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Polymer dynamics near the surface and in the bulk of poly(tetrafluoroethylene) probed by zero-field muon-spin-relaxation spectroscopy

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The results of many experiments on polymers such as polystyrene indicate that the polymer chains near a free surface exhibit enhanced dynamics when compared with the bulk. We have investigated whether this is the case for poly(tetrafluoroethylene) (PTFE) by using zero-field muon-spin-relaxation spectroscopy to characterize a local probe, the F–Mu$^+$–F state, which forms when spin-polarized positive muons are implanted in PTFE. Low-energy muons (implantation energies from 2.0 to 23.0 keV) were used to study the F–Mu$^+$–F state between $\sim$23 and 191 nm from the free surface of PTFE. Measurements were also made with surface muons (4.1 MeV) where the mean implantation depth is on the order of $\sim$0.6 mm. The relaxation rate of the F–Mu$^+$–F state up to $\sim$150 K was found to be significantly higher for muons implanted at 2.0 keV than for higher implantation energies, which suggests that the polymer chains in a region on the order of a few tens of nanometers from the free surface are more mobile than those in the bulk.

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I. INTRODUCTION

Poly(tetrafluoroethylene) (PTFE) is one of the most important commercial polymers for highly demanding applications. Its areas of use range from structural parts to low-friction bearings and nonstick frying-pan coatings. The versatility of PTFE is due to its unique physical and chemical properties, such as high hydrophobicity, very low friction coefficient, thermal stability, and chemical inertness. Bulk PTFE is highly crystalline, with helical chain molecules packed in essentially hexagonal arrangements. Four phases are known, with phase II being the stable state below 292 K. Phase II has a "pseudohexagonal" (triclinic) packing of alternating left- and right-handed helices with a conformation of $\sim$2.1598 CF_2 groups per turn of a helix with a pitch of 0.2808 nm [1]. The lattice parameters of phase II have been reported to be $a = b = 0.559$ nm, $c = 1.69$ nm, $\gamma = 119.3^\circ$ [2]. There have been several studies of the dynamics in bulk PTFE at low temperatures. David *et al.* observed a low-temperature relaxation peak close to 170 K at 0.1 Hz using a forced oscillation spectrometer [3]. Eby and Sinnott observed that the ^{19}F NMR linewidth of F nuclei in the amorphous regions of PTFE is approximately constant below 190 K and decreases rapidly above this temperature [4]. This temperature corresponds to the "glass-II transition" below which rotations about the C–C bonds freeze. In contrast, much less is known about dynamics near the surface of PTFE, which is the main subject of this paper. The near-surface properties of a polymer are critical to its performance in commercial applications. There have been several investigations of PTFE thin films produced by frictional deposition [5,6], but those were focused on the static and/or structural properties of the surface.

In general, the physical and chemical properties of materials near a surface or interface can be significantly different from the properties of the bulk [7–9]. These differences are even more important in thin films and nanostructures and could have significant implications for technological applications of materials. In supported polymer thin films, it has been found that the glass-transition temperature (T_g), which can be viewed as being related to the dynamics of the polymer chains, depends on the overall thickness of the film [10,11] and on the depth from the surface [12,13]. These experiments can be understood by assuming there is a surface layer with enhanced mobility relative to the bulk [14] and that the dynamics depends on the depth. De Gennes noted "future experiments should aim not at the determination of a single T_g, but at a distribution of T_gs" [15]. Several explanations of the T_g shift have been proposed [16–19] and these have been considered by de Gennes [15]. The enhanced dynamics of the polymer chains near the surface should occur for every polymer, although the range of the effect will likely depend on the molecular properties. There have been no studies of the thickness dependence of T_g or polymer dynamics in PTFE due to the inability to make films with well-defined surfaces and the fact that it is a mixture of amorphous and crystalline regions. In order to circumvent the problem of the macroscopic film quality, one would ideally like to use an atomic scale probe that can be implanted at specific depths from the polymer surface and is sensitive to the polymer dynamics. Such a technique would not depend on the macroscopic quality of the film. In this paper, we use muons as local probes of the dynamic properties near the surface of PTFE. We follow these gradually from the surface region (on the nm length scale) deep into the bulk of PTFE and find evidence for enhanced dynamics of the polymer chains in PTFE within $\sim$20 nm of the surface.

