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# High resolution electron energy loss spectroscopy study of Fomblin Z-tetraol thin films\*

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High resolution electron energy loss spectroscopy has been used to obtain vibrational spectra of Fomblin Z-tetraol lubricant films on a commercial magnetic hard disk. The energy loss intensities of the  $\nu(\text{CF}_2)$  stretching mode are roughly independent of scattering angle up to angles of  $\Delta\theta < 14^\circ$  indicating that they are excited by impact scattering. As a consequence there is little information that can be gleaned from the spectra about molecular orientation on the surface. A negative ion resonance enhances the energy loss cross section of the  $\nu(\text{CF}_2)$  stretching mode at the impact energy of  $E_1=4$  eV. It is possible that this resonance is associated with the known sensitivity of fluorocarbons to electron induced dissociation. Annealing the disk sample to  $T=700$  K causes a dramatic decrease in the intensity of C–F stretching modes and an increase of the loss features due to C–H stretching. This indicates that the Fomblin Z-tetraol has decomposed and is exposing the  $\alpha\text{-CH}_x$  overcoat on the magnetic media surface. © 2005 American Vacuum Society. [DOI: 10.1116/1.1861052]

## I. INTRODUCTION

Perfluoropolyalkylether (PFPE) thin films have been used for years as lubricants on the surfaces of magnetic data storage hard disks as a result of their high thermal stability, low viscosity and low vapor pressure.<sup>1–3</sup> One such PFPE lubricant is tetrahydroxy PFPE, or Fomblin Z-tetraol which is a random co-polymer having the following formula:



Such PFPEs typically have molecular weights in the range 2000–8000 amu corresponding to chain lengths on the order of 50–200 atoms. Thus the chain length is in the range 50–200 Å while the chain diameter is roughly 7 Å. The PFPE lubricant films on disk surfaces are 10–20 Å thick and so the PFPE chain must be oriented roughly parallel to the surface. Little spectroscopic data exist, however, to probe the structure and orientation of PFPE molecules on disk surfaces.

Vibrational spectroscopy has often been used as a tool for probing the orientations of molecules adsorbed on single crystalline surfaces.<sup>4</sup> In order to probe the structure and chemistry of PFPE lubricant films on hard disk surfaces, we have obtained high resolution electron energy loss spectra (HREELS) of Fomblin Z-tetraol films on a hard disk surface. HREELS provides vibrational spectra of adsorbed molecules. Although Fourier transform infrared (FTIR) is commonly used to measure the thicknesses of PFPE films on disk surfaces,<sup>5</sup> HREELS offers several potential advantages over FTIR spectra. HREELS allows one to obtain vibrational

spectra over a much wider frequency range (100–4000  $\text{cm}^{-1}$ ) than FTIR which cannot easily reach the frequency range below 800  $\text{cm}^{-1}$ . Thus HREELS allows one to observe the low frequency modes of the adsorbed PFPEs. In addition, HREELS does not require that one obtain a background spectrum as is commonly needed in FTIR measurements. This makes it relatively easy to observe changes to the PFPE film induced by heating. Finally, the impact scattering mechanism of HREELS makes it possible to detect modes that cannot be observed using FTIR due to the dipole-selection rules.<sup>4</sup> Taking advantage of these properties of HREELS, we have obtained the complete vibrational spectrum of Fomblin Z-tetraol lubricant thin films on a hard disk surface.

There have been several studies of PFPE films that have used vibrational spectroscopy. FTIR is commonly used as a means of calibrating the thickness of PFPE films dip coated onto disk surfaces. FTIR measurements of Fomblin Zdol ( $\text{R}=\text{CH}_2\text{OH}$ ) films have been obtained in order to study the effects of dc electric fields that may be present at the head-disk interface.<sup>5</sup> After exposing the thin film of Fomblin Zdol to electric fields of  $3\text{--}6 \times 10^4$  V/cm a new absorption band appeared in the frequency range 1640–1720  $\text{cm}^{-1}$ . This was attributed to C=O, suggesting that the lubricant degraded in the presence of the strong electric field. A previous HREELS study by Montei and Kordesch reported the vibrational spectra of Fomblin Y  $[\text{CF}_3\text{-OCF}_2\text{CF}(\text{CF}_3)]_m\text{-(OCF}_2)_n\text{-OCF}_3$  with  $m/n \sim 100$ ) and Fomblin Z ( $\text{CF}_3\text{-(OCF}_2\text{CF}_2)_m\text{-(OCF}_2)_n\text{-OCF}_3$  with  $m/n \sim 1$ ) that had been vapor deposited onto a polycrystalline Mo surface.<sup>6,7</sup> They were able to identify the  $\nu(\text{CF}_3)$  and  $\nu(\text{CF}_2)$  stretch modes as the most intense features in the spectrum.

