

Infrared Spectral Hole Burning of Polymers: A Probe of Local Structure

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Infrared hole-burning studies of the ionic polymers poly(ammonium styrenesulfonate) and ammonium Nafion are reported. The ammonium groups are doped with a few percent of deuterium, and the irradiation is in the N–D stretching bands. Both polymers show only broad spectral absorption bands, but the narrow spectral holes reveal details of the ammonium group interactions with their surroundings. The results are interpreted by comparison with the hole burning of the model compounds ammonium tosylate and ammonium triflate. Characteristic behavior of the holes shows that some of the local conformations of the models persist in the polymers. Particularly unusual are the changes of hole depth with time: for the Nafion, some holes decay for a period of time, then grow, and then continue to decay—a behavior also observed in the model triflate.

Introduction

Upon irradiating the N–D stretching band of the NH_3D^+ ion, the ion rotates the N–D bond to a new position. A hole results at the original spectral position of the N–D, and an antihole is produced at the new position.¹ The positions of the holes and antiholes and the rates of the hole production and decay are determined by the local environment of the ammonium ion. This makes spectral hole burning a powerful tool for investigating amorphous or partly amorphous materials such as ionic polymers.

To investigate polymers, most spectral hole burning and other spectral excitation methods such as fluorescence excitation have used dyes absorbing in the visible and doped into the polymer. Hole burning of dyes has been investigated for possible use in storing optical information, since polymers form a relatively rigid matrix that “freezes” the changes induced by the radiation.² The visible excitation can also be used to explore the polymer per se and this is what was done, for example, by studying the emission of a ruthenium complex in Nafion films.³ Basically the same idea has been used with a near-infrared absorbing dye in a Nafion film.⁴

Very few infrared studies of this type exist for polymers. The first is probably the hole burning of the OH bands of poly-(hexafluorocumyl alcohol) and similar compounds.⁵ Upon excitation, the OH bond probably rotates, often to weaken the O–H–F hydrogen bond, leading to an antihole at higher frequency. This can be concluded by studying the changes in the 2-haloethanols, which provide a model for the chromophore.⁶ Recently, we hole-burned poly(ammonium styrene sulfonate), which had been doped with a small amount of NH_3D^+ .⁷ At that time, our closest model compounds were various ammonium sulfates.⁸ However, these provide only a very crude model of the ammonium motions in the polymer. We needed to find a reasonable model compound that can be understood in detail, making it possible to elucidate the properties of the chromophore site in the polymer.

We have now investigated two crystalline compounds,⁹ which provide models for ionic polymers. The polymers are poly-(ammonium styrenesulfonate) (PASS) and the ammonium salt of Nafion (copolymerized poly(tetrafluoroethylene) and various perfluorosulfonic acids). Both are relatively simple soluble versions of polymers that in various forms—resins, films, and in solution—have a multitude of uses.^{10,11}

Our model compounds are ammonium tosylate (ammonium *p*-toluene sulfonate) and ammonium triflate (ammonium trifluoromethanesulfonate). The two models are very different from each other, as are the two polymers. In this paper, we describe the hole burning properties of the polymers, compare them to the models, and contrast them with each other.

Experiment

The poly(styrenesulfonic acid) was bought from Polyscience as a polymer of average molecular weight 70 000 in a water solution. The acid solution was neutralized with ammonia in water containing a small amount of D_2O . The sample solution was put on a clean watch glass and dried in a flow of nitrogen to form a film. We found that 3 days was required to form a mechanically stable film. The film was then lifted from the watch glass and sandwiched between two CaF_2 windows that were in turn clamped into the cold head of a closed-cycle refrigerator.

The Nafion was bought from Aldrich as 5 wt % polymer in an alcohol-water mixture. The number molecular weight is reported as 1100. The solution was concentrated about a factor of 2 by pumping away solvent, and then ammonium $\text{H}_2\text{O}/\text{D}_2\text{O}$ was added. The solution was placed on a ZnSe window (a CaF_2 window would probably be dissolved by the strong perfluorinated acid) and dried. Another piece of ZnSe was placed over the dried film, and the sample sandwich was placed into the cold head.

