH. Figs. 3ab, 4ab and 5ab directly compare the reflection and transmission IR spectra. Qualitatively they are different enough such that the spectra could be misinterpreted as originating from different materials. However, this is not the case. One needs to account for the fact that both transverse optical (TO) and longitudinal optical (LO) excitations are associated with each resonance term in the dielectric function that can be observed in the IR spectra [16,25,26]. When the IR radiation is normal to the sample surface, only TO vibrations are detected due to

the transverse character of the electromagnetic radiation. However, in reflection spectroscopy employing IR radiation at angles off-normal to the surface, both LO and TO surface modes can be excited in the thin film limit [16]. The TO and LO modes are separated in frequency by the Lyddane-Sachs-Teller relation [27] where the LO frequency is shifted to a higher wavenumber from that of the TO frequency by an amount that is approximately proportional to the absorption strength, i.e., the stronger the absorption the greater the shift of the LO frequency.

$$\frac{\nu_{LO}}{\nu_{TO}} = \left(\frac{S_o + \epsilon_o}{\epsilon_o} \right)^{1/2} \quad (17)$$

ν_{LO} and ν_{TO} are the LO and TO frequencies, respectively, and S_o is the absorption strength. One can then begin to understand why the experimental reflection and transmission spectra shown in Figs. 3-5 are so different. Fig. 9 compares the TO and LO energy loss functions that are calculated from the oscillator parameters given in Tables 3-5. The LO spectrum, $\text{Im}(-1/\epsilon)$, is calculated using Eq. 18 [28].

$$\text{Im}(-1/\epsilon) = \frac{\epsilon_i}{(\epsilon_i^2 + \epsilon_r^2)} \quad (18)$$

Fig. 8 The experimental and calculated transmission spectra for 0.060 mm TA-30, 0.037 mm D-4OH and 0.42 mm C4-4OH films on NaCl. The calculated spectrum is derived from the oscillator parameters specified in Tables 3-5

Fig. 9 The calculated LO ($\text{Im}(-1/\epsilon)$) and TO ($\text{Im}(\epsilon)$) spectra for TA-30, D-4OH and C4-4OH. All spectra are normalized to 1 (y-axis) for ease of viewing

For the reflection IR spectra, the incident infrared radiation for both simulated and observed cases is p-polarized with an angle of incidence equal to 71° . The experimental reflection spectrum (Figs. 3-5) contains an appreciable contribution from the LO vibrations.

Observed and computed specular reflection spectra are now discussed in Figs. 10-12 for TA-30, D-4OH and C4-4OH, respectively, as a function of film thickness between approximately 1 and 34 Å. This thickness range covers the actual film thicknesses typically used in hard-disk drives (HDDs). The monolayer thicknesses for TA-30, D-4OH and C4-4OH are 19, 18 and 16 Å, respectively [29,30]. Sub-monolayer film thicknesses are therefore included in this analysis. All of the experimental spectra were recorded using gold as the substrate. As shown by the results, excellent agreement between the observed and simulated reflectance IR spectra is qualitatively obtained for all PFPEs with one exception. In the experimental spectra, the band center of the main absorption band at 1270 cm^{-1} for TA-30, 1240 cm^{-1} for D-4OH, and 1250 cm^{-1} for C4-4OH, is

observed to shift to a lower wavenumber (cm^{-1}) with decreasing film thickness, Fig. 13. This experimental feature is not reproduced in the simulated reflectance spectra for these ultra-thin films. The shift in the band center with decreasing film thickness is experimentally observed for film thicknesses below approximately 15 Å for TA-30, and 11 Å for both D-4OH and C4-4OH, Fig. 13. The dispersive surface energy as a function of thickness is often used as an indicator for PFPE film coverage of the underlying substrate [31]. The asymptotic value in the dispersive surface energy is taken as an indication for full surface coverage. The dispersive surface energy versus PFPE film thickness on carbon films (not gold) is shown in Fig. 13 for TA-30, D-4OH and C4-4OH. Using the definition described above, the asymptotic value of the dispersive surface energies are approximately near 15 Å for TA-30, D-4OH and C4-4OH. We suggest that the shift in the IR band center originates from PFPE surface coverage effects. This band shift may be reproduced in the calculated reflection IR spectra by correcting the

