Positronium as a probe of transient paramagnetic centers in a-SiO_2

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A laser-pump, positron-probe technique has been developed for measuring the dynamics of laser-induced paramagnetic centers in porous materials. The basis of the technique is the fact that the annihilation rate of ortho-positronium may increase in the presence of unpaired spins. By using an intense positron pulse to create positronium atoms in a porous silica sample we have used this effect as a probe to measure the time dependence of the recombination of laser-induced paramagnetic centers. We have observed nonexponential postirradiation decay kinetics extending over ten orders of magnitude that are similar to those previously observed in silica glasses.

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I. INTRODUCTION

Amorphous silica (a-SiO_2) has been extensively studied due to its importance in electronic and optical components.[1] Indeed, it is difficult to overstate the importance of silicon and its oxides to modern technological applications; as the most common gate dielectric for metal-oxide-semiconductor devices, a-SiO_2 is practically indispensable. This material also plays a critical role in the fabrication of optical and laser components, lithographic photomasking, and fiber optics, to name just a few applications. Furthermore, monocomponent glassy systems like a-SiO_2 also serve as models for basic physics studies of the amorphous state.[2]

Considerable attention has been directed toward the effects of radiation on a-SiO_2,[3] and the subsequent creation of point defects. Many of these studies have been carried out using electron spin resonance[4] (ESR) and optical spectroscopy[5] (OS) techniques, which have yielded a great deal of information.

Understanding the mechanisms by which radiation-induced defects are created is extremely important for the development of radiation-resistant materials, and since a-SiO_2 is often used in devices subjected to high-radiation environments (for example, space applications, medical treatments, fusion reactor diagnostics, or nuclear waste containment) radiation damage in silica is an important field.

It is often the case that radiation-induced point defects are paramagnetic centers (that is, possessing an unpaired electron spin), and the measured g factors, hyperfine splittings, or fine-structure splittings obtained from ESR measurements can provide detailed structural information.[4,6] Some radiation-induced defects exhibit photoluminescence and/or absorption bands at well-defined energies, and both pulsed ESR[7] and pump probe laser[8] techniques can yield time-resolved information regarding paramagnetic centers.

We describe here a technique developed for studying radiation-induced damage in amorphous porous materials. A laser pump pulse was used to create paramagnetic centers in porous a-SiO_2 and a positron beam was used as a probe of these defects via the formation of ortho-positronium (o-Ps) atoms. When positrons are introduced into porous a-SiO_2 (or similar materials) o-Ps is formed in the pores[9] and interactions between o-Ps atoms and paramagnetic centers can lead to spin exchange quenching of the Ps, which increases the decay rate.[10] The initial formation of Ps may be inhibited[11] if there are many paramagnetic centers or scavenging electrons present when the positrons are implanted. In the present experiment there is no way to distinguish between these mechanisms. This means that the o-Ps decay rate and formation intensity can yield information about the paramagnetic center number density, although in the latter case the possibility of additional mechanisms should be considered. Because positronium in the pores of the sample cannot reenter the bulk, [9] this technique is *necessarily* surface selective, in contrast to ESR or OS measurements.

In most of the experiments we report the Ps was formed after the laser pulse and so the increased o-Ps decay rate could not then be due to a direct interaction between the laser and the o-Ps atoms. However, when the laser pulse was fired after the formation of Ps, it is likely that there was no direct effect since the interaction probability is vanishingly small. Similarly, the density of o-Ps atoms was so low as to preclude Ps promoting a longer-lived paramagnetic species by interaction with a short-lived species (for example, converting excitons from singlet to triplet states).

II. EXPERIMENTAL PROCEDURE

An integral part of the method we describe is the production of intense positron pulses. This was accomplished using a positron accumulator that has been described in detail elsewhere.[12] Briefly, positrons from a source were moderated using neon[13] and then trapped, accumulated, and compressed in a Surko-type trap.[14] In this way pulses containing around 2×10^7 positrons, with a full width at half maximum (FWHM) of $\sim$3.5 mm and temporal width of $\sim$15 ns FWHM were produced. Figure 1 shows a schematic of the laser-positron timing and detection layout. uv light (266 nm) was generated using the fourth harmonic of a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Quanta Ray DCR-1A). The output energy and pulse width were approximately 8.3 ± 1.4 mJ/pulse and 10 ± 1 ns (FWHM), re-