The cold head is mounted on a lathe tool carriage in the beam from a Nicolet 550 infrared spectrometer. A flat mirror in the optical path can be switched to allow the irradiation of the sample by one of a number of lasers. A mask over the sample with a 3 mm hole, together with the use of the same detector for both the lasers and the spectrometer beam, assures that the portion of the sample irradiated is the same as that seen by the spectrometer.

Two different infrared lasers were used for the hole burning. The PASS was burned with a diode laser using MDS 2020 lead-salt diodes (Boston Electronics Corp.) and a Laser Analytics-Spectra Physics SP5150 monochromator as a mode selector. The Nafion films were burned with our pulsed laser system, which uses a LiIO_3 crystal to produce a difference frequency from two visible laser beams.¹²

In previous work on Tutton salts,¹³ we checked carefully that the depth of holes on burning varies linearly with average power over the range that included both the diode and the difference-

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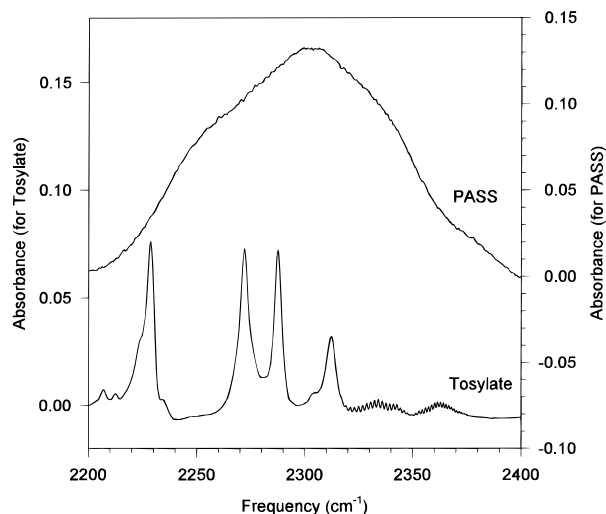


Figure 1. Infrared spectrum of PASS compared to that of ammonium tosylate. Only the N–D stretching region of the spectrum is shown. The spectra are taken at 7 K, the polymer is in the form of a film, and the tosylate is in the form of a mull with mineral oil. Both samples contain some deuterium, which forms NH_3D^+ ions.

frequency sources. Although the pulsed laser has a line width of about 1 cm^{-1} , the bands we have been burning are considerably broader than this.

For the PASS, the diode laser was used. The diode laser beam is linearly polarized and a grid polarizer was used to linearly polarize the analyzing FTIR beam. No polarization dependence of the spectra holes was found, perhaps because the polymer film depolarizes the beam. The power of the laser at the sample was estimated to be $10\text{--}60\text{ mW/cm}^2$. The polymer sample was kept at low temperature for 16 h or more to let it come to equilibrium before burning. The aging period of 3 days did not result in a totally stable film—temperature cycling of the film sometimes produced films with different relaxation times after hole burning. We did not systematically explore the effect of various temperature cycling regimes. After burning, raising the temperature to 45 K was found to be sufficient to erase the holes and antiholes.

For the Nafion, the pulsed laser system was used. Again, the sample was kept at low temperature at least overnight to stabilize. The pulsed laser system is more powerful than the diodes. The average power was limited to what we estimate is $40\text{--}60\text{ mW/cm}^2$ and could be kept approximately constant as the frequency was changed. Typical burning times were only 3–5 min.

Results

Poly(ammoniumstyrene sulfonate). The N–D stretching bands of PASS form a continuous band in the infrared from about $2200\text{ to }2400\text{ cm}^{-1}$ (Figure 1). This is about what is expected on the basis of investigation of ammonium tosylate, the spectrum of which is also shown in Figure 1. The various discrete bands of $(\text{NH}_4)_2\text{SO}_4$ also range from about $2230\text{ to }2440\text{ cm}^{-1}$. By comparing the intensity in the N–H spectral region to that in the N–D region, we estimate that about 10% of the “hydrogen” atoms are deuterium. The film is about $10\text{ }\mu\text{m}$ thick, as determined from the interference fringes in the spectrum. The broad PASS spectrum shows little change on cooling to low temperature, with only a small increase in the overall width of the N–D region.