II. EXPERIMENT

All of the muon-spin-relaxation (μSR) experiments reported here were performed at the Swiss Muon Source (SμS),

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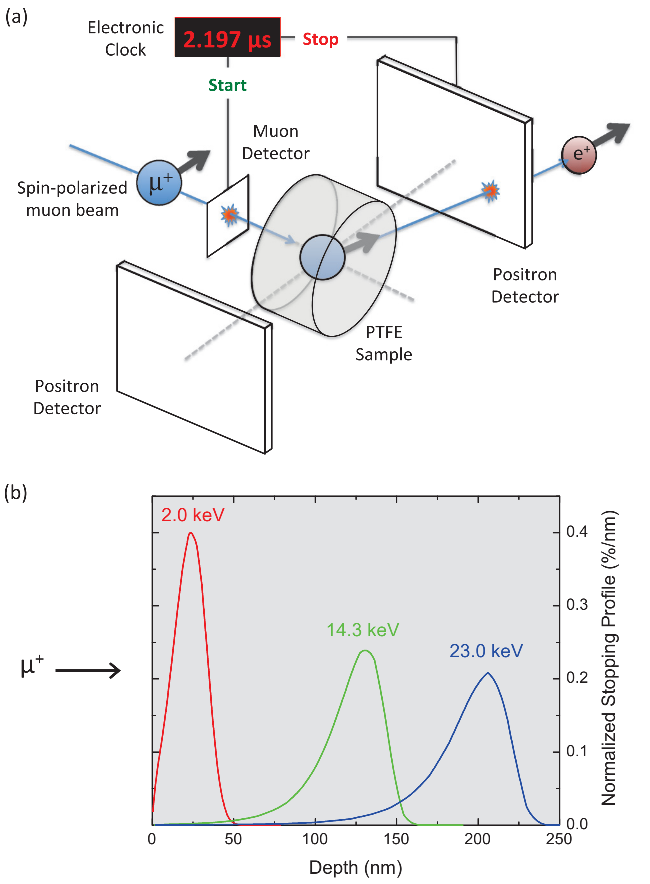

FIG. 1. (Color online) (a) Schematic of the zero-field muon-spin-relaxation experiment and (b) stopping profiles of low-energy muons in poly(tetrafluoroethylene) calculated with the program TRIM.SP [26].

Paul Scherrer Institute, Switzerland, on the Low-Energy Muon (LEM) [20] and the General Purpose Surface-Muon (GPS) spectrometers. Muon spin relaxation is a spectroscopic technique that has found widespread use in condensed matter physics, materials science, and chemistry [21,22] and has been used to investigate dynamics in insulating polymers and charge mobility in conducting polymers [23]. In a μSR experiment, a ~100% spin-polarized beam of positive muons (lifetime $\tau_\mu = 2.197\ \mu\text{s}$) is stopped in a target sample and the time evolution of the ensemble muon spin polarization is monitored by detecting the positrons produced by the radioactive decay of the muon in a pair of opposing detectors [Fig. 1(a)]. The asymmetry $A(t)$, which is determined from the number of positrons recorded in opposite pairs of detectors arranged around the sample, is proportional to the ensemble muon spin polarization. The near-surface measurements were performed on the LEM spectrometer [24], which has been previously used to study the depth-dependent dynamics in thin films of polystyrene [25]. Different regions of the sample are studied by controlling the implantation energy of muons (2.0–23.0 keV). The Monte Carlo simulation program TRIM.SP [26,27] was used to calculate the stopping profile as a function of implantation energy assuming a density of 2.2 g cm^{-3}. Implantation energies of 2.0, 14.3, and 23.0 keV correspond to weighted-mean implantation depths of 23, 120, and 191 nm, respectively, while the corresponding range straggling (square root of the variance of the stopping distribution) is 9, 22, and 27 nm, respectively [Fig. 1(b)]. Bulk measurements were performed on the GPS spectrometer. The range of surface muons in GPS is 130 mg cm^{-2}, which corresponds to a mean implantation depth of ~0.6 mm in phase II PTFE. Data analysis was performed using the MUSRFIT package [28].