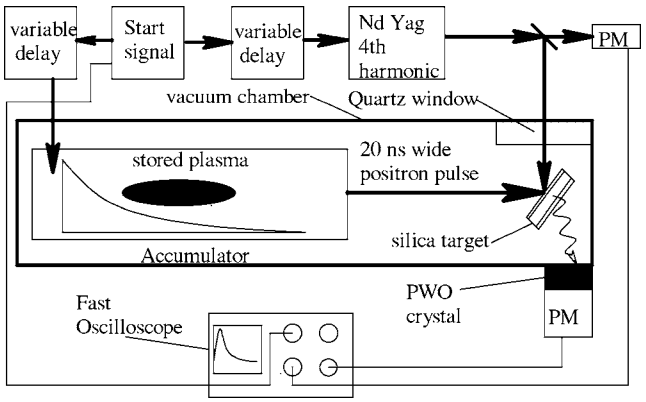

FIG. 1. Schematic of the laser and positron pulse timing and detection arrangement. The relative arrival times of the positron and laser pulses are determined by choosing appropriate delays for their trigger signals. The start signal is generated by a computer according to predetermined plasma filling conditions. The laser pulse timing is monitored by sending a fraction of the beam to a photomultiplier (PM). PWO indicates the lead tungstate crystal.

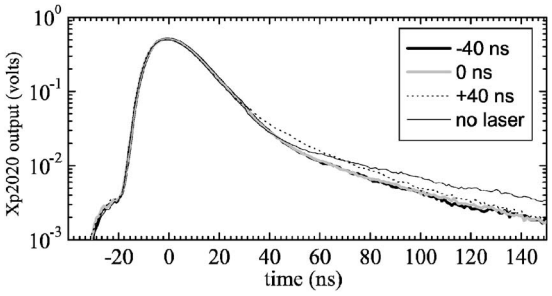

FIG. 2. Lifetime spectra for various laser delay times. By convention the positron pulse is always at $t=0$. The width of the prompt peak is determined by the detector response and the width of the primary positron pulse. These data are meant to highlight the difference between positive and negative laser delay times.

spectively. We note that all the data shown here are for 266 nm light. Similar effects were observed using 355 nm light; no effect was observed when 532 nm light was used.

The laser light entered the vacuum system via a quartz window with negligible absorption to impinge on a 300-nm-thick a-SiO_2 target. This sample was fabricated using a sol-gel spin-coating method on a silicon substrate.[15] A nonporous capping layer covered the porous film which had a porosity of ~50%. We estimate that at most ~10% of the laser light was applied to the region of the sample overlapping the incident positron beam. Thus, the maximum possible dose from each laser pulse was less than ~10 kGy. The actual dose was much less than this, since the absorption coefficient of pure silica glasses at 266 nm is typically only ~1 cm^{-1}.[16]

The laser and positron pulse arrival times were controlled via the appropriate trigger signals. For most of the work described here the laser pump pulse was fired first, and then after some delay the positron probe pulse was fired. However, for delay times greater than 10 s this procedure becomes impractical. At these longer times a single pump pulse was used, and the sample was then probed with many successive positron pulses. The time between the laser and positron pulses could be varied sequentially or randomly, with practically the same results. This means that the laser essentially "resets" the density of paramagnetic centers with each shot. This implies that there was no long-lived charging induced by the laser. Also, the positron beam itself did not produce any measurable paramagnetic centers. We estimate that the maximum possible change in the sample temperature due to the laser is less than 1 K.

The o-Ps formation fraction (I_{Ps}) and decay rate (Γ_{Ps}) were determined by fitting lifetime spectra obtained using single-shot positron annihilation lifetime spectroscopy.[17] The γ-ray detector used was a lead tungstate (PWO_4) scintillator coupled to an XP2020 photomultiplier (PMT). The output from the PMT was coupled directly to a fast digital storage oscilloscope (Agilent 54855A). Figure 2 shows lifetime spectra obtained in this way for different laser arrival times. We use the convention that $t=0$ refers to the arrival time of the positron pulse, so that the laser pulse arrival times may be positive or negative.

After a positron pulse has been implanted into the silica sample most of the positrons rapidly annihilate into two γ rays[18] which gives rise to the "prompt peak" centered at $t=0$. The width of this peak is determined, in this case, by the decay time of the scintillator convoluted with the width of the positron pulse (both of which are ~15 ns). Many of the positrons that do not immediately annihilate form positronium. The short vacuum lifetime ($\tau_{vac}=125$ ps) of parapositronium (p-Ps) means that it is indistinguishable from direct annihilation and will simply contribute to the prompt peak. Similarly, any quenching mechanisms that cause o-Ps ($\tau_{vac}=142$ ns) to decay at a sufficiently fast rate will also lead to counts in this peak.