Holes can be burned at any frequency from $2250\text{ to }2380\text{ cm}^{-1}$ at 7 K. (Below 2250 cm^{-1} , our diodes gave only very little power, and so we could not hole burn at the lower

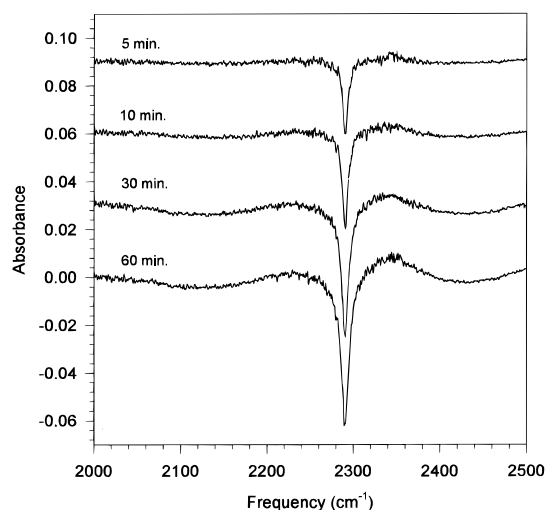


Figure 2. Formation of a spectral hole at 2298 cm^{-1} in PASS as a function of irradiation time at 7 K. The irradiation was with an infrared diode laser. The development of the broad antiholes at each side of the hole can be seen clearly.

TABLE 1: Hole Decay for PASS at 30 K

freq (cm^{-1})	k (10^{-3} min^{-1})	hole filling ^a (%)	frequency (cm^{-1})	k (10^{-3} min^{-1})	hole filling ^a (%)
2272	12.85	75	2310	10.27	64
2282	15.56	71	2318	22.69	56
2292	20.47	74	2327	43.11	54
2300	21.89	68			

^a The holes decay, filling asymptotically to the percentage indicated.

wavenumbers and higher temperatures.) The holes increase logarithmically in depth as the irradiation time increases, yielding Lorentzian-shaped holes. However, the rate of burning then decreases steadily and the hole reaches an asymptotic limit after about 180 min. Antiholes grow simultaneously with the hole and appeared as broad features about 50 cm^{-1} wide at either side of the hole (Figure 2). Note that these antiholes are a bit wider than the 30 cm^{-1} antiholes observed in the mixed sulfates.^{8,14} The mechanism for producing the hole is rotation of the NH_3D^+ ion, thus carrying the N–D bond to a new environment. The broad antiholes show that the polymer environment is somewhat more heterogeneous than that of the mixed, but still crystalline, sulfates, a point we discuss further below. The depth of the holes grows as the logarithm of the time over a large range of times from a few minutes to a few hours. However, the width of the holes grows in a more complicated fashion, reaching an asymptotic limit and, consequently, so does the hole area. This is shown in Figure 3 for irradiation at 2298 cm^{-1} for a sample at 7 K. The variation in the hole width with frequency at two temperatures is shown in Figure 4. This variation is distinctly nonmonotonic in contrast to the variation of width with frequency for holes burned in the mixed sulfates. For the PASS, the maximum of the width is near the region of the three mobile hydrogen bonds of the model tosylate, and we also comment on this below.