Another study quite relevant to this work is that of Akavoor *et al.* who used HREELS to obtain vibrational spec-

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tra from thin films of polytetrafluoroethylene (PTFE) rubbed onto a gold substrate.<sup>8,9</sup> The spectra obtained in that study are quite similar to those reported for PFPE films in this article but were obtained with higher resolution. That work suggested that the modes were excited by dipole scattering. Furthermore, because the PTFE films were oriented as a result of their application by rubbing, orientational effects were observable in HREEL spectra taken along different directions.

In this work, HREEL spectra of Fomblin Z-tetraol have been obtained from a commercial hard disk surface. The disk surface is coated with a thin film of amorphous hydrogenated carbon ( $a\text{-CH}_x$ ) that was deposited on the hard disk surfaces prior to deposition of the lubricant film. HREEL spectra have been obtained as a function of scattering geometry, incident beam energy and surface temperature in order to explore the scattering mechanism, molecular orientation and the effect of heating on the lubricant surface chemistry.

## II. EXPERIMENT

All experiments were performed in an UHV chamber with a base pressure of  $1 \times 10^{-9}$  Torr. The UHV chamber was equipped with an LK ELS3000 HREEL spectrometer and an UHV sample manipulator that allowed heating and cooling of the sample over a temperature range of  $T=100\text{--}1000$  K. Magnetic hard disk platters coated with amorphous hydrogenated carbon ( $a\text{-CH}_x$ ) and a 12-Å-thick film of Fomblin Z-tetraol (nominal MW=2000) were provided by Seagate Technology, Inc. These platters were punched out to create 12.5-mm-diam disk samples. The disk samples were bolted to a Ta plate which was mounted to the UHV sample manipulator and inserted into the chamber. The chamber bake-out was omitted to avoid any desorption or decomposition of the lubricant film.

The vibrational spectra were obtained using the LK ELS3000 HREEL spectrometer. Each spectrum was collected with a dwell time of 2 s/channel and an incident beam energy in the range  $E_1=3\text{--}9$  eV. In the specular scattering geometry, the incident and analysis angles were  $60^\circ$  from the surface normal. The highest resolution achieved was  $\Delta E=5$  meV ( $40\text{ cm}^{-1}$ ). Unless otherwise noted, all the spectra were taken at a sample temperature of 300 K. The effects of sample temperature were studied by heating the sample to temperatures up to 700 K for periods of 30 s and then cooling the sample back to 300 K before taking the HREEL spectrum.

## III. RESULTS AND DISCUSSION

### A. Energy loss mechanism

In principle, the vibrational spectrum of an oligomer such as Fomblin Z-tetraol is complicated by the fact that the molecule has many modes and the fact that it is polydisperse. Nonetheless, the HREEL spectra illustrated in Fig. 1 reveal a number of distinct energy loss features that can be assigned to distinct molecular motions. The most thorough attempt to assign the vibrational spectrum of perfluoropolyethers has