In porous materials the o-Ps decay rate depends on the pore size (or, more properly, the o-Ps mean free path). This is because of interactions with the pore walls ("pick-off"[19]). The sample used here had a pore size of ~4 nm,[15] and the o-Ps mean free path was ~6 nm, due to the interconnectivity of the pores. The lifetime in the absence of laser-induced paramagnetic centers was thus ~85 ns and we expect that the time for o-Ps to thermalize was around 10 ns.[20]

The sample was capped with a nonporous layer which acted as a diffusion barrier, ensuring that positronium remained within the sample. This meant that the incident beam had to be implanted at 2.5 keV to penetrate the top layer. Figure 3 shows the delayed fraction as a function of the beam impact energy. The delayed fraction is defined as the sum of the counts in the lifetime spectrum in the time interval 100–300 ns divided by the total number of counts in the spectrum. This quantity depends on both the o-Ps decay rate and formation fraction (see Fig. 4). The maximum in Fig. 3 indicates the beam impact energy for which Ps was formed primarily in the center of the porous region of the sample. At low energies positrons are implanted into the capping layer and do not form much Ps. At very low energies (<1 keV) Ps formation occurs on the surface of the top layer. When the laser was fired 1 μs before the positron pulse the delayed fraction was reduced, indicating an increase in the decay rate. The fact that the application of the laser leads to the

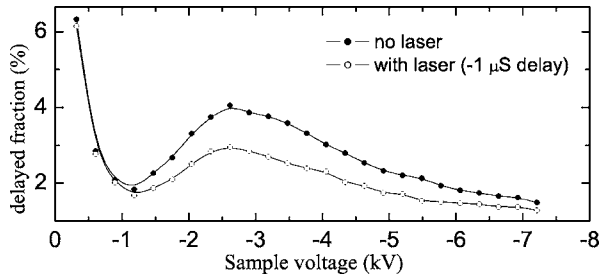

FIG. 3. Delayed fraction as a function of the positron implantation energy. At high energy the positrons are implanted into the silicon substrate and do not form much Ps. At low energies they are implanted into the capping layer and again do not form much Ps. At very low energies (<1 keV) Ps formation occurs on the surface of the top layer. When the laser was fired 1 μs before the positron pulse the delayed fraction was reduced, indicating an increase in the decay rate.

same decrease at all depths indicates that the paramagnetic centers are created throughout the target, although it should be remembered that as the implantation energy is increased the stopping profile of the beam spreads out and some of the porous region will be sampled.

The basis of our measurement is the increase in the decay rate of o-Ps due to the presence of paramagnetic centers on the internal surfaces of the porous sample. If a sample with very large pores had been used the self-annihilation of o-Ps might have dominated, and the measurement would then have been quite insensitive. This would be the case for pore sizes greater than ~100 nm. Conversely, in a sample with very small pores the intrinsic pick-off rate would dominate, and the measurement would again become very insensitive. This would occur for pore sizes less than around 1 nm. If the density of surface paramagnetic centers is n_p (cm^{-2}) then the o-Ps decay rate due to interactions with them is given by

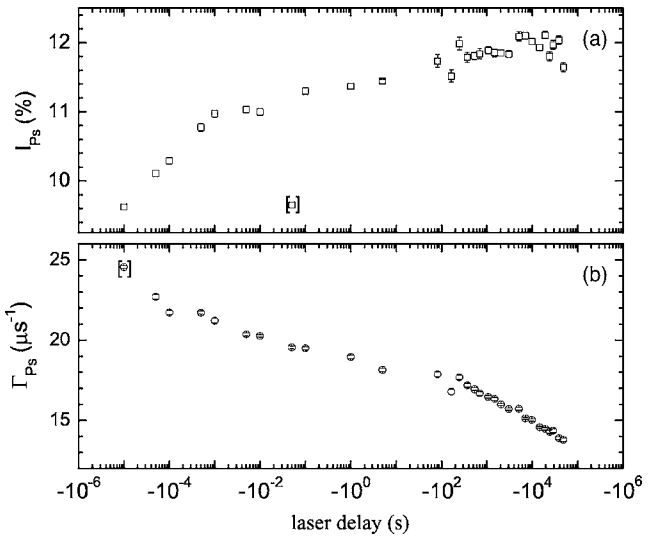

FIG. 4. o-Ps formation fraction (a) and decay rate (b) as a function of the time difference between the laser pulse and the subsequent positron pulse. Suspected anomalous data points are shown in parentheses.