The holes decay at a rate that depends on the frequency, and the decay rates are listed in Table 1. A typical decay is shown in Figure 5. A number of features of the decay are noteworthy. The decay of the holes takes on the order of 100 min at 7 K, but the system does not return to its original state. Instead, as shown in Figure 5, the hole fills only about halfway, and the new state is stable for days or longer. Remarkably, the ammonium tosylate shows similar behavior, with the holes

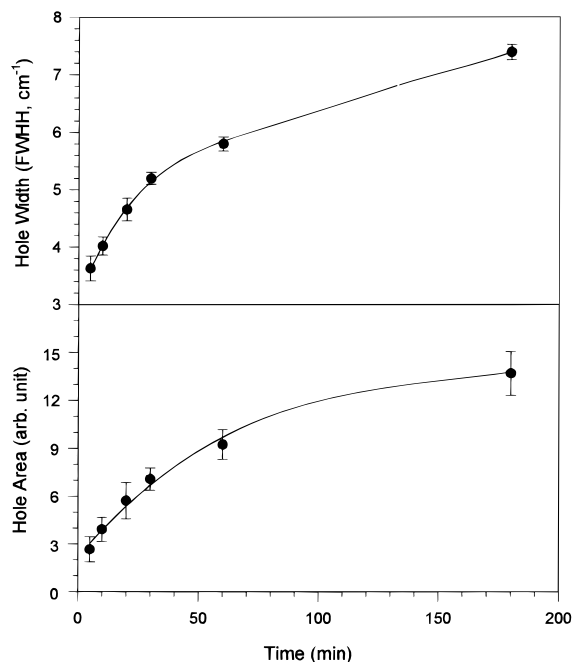


Figure 3. Width and area of a hole at 2290 cm^{-1} and 7 K as a function of time of irradiation. The hole depth grows as the log of the time over this range of times.

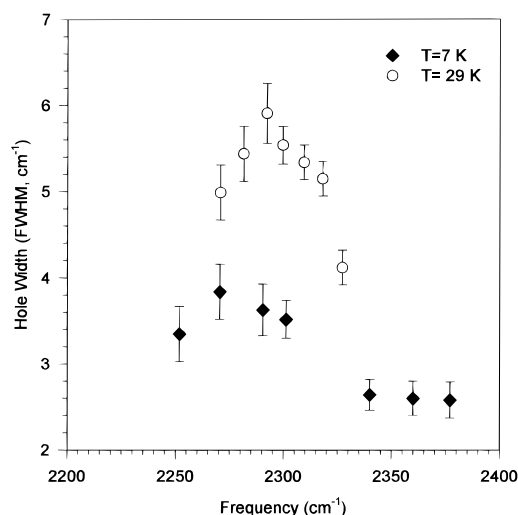


Figure 4. Variation in the hole width with frequency at 7 and 29 K. The width reaches a maximum between 2250 and 2300 cm^{-1} . This behavior is in marked contrast with the monotonic dependence of the width of holes burned in the broad bands of the mixed sulfates.

filling only partway. However, the rates of decay in the polymer are at least 2 orders of magnitude faster than those in the tosylate. Examination of Table I shows that the rate of the faster decay varies almost monotonically with frequency with the faster decay rates at higher frequency. This is similar to the variation in decay rates for the mixed sulfates—the weaker hydrogen bonded N–D sites decay faster. The hole at 2310 shows a marked exception to this trend—similar to the situation in the tosylate, in which band IV (2312 cm^{-1}) decays much more slowly than the other bands.

As the temperature is raised, the holes decay more rapidly, with an abrupt increase in rate at temperatures over 40 K. This type of temperature dependence is typical of most of the systems we have examined previously and is characteristic of decay by tunneling.¹

Ammonium Nafion. The infrared spectrum of the ammonium Nafion is compared with that of its model compound,

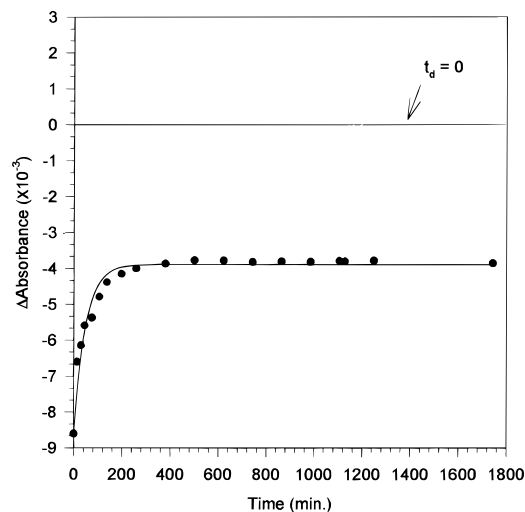


Figure 5. Recovery of a hole at 2275 cm^{-1} and 7 K as a function of time after irradiation. The hole does not fill in completely, but instead the filling reaches a limit after a few hundred minutes.