The sample used in the LEM measurements was a 5-μm-thick PTFE film (Goodfellow Inc., catalog no. FP301050) and was used without further modification. The PTFE film was studied in order to eliminate the possibility of thermal gradients. The surface of the film was determined to have an average roughness of 4.3 nm over regions of 500 × 500 nm from atomic force microscopy measurements. This length scale is comparable to the implantation depths used in this experiment and we contend that roughness over a larger area is not important as the muon is a local probe. A crude estimate of the number-averaged molecular weight $\overline{M}_\text{n}$ was determined by measuring the heat of crystallization using a Perkin-Elmer DSC7 and the empirical relationship proposed by Weigel and Garske [29] and endorsed by Lappan *et al.* [30]. The $\overline{M}_\text{n}$ of the film was estimated to be approximately 2×10^7 g/mol, which corresponds to an average degree of polymerization, N, of $\sim 2 \times 10^5$. The radius of gyration of the unperturbed polymer chain, $\langle S^2\rangle^{1/2}$, is equal to $\sqrt{Nb^2/6}$, where b is a monomer size, and was found to be ~20 nm for the PTFE film. The PTFE film was mounted with a thin layer of Apiezon grease on a high-purity Al backing plate, which was then mounted on a cold finger cryostat. A silver mask with a circular hole with a diameter of 3 cm was placed in contact with the side of the sample facing the muon beam in order to ensure proper thermalization.

The PTFE sample studied using the GPS spectrometer was a disk with a diameter of 25 mm and a thickness of 3 mm. This was cut from a rod of PTFE (Goodfellow Inc., catalog no. FP307975). The heat of crystallization suggests that $\overline{M}_\text{n} \sim 1.3 \times 10^8$ g/mol, although this is outside the range where the Weigel and Garske relationship has been verified experimentally. The radius of gyration of the unperturbed polymer chain for the PTFE disk is ~47 nm. The sample was determined to be ~68% crystalline from Wide-angle X-ray scattering (WAXS) measurements. The PTFE disk was mounted in a He flow cryostat.

Density functional theory (DFT) calculations were performed with the GAUSSIAN 09 package of programs [31]. All calculations were performed with the B3LYP functional and the 6-311+G(d,p) basis set.

III. RESULTS AND DISCUSSION

Typical zero-field muon-spin-relaxation (ZF-μSR) spectra of PTFE obtained using the LEM and GPS spectrometers are presented in Fig. 2. Note the clear oscillation in the low-temperature spectra, both near the surface and in the bulk, which is due to the formation of a linear "hydrogen bond" between the muon and the two fluorine atoms and that we call the F–Mu$^+$–F state (sometimes also called F–μ^+–F). This state is typically formed in fluorinated materials, where the muon is preferentially drawn towards the electronegative fluorine atoms, and the muon spin interacts strongly with a small number of fluorine spins via dipole-dipole coupling.