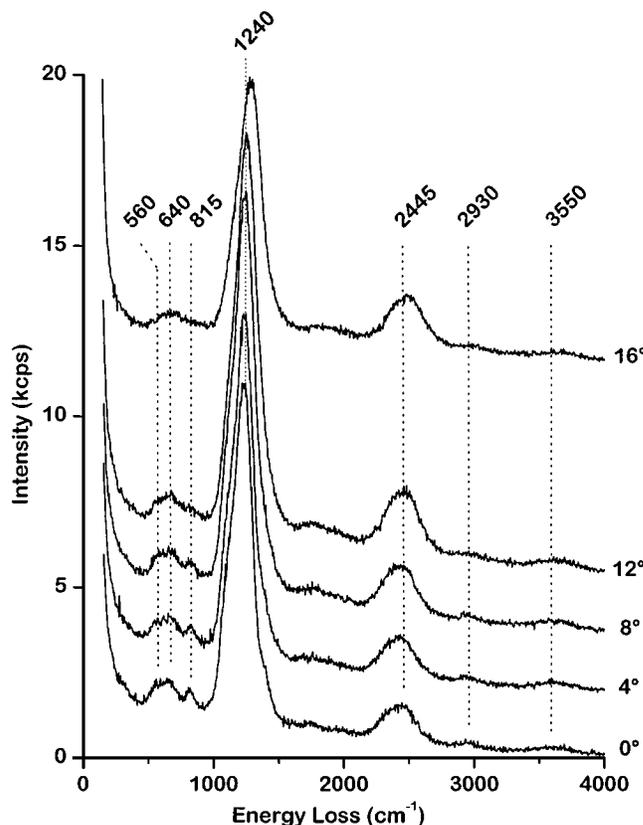


FIG. 1. HREEL spectra of Fomblin Z-tetraol at scattering angles,  $\Delta\theta = \theta_1 - \theta_2$ , in the range  $\Delta\theta=0\text{--}16^\circ$ . The spectra have been offset from one another for clarity. The vibrational mode assignments are given in Table I.  $E_1 = 6.0$  eV.

been made by Pacansky *et al.* who compared the results of electronic structure calculations with the vibrational frequencies and intensities measured by infrared absorption.<sup>10</sup> The assignments of the vibrational modes observed in the spectrum obtained at the specular scattering angle,  $\Delta\theta=0^\circ$ , are summarized in Table I. These assignments were made based on comparison with previous HREELS measurements of Fomblin Z and Fomblin Y deposited on polycrystalline Mo,<sup>6,7</sup> the gas phase spectrum of  $\text{CF}_3\text{CH}_2\text{OH}$ <sup>11</sup> and the results of Pacansky *et al.*<sup>10</sup> Our HREEL spectrum is quite similar to their infrared absorption spectrum of Fomblin Z which has the structure



The modes at 560 and  $640\text{ cm}^{-1}$  are attributed to the  $\text{CF}_2$  deformation motions.<sup>10</sup> The mode at  $815\text{ cm}^{-1}$  is probably due to the  $\nu(\text{CO})$  stretch as assigned in the HREEL spectrum of Fomblin Z at  $840\text{ cm}^{-1}$  by Montei and Kordesch.<sup>6</sup> The symmetric and asymmetric  $\nu(\text{CF}_2)$  stretching modes are observed in an unresolved feature at  $1240\text{ cm}^{-1}$  and as an overtone at  $2445\text{ cm}^{-1}$ . Finally, there are weak signals at 2930 and  $3550\text{ cm}^{-1}$ , corresponding to  $\nu(\text{C-H})$  and  $\nu(\text{O-H})$  stretching modes, respectively.

TABLE I. Vibrational modes and frequencies of Fomblin Z-tetraol ( $\text{cm}^{-1}$ ).

| Mode                  | Fomblin Z-tetraol<br>300 K | Fomblin Z/Mo<br>300 K <sup>a</sup> | Fomblin<br>Y/Mo<br>300 K <sup>b</sup> | Fomblin Z<br>IR <sup>c</sup> | CF <sub>3</sub> CH <sub>2</sub> OH<br>IR <sup>d</sup> |
|-----------------------|----------------------------|------------------------------------|---------------------------------------|------------------------------|---|
| $\delta(\text{CF}_2)$ | 560                        | 560                                | 544 (CF <sub>3</sub> )                | 530                          | 546 (CF <sub>3</sub> )                                |
| $\delta(\text{CF}_2)$ | 640                        |                                    |                                       | 680                          | 660 (CF <sub>3</sub> )                                |
| $\nu(\text{CO})$      | 815                        | 840                                |                                       | 830                          |   |
| $\nu_s(\text{CF}_2)$  | 1240                       | 1232                               | 1256                                  | 1050–1200                    | 1195  |
| $2\nu_s(\text{CF}_2)$ | 2445                       | 2432                               | 2512                                  |                              |   |
| $\nu_s(\text{CH})$    | 2930                       | 2912                               |                                       |                              | 2977  |
| $\nu_s(\text{CH})$    | 3025 (700 K)               |                                    |                                       |                              | 3012  |
| $\nu(\text{OH})$      | 3550                       |                                    |                                       |                              |   |

<sup>a</sup>Reference 6.<sup>b</sup>Reference 7.<sup>c</sup>Reference 10.<sup>d</sup>Reference 11.