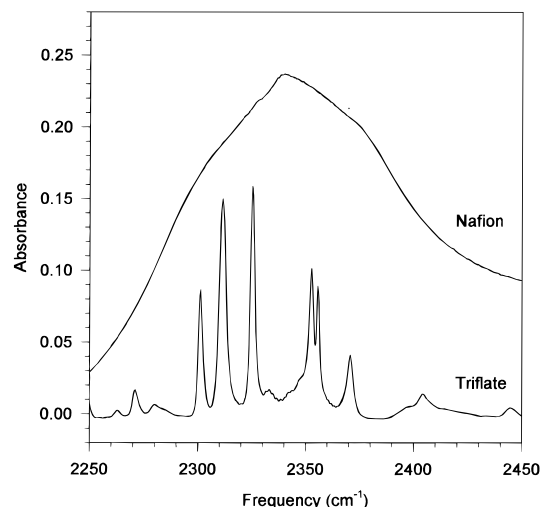


Figure 6. Infrared spectrum of ammonium Nafion and ammonium triflate in the N–D stretching region. Both compounds have been doped with a few percent deuterium. The spectra are at 7 K, and the zero of absorbance is arbitrarily taken at the level of background absorption.

ammonium triflate, in Figure 6. As expected, the polymer band is broad and covers about the same range as the model compound. As for the PASS, the polymer band hardly changes with temperature, with no detectable change in the position of the band maximum.

Holes could be burned at any frequency over the range $2242\text{--}2410\text{ cm}^{-1}$. Figure 7 shows typical holes for a sample at 7 K and 5 min irradiation time. (The laser system used in these experiments could be set to approximately equal power at all the frequencies at which holes were burned.) A broad antihole can be seen to the high-frequency side of the 2242 cm^{-1} hole, even after the short irradiation, and such holes grow on both sides of the holes on longer irradiation. Figure 8 shows the result of increasing irradiation at 7 K and 2300 cm^{-1} . At short times, the hole is accurately Lorentzian. At longer times up to at least 30 min, the width does not change but the hole depth, and therefore also the area, increase. At longer times the width increases. The changes are similar to those observed in the mixed sulfates.

The width of the holes increases markedly with decreasing frequency (Figure 9). Decreasing frequency corresponds to increasing hydrogen-bond strength, and the general trend of increasing width is similar to that seen in the sulfates. The linear

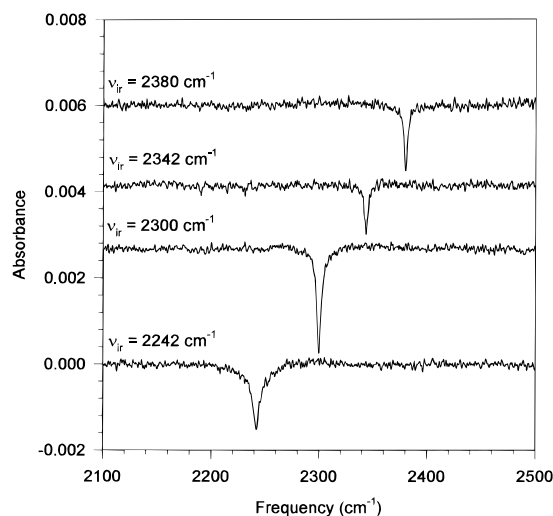


Figure 7. Holes burned in the ammonium Nafion at 7 K by irradiating for 5 min. Note the antihole forming on the high-frequency side of the 2242 cm^{-1} hole.