$$\Gamma_p = \frac{n_p \sigma v_{Ps}}{l}, \tag{1}$$

where v_{Ps} is the positronium speed (which we assume to be thermal, i.e., 8×10^6 cm s^{-1}), σ is the spin exchange cross section, and l is the Ps mean free path with respect to interactions with paramagnetic centers. Thus, the sensitivity of the technique depends on the pore size used and the accuracy with which the decay rate can be measured. In similar experiments Saito and Hyodo measured a spin exchange cross section of $\sim1\times10^{-17}$ cm^{-2} for Ps interactions with $-OCH_2^{\bullet}$ radicals[21] (where the superscript • denotes an unpaired electron). If the cross section for spin exchange quenching with any paramagnetic center is of this order then, assuming that changes in the decay rate can be measured with a precision of ±0.3 μs^{-1}, the sensitivity of the technique is $n_p\sim3\times10^9$ spins cm^{-2}.

III. RESULTS AND DISCUSSION

There are two parameters obtained from fits to the lifetime spectra: the o-Ps formation intensity and decay rate. These are shown in Fig. 4 for various laser delay times. The formation intensity should be treated with caution because any quenching effects that cannot be resolved will be indistinguishable from an actual reduction in the initial formation of Ps.

Figure 5(a) shows lifetime spectra obtained with the laser fired *after* the positron pulse. There is an initial rapid decay which occurs when the laser pulse arrives, followed by a slower decay. This is made clearer in Fig. 5(b) which shows the difference signal between spectra with the laser fired at various positive times and at $t=0$. The exact mechanisms producing these two decay rates remain unknown; they may be due to paramagnetic centers that decay quickly, a short-lived laser-induced scavenger effect, or some combination of these. Empirically fitting the difference spectra with a single exponential yields a common decay rate of ~40 μs^{-1} for all three. However, without knowing the actual mechanisms occurring it is not clear what this really means.

Figure 6(a) shows the data of Fig. 4 replotted as the change in I_{Ps} with respect to the long-time value, which approximates the value with no laser fired. This curve is regarded as describing the number of paramagnetic centers responsible for o-Ps decays taking place in times shorter than ~40 ns. Figure 6(b) shows the o-Ps decay rate due solely to laser-induced paramagnetic centers. Both of these decay curves exhibit nonexponential behaviors which are similar to previously observed postirradiation decay kinetics of defect centers in silica-based glasses.[22]

In fact all of the data of Fig. 6 can be fitted by fractal kinetics formalisms derived by Griscom.[22] This approach has been very successful in describing γ-ray-induced defect formation and decay in both pure and Ge-doped silica-core optical fibers.[22] First-order fractal kinetics is synonymous with the so-called stretched exponential or Kohlrausch[23] formalism, which describes diffusion-controlled or hierarchical reactions in stochastic systems:

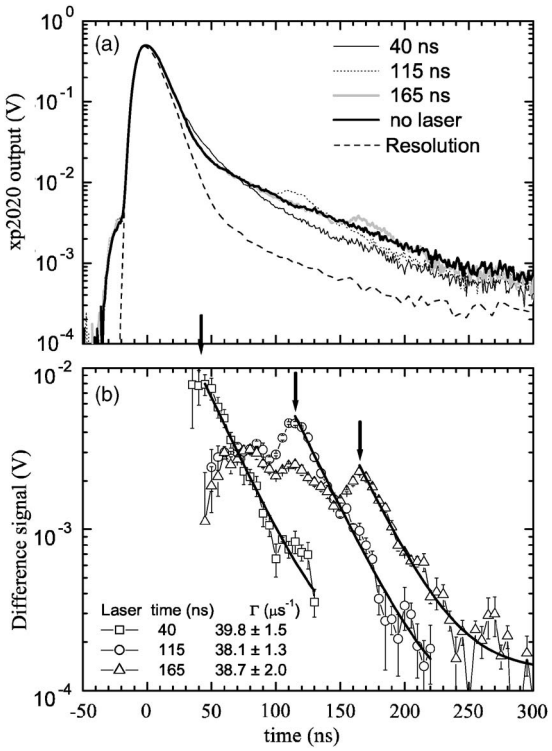

FIG. 5. (a) Lifetime spectra observed for laser shots just after the positron implantation, with the time delays shown in the legend. (b) Expanded view of the difference between various spectra with the laser fired at various times and at $t=0$. The dashed line in (a) is a resolution function obtained by implanting the positrons at 7 kV into a pure silicon sample. These data (from which practically no Ps is expected) were used to perform the fitting procedures and obtain the positronium decay rate and intensity for the data shown in Fig. 4. Shown in (b) are single-component exponential fits to the immediate decay (plus a constant background) following the laser pulses. The calculated decay-time constants from these fits are shown in the legend. The vertical arrows indicate the arrival time of the laser pulse for the appropriate spectra.

$$N(t) = N(0)\exp[-(t/\tau)^{\beta}], \tag{2}$$

where $N(t)$ is the number of (paramagnetic) centers at time t, $N(0)$ is the number at $t=0$, τ is an effective time constant, and β is the "stretching parameter," which is a number between 0 and 1. Second-order fractal kinetics describing thermally activated bimolecular processes in amorphous materials can be cast in an analogous form,[22]

$$N(t) = N(0)\{1 + [N(0)/N^{*}](t/\tau)^{\beta}\}^{-1}, \tag{3}$$

where the symbols have the same meanings as in Eq. (1) except that N^{*} is a quantity with the same dimensions as $N(t)$ but unit value.

We found that fits to the data could be made using two fractal-kinetic functions comprising first- and/or second-order components. The quality of the fit to the data in Fig. 6(a) was slightly better when a function that was the sum of two second-order terms was used. This fit is shown in the figure. Similarly, for the data of Fig. 6(b) a slightly better fit was obtained using a function that was a sum of a first- and

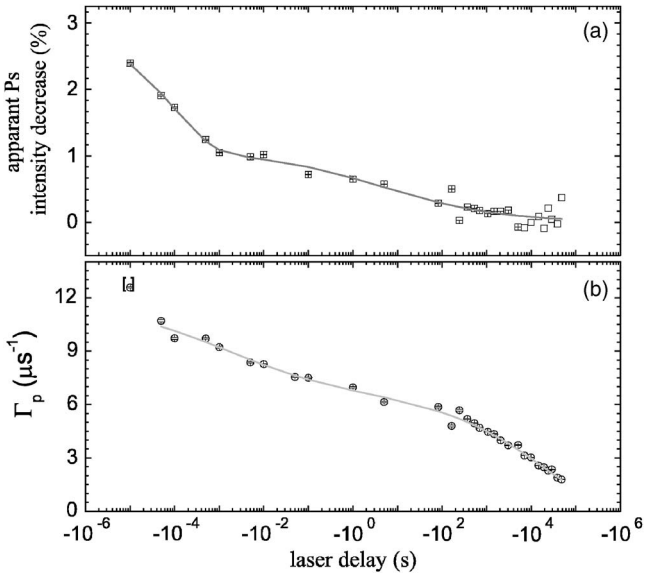

FIG. 6. The same data as in Fig. 4 but recast as the apparent decrease in I_{Ps} (a) and the decay rate Γ_p (b) induced by the laser as a function of the time difference between the laser pulse and the subsequent positron pulse. In both cases the solid lines are fits made according to the procedure described in the text. A suspected anomalous point in (b) is shown in parentheses and was not included in the fit.

a second-order component. This fit is shown in the figure. In both cases the difference between the fit qualities for various combinations of first- and second-order components was marginal, and it was not possible to unambiguously identify the kinetic order of the decay curves. This type of ambiguity is not uncommon since this pair of functions can yield equally good fits regardless of the true kinetic order if reliable decay data for times one or two orders of magnitude greater than τ should be unavailable.[1]

Girard and co-workers have recently measured the decay kinetics of induced optical bands in silica fibers following irradiation by pulsed x rays at room temperature.[24] They were able to fit their data to equations of the form of either (2) and (3) with similar efficacy. They argued, as in Ref. 22, that since the second-order formalism describes free-electron–hole recombination [Eq. (2)] it can be anticipated that there should be a change over to first-order kinetics at long times when the electron-hole density has been reduced to the point that the remaining pairs recombine geminately (pseudo-first-order kinetics).