HREEL scattering can occur by either dipole or impact scattering mechanisms. Modes that are excited by dipole scattering have intensities that obey the dipole selection rule and thus can be used to provide orientational information about the adsorbed molecule.<sup>4</sup> Impact and dipole scattering cross sections have different dependence on scattering geometry and the scattering mechanism of a given mode can be determined by examining the dependence of its loss intensity on scattering angle,  $\Delta\theta$ . The cross section for dipole scattering is peaked sharply about the specular scattering direction, whereas, the intensities of modes excited by impact scattering are only weakly dependent on scattering angle. Figure 1 shows spectra taken at an incident beam energy of  $E_1 = 6$  eV and scattering angles in the range  $\Delta\theta = 0$ – $16^\circ$ . For the most part, the loss intensities do not appear to depend strongly on scattering angle. Figure 2 presents the dependence of the elastic peak intensity on scattering angle. On well-defined surfaces such as those of single crystalline metals, one would expect the elastic peak intensity to decay very rapidly. For example, on the W(100) surface modified by the adsorption of hydrogen atoms the elastic peak drops to 10% of its specular intensity at  $\Delta\theta \approx 5^\circ$ .<sup>12</sup> On the hard disk surface the intensity appears to decrease linearly and fairly slowly with  $\Delta\theta$ , falling to 10% of the specular intensity at  $\Delta\theta \approx 18^\circ$ . This slow decay of the elastic peak intensity may arise from the disordered nature of the PFPE film on the surface. It is not likely to arise from overall surface roughness since the hard disk surfaces are prepared to have roughnesses of  $< 5$  Å rms and are as flat or flatter than most single crystalline metal surfaces.

The energy loss mechanism of specific vibrational modes is determined by examining the dependence of their intensity on scattering angle and comparing that to the dependence of the elastic peak intensity on scattering angle. Figure 3 shows the absolute intensities of the  $\nu(\text{CF}_2)$  stretching modes, the  $\text{CF}_2$  deformation, and the C–O stretch plotted as a function of scattering angle. The intensities of all these modes are only weakly dependent on scattering angle up to  $\Delta\theta \approx 14^\circ$  and certainly do not exhibit the linear decay of intensity displayed by the elastic peak. The only interesting feature is

the apparent rise in the intensity at scattering angles of  $\sim 8^\circ$ – $12^\circ$  of the peak at  $1245 \text{ cm}^{-1}$  and its overtone at  $2440 \text{ cm}^{-1}$ . The origin of this is not clear. The conclusions drawn from the dependence of loss intensities on scattering angle is that the modes observed in these spectra are excited by impact scattering. Unfortunately, this precludes the use of these modes as probes of the molecular orientation on the surface.