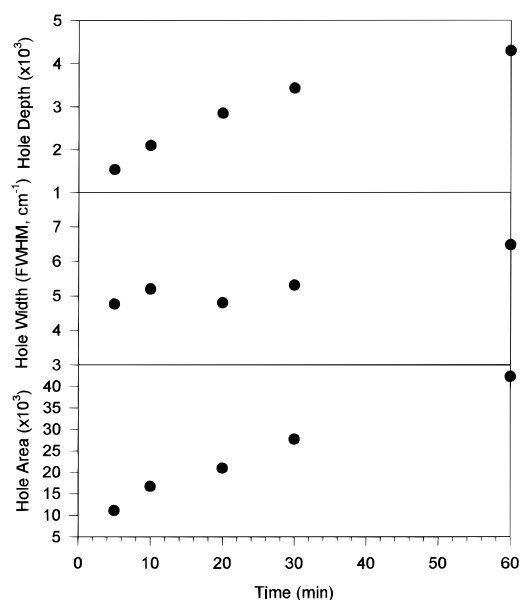


Figure 8. Variation of the hole at 2300 cm^{-1} and 7 K with time of irradiation. The hole depth in absorbance units, the width in wave-numbers, and the area in absorbance units times wavenumbers are plotted as a function of time. Note that all the holes are shallow, amounting to only a few thousandths of an absorbance unit. The width of the hole does not change for about the first 30 min.

dependence of width on frequency is not, however, reproduced in the polymer.

After irradiation, the holes decay. In the ammonium triflate the decay is complicated and involves a number of different ammonium sites (discussed further below), which can grow and decay. The different modes of decay can be classified as one of three types, I, II, and III (Table 2). Type I holes show an approximately exponential decay with a rate constant of 10^{-2} min or larger. Type II are similar but with a smaller rate constant. Type III decays are distinctly biphasic with a slower and a faster decay. The slower decay takes over at about 80–150 min and often the hole *grows* for a short period of time before resuming the decay. This is shown in Figure 10 for a hole at 2275 cm^{-1} at 7 K. The growth interval is reproducible. We have fit these decays by a combination of two exponentials (Table 2), but the time dependence of the hole is more complicated, involving growth terms as well as decays. We have not tried to model this in detail.

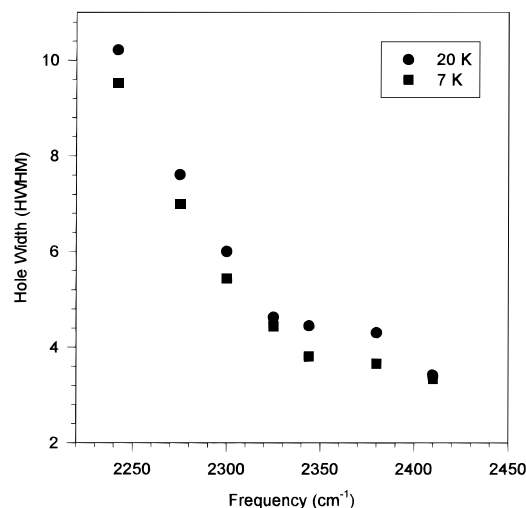


Figure 9. The hole width as a function of frequency at two temperatures. Note the monotonic variation of the hole width in contrast to the PASS (Figure 4).

TABLE 2: Hole Decay Rate Constants for the Nafion at 7 K

freq (cm^{-1})	type ^a	$k[t < 80 \text{ min}]$ (10^{-2} min^{-1})	$k[t > 80 \text{ min}]$ (10^{-3} min^{-1})	$k[\text{overall}]$ (10^{-2} min^{-1})	hole filling ^b (%)
2242	III	7.58	8.69		38
2275	III	5.77	2.29		88
2300	III	3.41	5.78		50
2325	II			0.65	39
2344	III	1.05	4.43		78
2380	I			2.25	77
2410	I			1.48	92

^a The various decays are qualitatively different; see text and Figure 10. Type III decays are fit by two time constants. ^b The holes decay, filling asymptotically to the extent indicated.