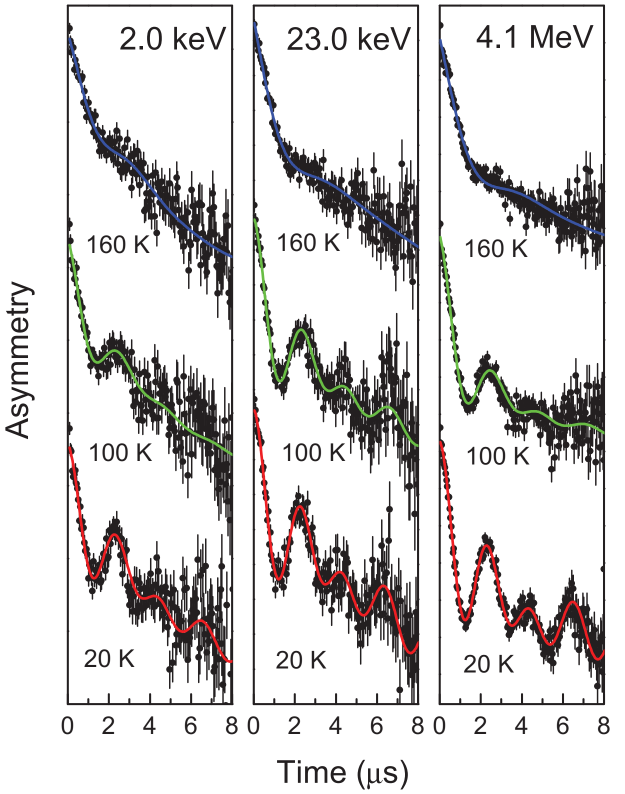

FIG. 2. (Color online) ZF-μSR spectra of PTFE at 20, 100, and 160 K for muons implanted near the free surface (2.0 and 23.0 keV) and in the bulk (4.1 MeV). The spectra were fit using Eq. (4).

This was first observed in several alkali-metal and alkaline-earth fluorides [32] and has since been observed in several fluoropolymers [33–35] and magnetic systems [36,37]. Möller *et al.* have used *ab initio* calculations to study the F–Mu$^+$–F state in several insulating fluoride compounds [38]. The fluorine atoms in the F–Mu$^+$–F state are usually separated by approximately twice the F$^-$ ionic radius of 0.117 nm. Most importantly, this state is extremely sensitive to the local dynamics and structure and therefore can be used to accurately determine these properties.

The muon spin oscillation function of the linear F–Mu$^+$–F state is given by [32]

$$G_{\mathrm{F-Mu^+-F}}(\omega_{\mathrm{d}}t) = \frac{1}{6}\left[3 + \cos(\sqrt{3}\omega_{\mathrm{d}}t + \phi) + \left(1 - \frac{1}{\sqrt{3}}\right)\cos\left(\frac{3-\sqrt{3}}{2}\omega_{\mathrm{d}}t + \phi\right) + \left(1 + \frac{1}{\sqrt{3}}\right)\cos\left(\frac{3+\sqrt{3}}{2}\omega_{\mathrm{d}}t + \phi\right)\right], \tag{1}$$

where

$$\omega_{\mathrm{d}} = \frac{\mu_0\gamma_\mu\gamma_{\mathrm{F}}}{4\pi}\left\langle\frac{1}{r^3}\right\rangle, \tag{2}$$

γ_μ is the muon gyromagnetic ratio, γ_{F} is the ^{19}F gyromagnetic ratio, r is the Mu$^+$–F bond length, and the brackets indicate an average over the bond lengths that result from the motion of the polymer chains. The effective phase ϕ is an instrumental effect in the LEM spectrometer.

Muons that do not form the F–Mu$^+$–F state will experience a random quasistatic distribution of local magnetic fields due to the surrounding ^{19}F nuclear moments. The time dependence of the muon spin polarization in such a situation is given by the static Gaussian Kubo-Toyabe function,

$$G_{\mathrm{KT}}(t) = \frac{1}{3} + \frac{2}{3}(1 - \Delta^2t^2)\exp\left(-\frac{\Delta^2t^2}{2}\right), \tag{3}$$

where Δ is proportional to the second moment of the local magnetic field distribution [39]. The 1/3 term is often not observed due to the presence of slow dynamics in the field distribution and the overall behavior can be approximated by a Gaussian function at early times.