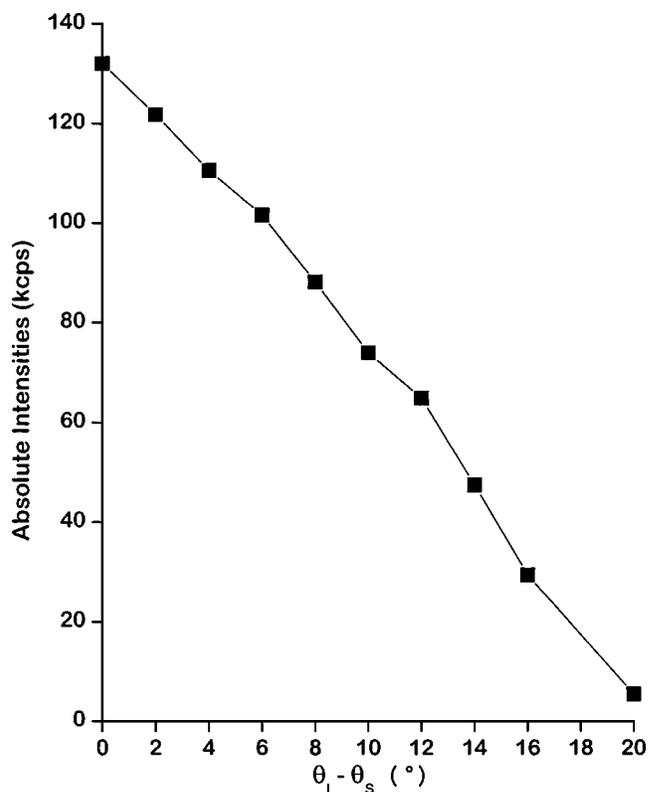


Fig. 2. Absolute intensity of the elastically scattered peak as a function of scattering angle,  $\Delta\theta$ . The intensity decreases roughly linearly with  $\Delta\theta$ . The decrease in the elastic peak intensity is slower than usually observed from single crystal surfaces.

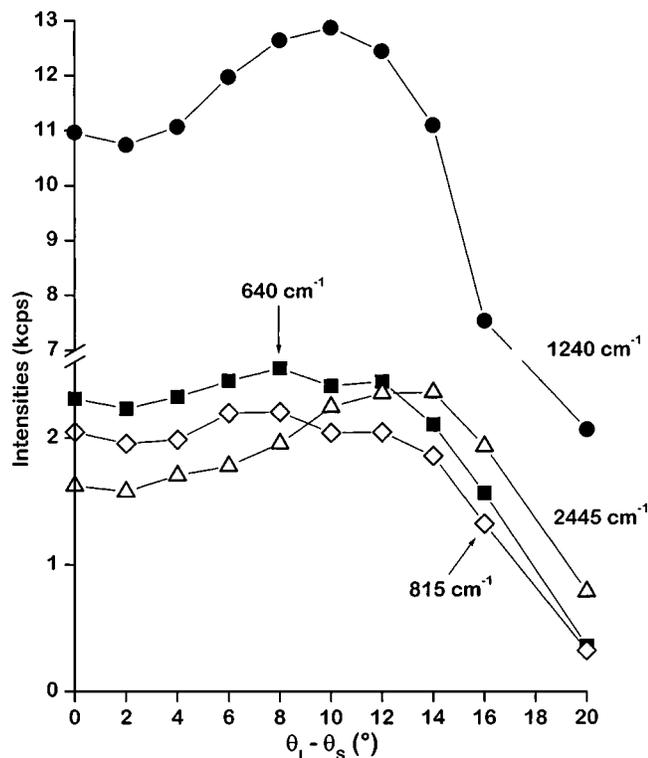


FIG. 3. Absolute intensities of the  $\nu(\text{CF}_2)$  (at  $1240\text{ cm}^{-1}$ ),  $2\nu(\text{CF}_2)$  ( $2445\text{ cm}^{-1}$ ),  $\nu(\text{CO})$  ( $815\text{ cm}^{-1}$ ) and  $\delta(\text{CF}_2)$  ( $640\text{ cm}^{-1}$ ) modes observed for Fomblin Z-tetraol as a function of  $\Delta\theta$ . The intensities are roughly independent of scattering angle for  $\Delta\theta < 14^\circ$  indicating that they are due to impact scattering.  $E_i = 6.0\text{ eV}$ .

It is worth noting that our conclusion that the modes in our HREEL spectra are predominantly impact scattered differs from the conclusions of Akavoor *et al.* derived from their HREELS study of PTFE films on gold.<sup>8,9</sup> The origin of the difference is not clear. It is likely that the disorder in our system is much higher than in the PTFE films as the PFPEs are liquid films.

## B. Energy dependence of the HREEL intensity

The dependence of vibrational energy loss intensities on incident beam energy,  $E_i$ , can be used to probe various adsorbate properties. For the dipole scattering mechanism, theory predicts that the energy loss cross section should decrease with increasing incident beam energy  $E_i$ , whereas, for impact scattered modes the excitation efficiency increases as  $E_i$  increases.<sup>4</sup> In reality the energy dependence of energy loss cross sections can be more complicated functions of energy. HREEL spectra of Fomblin Z-tetraol were obtained with  $E_i = 3\text{--}9\text{ eV}$  at  $300\text{ K}$  (Fig. 4). For the most part, the intensities of the modes are independent of incident beam energy. The most distinct feature is that the intensity of the  $\nu(\text{CO})$  stretching mode at  $815\text{ cm}^{-1}$  grows with incident beam energy suggesting that it arises from impact scattering.