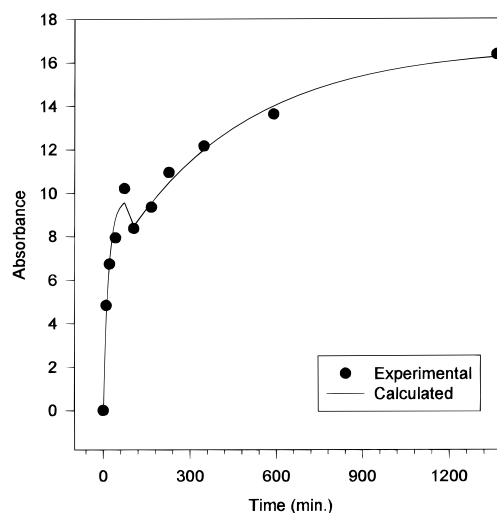


Figure 10. Decay of the hole at 2275 cm^{-1} and 7 K. The downturn in the curve near 150 min is real and is typical of the decay curves we have labeled type III. The drawn curve is just to guide the eye.

Discussion

The two polymers we have studied, PASS and ammonium Nafion, show broad, nearly featureless absorption in the N–D stretching region. The use of dilute deuterium in the ammonium ions is designed to reveal any discrete features, if there are any. Since the N–D bonds are dilute, there is very little N–D, N–D energy exchange which would lead to broad bands, and of course there are only individual N–D stretches and not

collective vibrations such as symmetric and antisymmetric stretches.

The broad band in the polymers then represents the inhomogeneous distribution of the N–D bonds. To resolve the information implicit in the spectrum, we burn holes into the broad distribution and use the parameters of the holes: the efficiency of burning, the nature of the antihholes, the widths of the holes, and the properties of the hole decays to unravel the N–D distribution.

We have studied three systems that can provide information of the holes in our polymers. The first are the mixed sulfates of the form $(\text{NH}_4)_x\text{K}_y\text{SO}_4$ or $(\text{NH}_4)_x\text{Rb}_y\text{SO}_4$. These sulfates are crystalline at all proportions of the ammonium and alkali metal, but they have disordered cation sites, “substitutional cellular disorder.”¹⁵ The result is a broad N–D band in which the properties of the holes vary systematically with frequency and hydrogen bond strength—lower frequency corresponds to stronger hydrogen bonds.

The other two reference systems are ammonium toluene-sulfonate, a model for PASS, and ammonium trifluoromethanesulfonate, a model for the Nafion. These two salts form crystals with discrete N–D stretching bands. The relaxation properties of these bands are complicated, and remarkably, some aspects are reproduced in detail by the polymers.

Both the N–D spectra of the PASS and the Nafion change little, if at all, with temperature. This is in contrast with the O–H bands of the polyfluorinated cumyl alcohols.⁵ These show separate bands due to the free O–H bonds and hydrogen-bonded O–H bonds, and the latter shift with temperature. The O–H bands hole burn much like the bands in the polymers we consider, and it is not clear why there is such a difference in the temperature coefficients of the bands.

On burning the holes, antihholes are formed. These are typically much broader than the holes. This indicates that the narrow distribution of sites burned by the laser changes into a much wider, more disordered distribution. Thus, the bonds that absorb in some narrow frequency range belong to an inhomogeneous distribution. The width of the antihholes is a direct measure of the disorder in frequency space of the sites. For the polyalcohols, the antihholes are on the order of 50 cm^{-1} wide and show considerable structure. This is consistent with the relatively narrow O–H stretching band which contains recognizable structure of both free and hydrogen-bonded O–H and which changes with temperature. The mixed sulfates show featureless antihholes of about 30 cm^{-1} width.^{8,13} In the pure sulfates the antihholes are at the position of the three N–D bands not being irradiated. The N–D bands belonging to the same ammonium group are about 20 cm^{-1} apart in the middle of the spectrum,¹⁶ and this is the width of the antihhole in the mixed sulfates corresponding to the expected result from burning in a situation in which each band is broadened by inhomogeneity. However, the inhomogeneity affecting the irradiated band is not the same as that affecting the bands that form antihholes. The two polymers show wider featureless holes with a width of about 50 cm^{-1} and are thus similar to the mixed sulfates with a bit more inhomogeneity.