All of the ZF-μSR spectra were fit with the following model:

$$A(t) = A_1G_{\mathrm{F-Mu^+-F}}(\omega_{\mathrm{d}}t)\exp(-\lambda t) + A_2\exp\left(-\frac{\Delta^2t^2}{2}\right) + A_{\mathrm{Bg}}, \tag{4}$$

where A_1 is the amplitude of the F–Mu$^+$–F state, λ is the relaxation rate of the F–Mu$^+$–F state due to dynamics, A_2 is the amplitude of the muons not incorporated in the F–Mu$^+$–F state, and A_{Bg} is attributed to a nonrelaxing background contribution, such as muons stopping in the silver mask. There is a missing fraction due to the formation of muonium, which was observed by Pratt *et al.* from repolarization measurements [33]. Lancaster *et al.* studied the F–Mu$^+$–F state in a number of fluoropolymers, including PTFE, with ZF-μSR. They were able to distinguish two separate ω_{d} frequencies, which were assigned as different stopping sites [35]. Lancaster *et al.* proposed that one F–Mu$^+$–F state forms from fluorine atoms on the same PTFE chain and that the other F–Mu$^+$–F state forms from fluorine atoms on adjacent PTFE chains. In contrast, we found only one ω_{d} frequency at each temperature.

The μSR spectra at each implantation energy were fit simultaneously with a common background, phase, and total asymmetry. Near the surface and in the bulk, the frequency (Fig. 3) and amplitude of the F–Mu$^+$–F state decreased with increasing temperature, while the amplitude of the Gaussian component increased with increasing temperature. At all implantation energies, the oscillating signal disappeared at ~180 K. The Mu$^+$–F separation was calculated using Eq. (2) and increases with increasing temperature. There was no apparent dependence of the vibrationally averaged Mu$^+$–F distance on the implantation energy (Fig. 4). The Mu$^+$–F distance increases approximately quadratically with temperature [40], but cannot be modeled by a single T^2 scaling, with the appearance of a crossover in behavior around 120 K. This scaling for the Mu$^+$–F bond length agrees with what was previously observed by Lancaster *et al.* [35]. The lack of any discernible dependence on the implantation energy for the Mu$^+$–F distance does not confirm or refute the hypothesis that polymer chains are more mobile near the surface than in the bulk.

We performed DFT calculations on model systems in order to determine the form of the F–Mu$^+$–F state. The optimized structures of tetrafluoromethane (CF$_4$), FHF$^-$, and

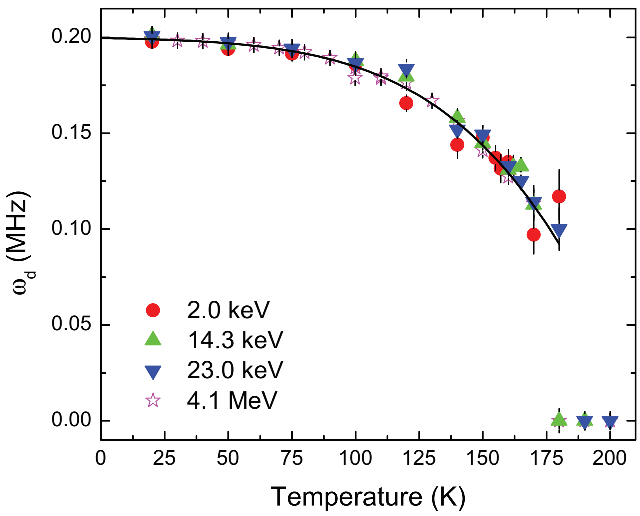

FIG. 3. (Color online) Fitted dipolar frequency ω_d of the F–Mu$^+$–F state as a function of temperature for different implantation energies. The solid line is a guide for the eyes.

$[CF_4 \cdots H \cdots CF_4]^+$ are shown in Fig. 5, along with the relevant bond lengths. The proton/muon clearly distorts its local environment and pulls nearby fluorines towards it when it is between two CF_4 molecules. The H–F separation in $[CF_4 \cdots H \cdots CF_4]^+$ is nearly the same as in the FHF^- molecule and both values are similar to the measured Mu–F separation. The proton/muon significantly distorts the CF_4 molecule, with the C–F bond pointed towards the proton being considerably lengthened and the remaining bond lengths decreasing. DFT calculations were also performed on protonated decafluorobutane in order to determine whether intrachain F–Mu$^+$–F states can form. Initial structures with the proton between both geminal and vicinal fluorines did not produce an F–Mu$^+$–F state. Instead, HF was formed in addition to a carbenium ion. Based on the DFT calculations, we propose that the observed F–Mu$^+$–F state is due to fluorines on adjacent polymer chains and that there are no intrachain F–Mu$^+$–F states.