The relative intensities ( $I_{\text{loss}}/I_{\text{elas}}$ ) of some peaks in the spectra are plotted as a function of the incident beam energy in Fig. 5. One interesting observation is that the relative intensity of the  $\nu(\text{CF}_2)$  stretching mode at  $1240\text{ cm}^{-1}$  and its

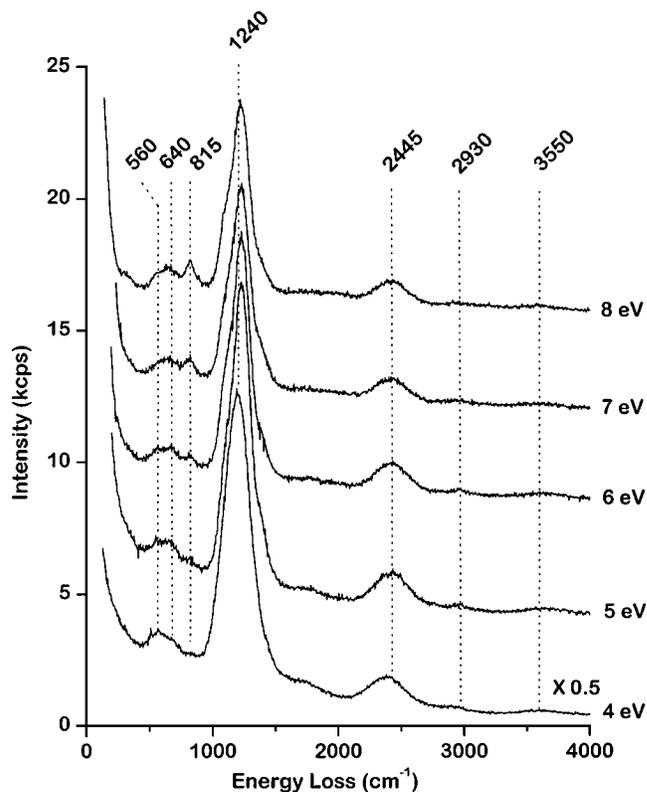


FIG. 4. HREEL spectra of Fomblin Z-tetraol with varying impact energy,  $E_i$ . The  $\nu(\text{CF}_2)$  stretching mode at  $1240\text{ cm}^{-1}$  and its overtone at  $2445\text{ cm}^{-1}$  are selectively enhanced by anion resonance at  $E_i = 4.0\text{ eV}$ .

overtone at  $2445\text{ cm}^{-1}$  are enhanced at an incident energy of  $E_i = 4.0\text{ eV}$ , suggesting the formation of a negative ion resonance at this energy. This phenomenon is well known in HREELS studies of adsorbed molecules<sup>13</sup> and in electron scattering from gas phase atoms and molecules.<sup>14,15</sup> At certain beam energies, an incident electron is temporarily trapped in an unoccupied orbital of the target molecule to form negative ion states with lifetimes on the order of  $10^{-14}\text{--}10^{-12}\text{ s}$ . This results in an enhancement in the excitation cross sections of specific, symmetry-allowed vibrational modes.<sup>16</sup> Previous studies have shown that temporary negative ion resonance scattering plays a major role in electron scattering from polymer films.<sup>17,18</sup> Perfluoroalkanes have been shown to possess temporary anion states.<sup>15</sup> Electron transmission spectroscopy studies yield energies in the range of  $1.2\text{--}4.6\text{ eV}$  for the lowest energy anion states of  $\text{C}_n\text{F}_{2n+2}$  with  $n = 2\text{--}6$ . The exact incident beam in our HREEL spectrometer is not known and would require knowledge of the difference between the spectrometer work function and the work function of the disk surface. Nonetheless, the energy range of the apparent resonance that we observe is consistent with the energy range observed for the anion resonances in perfluoroalkanes.