The radiation dose applied in the present work was in all likelihood rather low when compared with most other similar studies. For example, optical and ESR studies of point defects in a-SiO_2 have been carried out using γ-ray doses as high as 10^8 Gy.[25] However, in the work of Girard *et al.* mentioned above the absorbed dose was only 2 Gy, and these authors showed that their data were most likely due to creation of metastable self-trapped holes in the bulk material. In the present work we have no way to identify the paramagnetic centers observed, although we do know that they must be surface centers.

It has been well established that photoirradiation of a-SiO_2 can lead to the formation of a number of stable point

defects (e.g., E' centers and peroxy radicals[26]), provided that the photon energy is close to or larger than the ~9 eV photoconductivity band gap in silica[27] or, for lower-energy photons, provided that the pulse energy density is sufficient to give rise to significant two-photon absorption.[25] It is possible that the data shown here are due to a two-photon excitation process, and in future studies a more careful measurement of the paramagnetic center number density as a function of laser power will elucidate this.

Because the technique we describe is sensitive only to surface paramagnetic centers there may be some surface-specific formation mechanisms of point defects that should be considered. In previous studies of a-SiO_2 it has been found that the same type of chemical centers are present on surfaces as are found in the bulk but may have slightly different structural properties due to their different spatial environments.[28] Radzig[29] has garnered major insights from his studies of diamagnetic silylene centers on freshly fractured silica surfaces using several spectroscopic methods, and has catalogued many additional paramagnetic defects formed by reactions of the intrinsic surface silylene structures, as well as surface E' centers, with various gas molecules.

However, in the present case, the sample was a silica-gel thin film possessing high porosity. Thus, its high surface area was not due to fracturing but rather to details of the sol-gel method. Unfortunately, to date we have been unable to retrieve a detailed history of this sample. However, we note that porous silica (aerogel) films can be prepared by vacuum drying or by ambient-pressure methods reviewed in Ref. 30.

In any event, sol-gel silicas that have not been heated to temperatures as high as 600 °C are known to retain significant amounts of organics, which are responsible for some of the radiation-induced defects reported therein (e.g., Ref. 31). Indeed, one subpopulation of the laser-induced surface defects in our sample could possibly be the same as the $–OCH_2^{\bullet}$ radicals observed by Saito and Hyodo.[21] We note that related radiation-induced $–CH_2^{\bullet}$ radicals have been unambiguously detected by ESR in certain bulk silica glasses.[32]

IV. CONCLUSION

The experiments we describe here constitute pump-probe measurements in which a pump laser has been used in conjunction with a positron-based probe. This has become possible because of a recently developed intense positron pulsed beam system.[12] Some work has been done in which a laser pump has used electrons as a probe in diffraction or microscopy experiments,[33] but the radiation from positron annihilation has not previously been used in the present manner to our knowledge.

One of the advantages of this technique is that any paramagnetic center can be observed, so long as it is present on the surface of the porous material. Thus, paramagnetic centers without well-defined ESR or optical signals can still be studied. However, the indiscriminate nature of the positronium probe means that no structural information can be directly obtained via this method. For this reason it may be advantageous in some experiments to perform this type of measurement in conjunction with an ESR or OS measurement.

There may also be situations where surface selectivity is an advantage. ESR measurements are sensitive to paramagnetic centers in the bulk and on the surface, but defects on the surface can be recognized by their reactions with gas admitted into the sample.[29,34] It is not clear if this methodology would be suitable for time-resolved measurements. The method we describe is sensitive to isolated internal structures which may not be accessible to a quenching gas. This could prove useful for studies of silanol groups on the surface of silica dust particles, which are thought to be responsible for the lung disease silicosis.[35] Another area in which surface selectivity might be useful is in the study of catalysts for which the surface centers might be studied at various stages during a chemical reaction.

We have presented a technique for studying laser-induced paramagnetic centers in porous materials. This preliminary work has highlighted the efficacy of the technique, although uncertainty regarding surface impurities in the sample meant that we could not even speculate on the types of paramagnetic centers observed. These uncertainties, as well as the time resolution of the system, have made it impossible to elucidate some of the prompt processes occurring directly after laser irradiation. In future work it would be desirable to use well-defined samples, to vary the sample temperature, and to perform complementary studies using ESR or OS. Improvements in the detector resolution and positron beam pulse width would also be helpful for studying fast-decay components.

ACKNOWLEDGMENTS

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