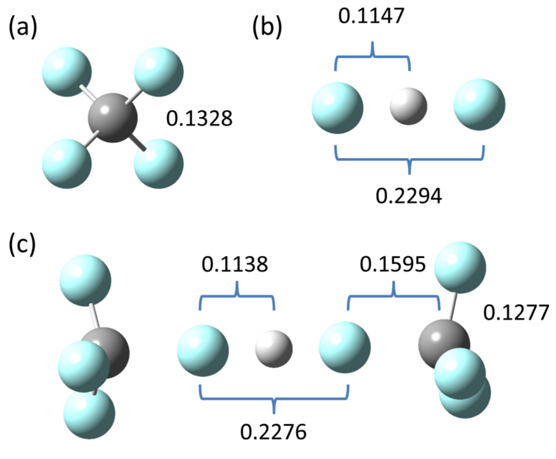

FIG. 5. (Color online) Calculated [B3LYP/6-311+G(d,p)] minimum energy structures and bond lengths (in nm) of (a) CF_4 (b) FHF^-, and (c) $[CF_4 \cdots H \cdots CF_4]^+$. Carbon atoms are gray, fluorine atoms are turquoise, and protons are white.

The relaxation rate of the F–Mu$^+$–F state, shown in Fig. 6, increases approximately exponentially with increasing temperature. In NaF and other ionic fluorides, the relaxation of the F–Mu$^+$–F signal is due to Mu$^+$ hopping from one site to another, but there is a large activation energy ($E_a/k_B = (1.7 \pm 0.2) \times 10^3$ K in NaF [41]), so this is only significant at high temperature. The activation barrier for hopping in PTFE is likely less than in the ionic fluorides, especially when the Mu$^+$–F distance is larger, but still large enough that we consider it unlikely for hopping to be the cause of the relaxation observed at very low temperatures.

The observation of relaxation at 20 K is surprising given that at this temperature, the polymer dynamics is expected to be very slow. This is not an experimental artifact as Pratt *et al.* observed λ on the order of 0.1 μs^{-1} at 25 K in bulk PTFE

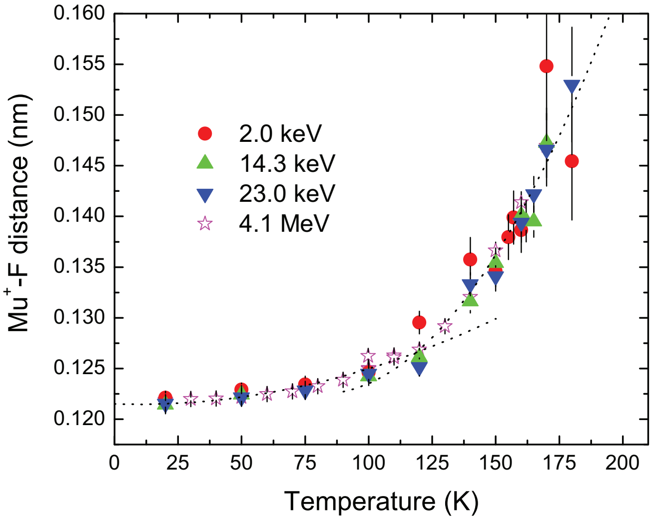

FIG. 4. (Color online) Fitted Mu$^+$–F distance as a function of temperature. The dotted lines are a guide to the eye, illustrating the T^2 scaling laws and the crossover in behavior at ∼120 K.