The observation of the anion resonance at  $E_i = 4\text{ eV}$  may have important implications for the electron induced decomposition of PFPE lubricants on hard disk surfaces.<sup>19</sup> Electron induced dissociation was studied by Lin, Bhatia, and Yates<sup>19</sup> by irradiating disk surfaces with electrons having energies up

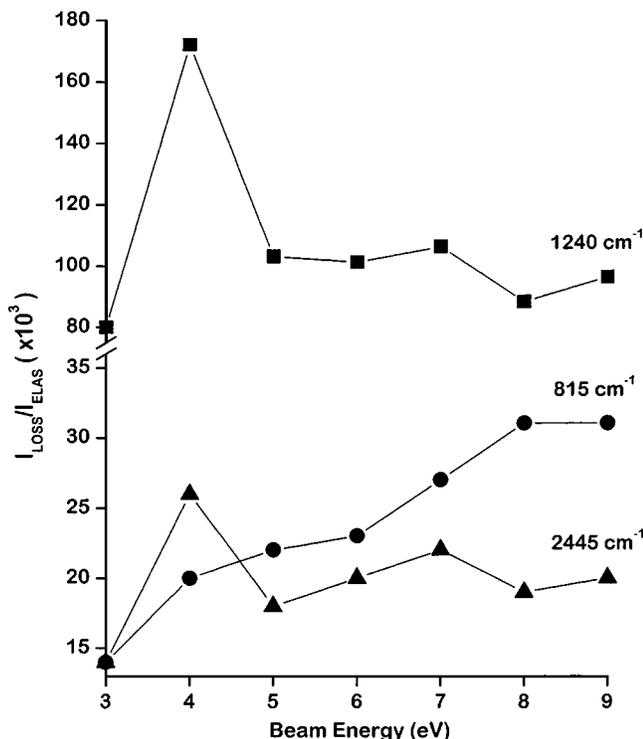


FIG. 5. Relative intensities ( $I_{\text{loss}}/I_{\text{elas}}$ ) of the  $\nu(\text{CF}_2)$  and the  $\nu(\text{CO})$  stretching modes as a function of the incident beam energy,  $E_i$ . The intensity of the  $\nu(\text{CF}_2)$  stretching modes increase at  $E_i=4.0$  eV suggesting the existence of a negative ion resonance. The intensity of the  $\nu(\text{CO})$  stretching mode at  $815\text{ cm}^{-1}$  increases with  $E_i$  characteristic of the impact scattering mechanism.

to 20 eV. They observed that the cross section for dissociative electron impact was highest at energies above the ionization potential of the PFPEs ( $\sim 14$  eV), decreased with decreasing electron energy, and then appears to increase again at low energies. They suggested that an anion resonance in which the electron attaches to the PFPE in an unoccupied anti-bonding state might be responsible for the enhanced dissociative electron impact at low energies. Our observation of an anion resonance at  $E_i=4$  eV is consistent with that suggestion and the observation of electron induced dissociation.

### C. HREELS of Fomblin Z-tetraol annealed to different temperatures

As the last part of this study, we have investigated the thermal decomposition of Fomblin Z-tetraol by obtaining HREEL spectra of the disk surface following annealing at temperatures in the range 100–700 K (Fig. 6). One spectrum was obtained with the sample held at 100 K. The remaining spectra were obtained at 300 K after annealing the sample at the temperatures indicated for periods of 30 s. The Fomblins are known to be chemically stable on hard disk surfaces at room temperature and below although it is possible that their conformations on the surfaces may be temperature dependent. In principle, the spectra obtained at 100 and at 300 K might exhibit different loss intensities, if the orientation of the adsorbed Fomblin Z-tetraol was temperature dependent. The HREEL spectra at 100 and 300 K are, however, almost