Next we compare to the mixed sulfates. The properties of the holes, the widths, and decay rates are monotonic functions of the frequencies and furthermore vary monotonically with composition and temperature. Particularly simple is the linear relation between the frequency and the hole width. This relation holds regardless of composition and thus represents an intrinsic property of the hydrogen (deuterium)–nitrogen bonds that are burned at a given frequency. These bonds are of a given hydrogen bond strength. In the polyalcohols mentioned above,

the width is a monotonic, though nonlinear function of the frequency. For the Nafion, widths are again nonlinear monotonic functions of frequency (Figure 9).

PASS shows a very different relationship, with the plot of width vs frequency showing a distinct maximum (Figure 4). As a given frequency is burned, the ammonium ions at that frequency rotate. The maximum line width of the holes corresponds approximately to the position of the three closely spaced N–D bands in the tosylate (Figure 1). These three bands also are the ones that interchange with one another in burning. The close proximity of the three bands must give lead to relaxation pathways not available to bands that, because of a more strained local environment, are far from the center of the frequency distribution.

Next, we consider hole filling. For the sulfates, the hole filling is a monotonic function of the NH_4^+ concentration, with the slower rates at higher concentrations. The crystals with more NH_4^+ ions form more hydrogen bonds, and so present higher barriers to some modes of motion. For the PASS, the hole filling is also monotonic (Table 1), with the striking exception of the hole at 2310 cm^{-1} . This hole fills about a factor of 2 more slowly than the holes at the neighboring positions. Remarkably, the slowly filling hole is exactly at the position of one of the bands in the tosylate, 2312 cm^{-1} . If this band is burned, the band recovers intensity very slowly, much more slowly than for the other two burnable bands.

The hole filling for the Nafion is even more unexpected. Holes at different frequencies fill at different rates (Table 2). Most distinctive are the holes which fill, then grow for a while, before resuming their filling (Figure 10). This behavior is similar to that of the A holes in the ammonium triflate. The A holes grow at the expense of B holes after excitation, i.e., the B ammonium ions become A ammonium ions. For the ammonium triflate crystal, we suggested that the A and B sites differ by the arrangement of the triflate ion, possibly by the reorientation of the CF_3 . The transfer from B to A then occurs on this reorientation of the CF_3 . For the ammonium Nafion polymer, we do not have an obvious CF_3 group to reorient, but a similar process occurs nonetheless; that is, we postulate that the reorientation of the first ammonium ion leaves the system in a nonequilibrium conformation. The conformation then relaxes toward equilibrium, moving the polymer and changing the local environment of the ammonium ion. The change occurs slowly because some of the conformational changes are by tunneling. We have shown that a similar change happens in mixed Tutton salts $[(\text{NH}_4)_2(\text{Co,Ni})(\text{H}_2\text{O})_6(\text{SO}_4)_2]$. Here, burning of the N–D bands of the ammonium ions (i.e., NH_3D^+) results, after a few hours in the dark, in motion of the water molecules. The water and the ammonium ions are not in direct contact but are separated by the sulfate ions, and the water motion must be driven by propagating strain.¹³

Conclusions

Infrared hole-burning spectroscopy reveals remarkably specific features of the N–D vibrations of our polymers. Comparison with model compounds identifies these features—mostly characteristic modes of decay with specific features of the models. Both polymers must have N–D bonds in the same local environment as the models—for example, the 2310 cm^{-1} in both the PASS and the tosylate. In the ammonium Nafion polymer, the most characteristic feature is the decay with an interval of growth. Details of these features are given in the body of the paper.

The broad antihholes seen in the polymers studied here as well as in the polyalcohols and the mixed sulfates contain information

on the amount of disorder. Finding a quantitative relation between the spectral features and the disorder is a project for the future.

Polymers. The poly(styrenesulfonic acid) solution from Polysciences is CAS No. 28210-41-5 (as 30% in water solution).

The Nafion solution from Aldrich is CAS NO. 66796-30-3 and is a solution with water and low molecular weight aliphatic alcohols.

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