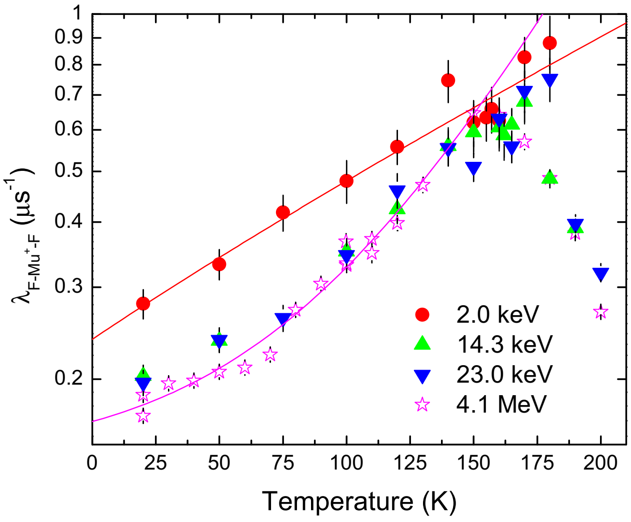

FIG. 6. (Color online) Fitted relaxation rates λ of the F–Mu$^+$–F state as a function of temperature for different implantation energies. The solid lines are guides for the eyes.

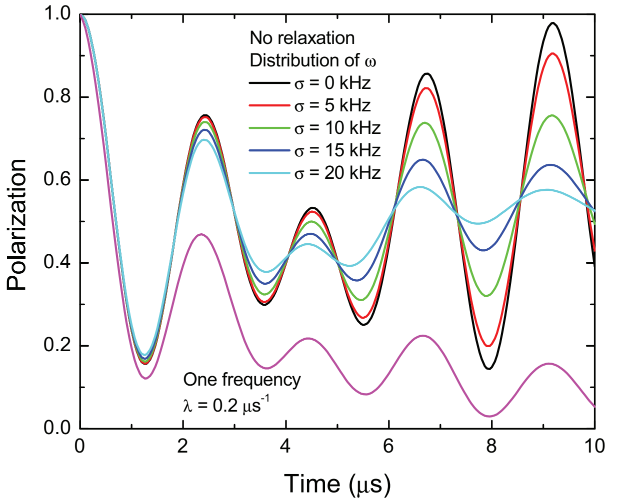

FIG. 7. (Color online) Simulated ZF-μSR spectra of the F–Mu$^+$–F state for Gaussian distributions of the dipolar frequency with no relaxation and for a single dipolar frequency with a relaxation rate of 0.2 μs^{-1}.

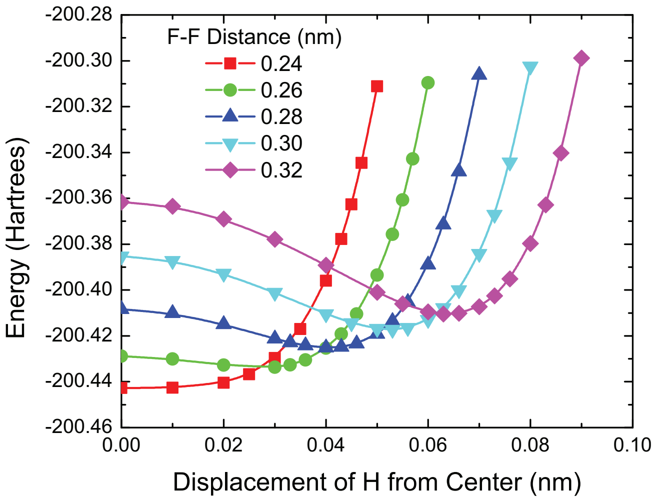

FIG. 8. (Color online) Calculated [B3LYP/6-311+G(d,p)] energy of the linear FHF$^-$ system as a function of H displacement from the center for several fluorine-fluorine distances.

using the EMU spectrometer at ISIS [33] and Nishiyama *et al.* noted that "Even at the lowest measured temperature, 5 K, a hopping rate of 0.1 μs^{-1} is needed to explain the μSR results for both Teflon and Fluorinert" from measurements made at KEK, Japan's National Laboratory for High Energy Physics [34]. We have considered the effect of a distribution of dipolar frequencies, possibly due to a static random field distribution from fluorine atoms far away from the F–Mu$^+$–F state, and found that this causes a damping of the F–Mu$^+$–F oscillations but does not match the relaxation observed experimentally (Fig. 7). The fact that a nonzero λ was observed at low temperatures in four different spectrometers suggests that the cause of the relaxation is intrinsic to PTFE.