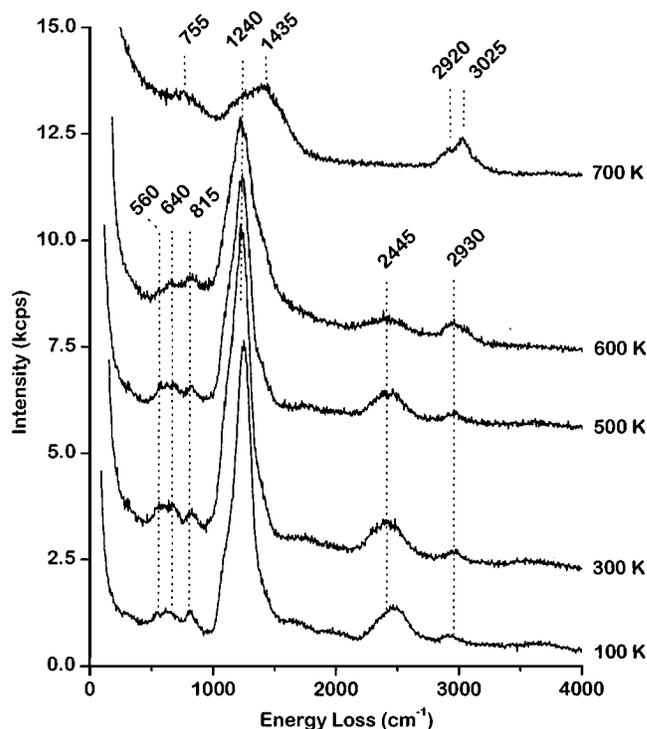


FIG. 6. HREEL spectra of Fomblin Z-tetraol obtained after annealing to temperatures in the range 100–700 K. The intensities of the  $\nu(\text{CF}_2)$  stretching mode at  $1240\text{ cm}^{-1}$  and its overtone at  $2445\text{ cm}^{-1}$  drop dramatically after annealing to 700 K. Most of the Fomblin Z-tetraol lubricant film decomposes during heating to 700 K exposing the  $\alpha\text{-CH}_x$  overcoat.

identical. This may be due to the fact that the modes are predominantly impact scattered and thus their electron energy loss cross sections are not dependent on orientation. It might also arise from the fact that these molecules are likely to be quite disordered on these surfaces. There are no significant changes in the spectra after heating to 500 K. After heating to 600 K, however, the intensities of the  $\nu(\text{CF}_2)$  stretching mode at  $1240\text{ cm}^{-1}$  and its overtone at  $2445\text{ cm}^{-1}$  begin to decrease significantly. At the same time, the intensities of the  $\nu(\text{CH})$  stretching modes at  $\sim 2930\text{ cm}^{-1}$  increase and all signal from the  $\nu(\text{OH})$  stretch disappears. After annealing at 700 K the intensity of the  $\nu(\text{CF}_2)$  stretching mode at  $1240\text{ cm}^{-1}$  drops dramatically and its overtone at  $2445\text{ cm}^{-1}$  disappears completely, indicating the loss of most of the C–F bonds at the surface.

Meanwhile, the  $\nu(\text{CH})$  stretching mode at  $2930\text{ cm}^{-1}$  splits into peaks at  $2920$  and  $3025\text{ cm}^{-1}$ , corresponding to symmetric and anti-symmetric  $\nu(\text{CH}_x)$  stretching modes, respectively. This suggests that heating to 700 K has resulted in substantial loss of Fomblin Z-tetraol and exposure of the  $\alpha\text{-CH}_x$  layer below. Previous temperature programmed desorption studies of Fomblin Z-dol have observed fluorocarbon fragments desorbing from the surface over the temperature range 600–750 K.<sup>19,20</sup> Our HREEL spectra of the surface after heating to these temperatures are consistent with those studies in suggesting that this is the temperature range in which Fomblin decomposition occurs.

#### IV. CONCLUSIONS

HREEL spectra of Fomblin Z-tetraol lubricant films on magnetic data storage media have been presented in this article. The angle dependent studies reveal that impact scattering is the principal energy loss mechanism for most of the modes observed. Unfortunately, this precludes use of the dipole selection rule as a means for probing the orientation of PFPEs such as Fomblin Z-tetraol on the surface. The  $\nu(\text{CF}_2)$  stretching mode shows an enhancement in electron energy loss cross section at an incident electron energy of  $E_1 = 4$  eV suggesting the existence of a negative ion resonance. This anion resonance may be the reason for the enhanced electron induced decomposition observed for PFPEs on hard disk surfaces.<sup>19</sup> Upon annealing to 700 K, the intensities of the  $\nu(\text{CF}_2)$  and the  $\nu(\text{OH})$  stretching modes drop dramatically while the intensity of the  $\nu(\text{CH}_x)$  stretching modes grow suggesting that heating to 700 K results in significant loss of the Fomblin Z-tetraol lubricant film and exposure of the  $\alpha\text{-CH}_x$  overcoat.

#### ACKNOWLEDGMENTS

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