Fig. 10 Plots comparing the experimental and calculated specular reflection infrared spectra of TA-30 on gold as a function of film thickness for p-polarized light at $\theta = 71^\circ$. The experimental film thicknesses in figure (a) are: 1.6, 3.1, 3.7, 5.0, 6.5, 8.6, 10.7, 13.4, 14.8, 19.7, 21.7, 27.2, 33.8 Å in increasing reflectivity. The calculated reflection spectra are shown in figure (b) at the identical experimental film thicknesses (black traces). The calculated reflectance spectra corrected via EMT (effective medium theory) are shown in the blue traces. The fractional coverage used to match the band center was 0.57, 0.66, 0.70, 0.75, 0.80, 0.85, 0.91, 0.96 and 0.98 for the 1.6, 3.1, 3.7, 5.0, 6.5, 8.6, 10.7, 13.4, 14.8 Å films, respectively

Fig. 11 Plots comparing the experimental and calculated specular reflection infrared spectra of D-4OH on gold as a function of film thickness for p-polarized light at $\theta = 71^\circ$. The experimental film thicknesses in figure (a) are: 0.7, 1.2, 2.1, 5.2, 7.8, 9.8, 11.4, 14.0, 17.3, 29.0 Å in increasing reflectivity. The calculated reflection spectra are shown in figure (b) at the identical experimental film thicknesses (black traces). The calculated reflectance spectra corrected via EMT (effective medium theory) are shown in the blue traces. The fractional coverage used to match the band center was 0.35, 0.37, 0.47, 0.68, 0.84 and 0.99 for the 0.7, 1.2, 2.1, 5.2, 7.8, 9.8 Å films, respectively

Fig. 12 Plots comparing the experimental and calculated specular reflection infrared spectra of C4-4OH on gold as a function of film thickness for p-polarized light at $\theta = 71^\circ$. The experimental film thicknesses in figure (a) are: 4.1, 5.4, 6.8, 7.9, 11.2, 14.0, 17.6, 22.1 Å in increasing reflectivity. The calculated reflection spectra are shown in figure (b) at the identical experimental film thicknesses (black traces). The calculated reflectance spectra corrected via EMT (effective medium theory) are shown in the blue traces. The fractional coverage used to match the band center was 0.75, 0.78, 0.88 and 0.89 for the 4.1, 5.4, 6.8, 7.9 Å films respectively

computed dielectric constant as a function of wavenumber using the effective medium theory (EMT). EMTs describe randomly mixed composites in terms of a spatially homogeneous electromagnetic response. Assuming an increasingly “patchy coverage” with decreasing PFPE film thickness below the monolayer thickness, the averaging effects in the dielectric constant as a function of wavenumber are simulated by mixing the refractive indexes for air and each PFPE. Here we employ the “power law” approximation [32]:

$$\epsilon_{\text{eff}}^\alpha = \sum_{i=1}^N f_i \epsilon_i^\alpha \quad (19)$$

$\epsilon_{\text{eff}}^\alpha$, f_i , and ϵ_i are the effective dielectric constant of the composite, volume fraction, and the dielectric constant of the i^{th} phase. In our calculations, we have chosen to use $\alpha = 1/2$ for no reason other than to demonstrate that the band center shift could be corrected using an EMT treatment. The value of α is related to the geometry of the scatterers where $\alpha = 1/2$ is attributed to cylindrical shaped scatterers [32]. The power law is used here since it can be applied to both dilute and dense mixture composites and is appropriate for the thickness range covered in these studies [33]. The result of applying the EMT to the calculated reflection spectra below full surface coverage is shown in Figs. 10-12. Fractional coverage values were iteratively assigned until the computed band center converged to the experimental band center for each experimental film thickness. Note the shift in the band center to lower wavenumbers with decreasing film thickness. The fractional coverage required to simulate the experimental reflection spectrum is plotted in Fig. 13. The plot is correlated to the band center shift and the changes in the dispersive surface energy.

Fig. 13 Plots comparing the changes in the (top) band centers, (middle) fractional coverage via effective medium theory, and (bottom) dispersive surface energy, as a function of the PFPE film thicknesses for (a) TA-30; (b) D-4OH; and (c) C4-4OH

5. Conclusions

This study reports useful spectroscopic data for the TA-30, D-4OH and C4-4OH perfluoropolyethers. The oscillator parameters reported herein can be used to calculate reflection spectra for any film thickness and any angle of incidence. We have shown that reflection and transmission spectra do not necessarily match since LO excitations are possible in the thin film limit of off-normal reflection spectroscopy. In the sub-monolayer film thickness regime, the reflection IR spectrum is further complicated by “patchy coverage”. This could be corrected by using effective medium theory and treating the composite film dielectric constant as deriving from a film/air mixture.

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