Lancaster *et al.* noted that the disappearance of the F–Mu$^+$–F signal coincides approximately with the bulk glass-II transition as determined by other techniques (192 K) and proposed that the F–Mu$^+$–F state breaks up due to rotation around the C–C bonds. This is unlikely to be important here as the γ process, which is responsible for the glass-II transition, is only on the order of kHz near 200 K [42], so it is too slow to break up the F–Mu$^+$–F state during the observation period (∼10 μs). We propose that the F–Mu$^+$–F state disappears because the increased average distance between fluorine atoms changes the shape of the potential with the preferred symmetric structure at short F–F distances, changing to F–Mu$^+\cdots$F for larger distances; see Fig. 8. This was confirmed with DFT calculations on the linear FHF$^-$ system where the change in the preferred structure occurs when the F–F distance is approximately 0.25 nm. The asymmetric structure does not result in muon spin oscillation in the zero field but in a Gaussian Kubo-Toyabe function, similar to what was observed in poly(vinyl fluoride) [35], and this explains the abrupt disappearance of the F–Mu$^+$–F signal and the increase in amplitude of the Gaussian component.

We propose that λ is the zero-order rate constant for change from the symmetric F–Mu$^+$–F structure to the asymmetric F–Mu$^+\cdots$F structure and is most likely caused by changes of the F–F distance due to *local* high-frequency vibrational motion. Motions such as the α, β, or γ processes are much too slow to have an impact during the muon lifetime. Our measurements were unable to distinguish between the F–Mu$^+$–F in crystalline and amorphous environments. Although IR studies have shown that local vibrational motions in amorphous state and crystalline states are different [43], they do not appear to be resolvable with the μSR technique. The change in structure leads to dephasing of the F–Mu$^+$–F oscillation signal. It appears that λ increases with increasingly rapid conformational fluctuations, but we cannot fully justify the observed exponential temperature dependence of λ.

We have observed that the values of λ measured for muons implanted at 2.0 keV are significantly higher than the corresponding relaxation rates measured at the higher implantation energies (Fig. 6). This implies that the polymer chains are more mobile within a few tens of nanometers of the free surface, i.e., on a length scale comparable to the stopping distribution at 2.0 keV. The difference in λ between the 2.0 keV data and the higher implantation energies disappears at approximately 150 K, which suggests that at this temperature there is no difference in the polymer chain dynamics near the surface and in the bulk.

Our finding that the polymer chains are more mobile within a short distance from the surface is in agreement with several theoretical models in the literature, where the thickness of the surface layer was assumed to be on the order of $\sim 2\langle S^2\rangle^{1/2}$ [44] to $\sqrt{6}\langle S^2\rangle^{1/2}$ [15], which for our film is between ∼40 to 50 nm and is comparable to the stopping distribution of positive muons implanted at 2.0 keV. Further measurements are needed at a range of implantation energies in order to more fully map the depth dependence of the polymer dynamics.

IV. CONCLUSION

The F–Mu$^+$–F state was observed in PTFE both in the bulk and within ∼200 nm of the surface using ZF-μSR spectroscopy. The F–Mu$^+$–F state disappears at ∼180 K in both the surface region and the bulk due to conversion to the asymmetric F–Mu$^+\cdots$F structure as a result of increasing separation between fluorine atoms. Motions such as the α, β, or γ processes are much too slow to have an impact during the muon lifetime and the relaxation of the F–Mu$^+$–F is likely due to local vibrational motion. Our depth-resolved measurements suggest that the polymer chains within a few tens of nanometers of the free surface of PTFE are more mobile compared with those in the bulk. This conclusion is based on the consistently faster relaxation of the F–Mu$^+$–F state at 2.0 keV compared with the higher implantation energies. Our results are compatible with theoretical predictions and show that an enhancement of polymer chain dynamics occurs within a region of $\sim 2\langle S^2\rangle$ from the free surface.

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