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Infrared Hole Burning and Crystal Structures of Ammonium Tosylate and Ammonium Triflate

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Spectral hole burning the N−D bands of the title compounds doped with a small amount of deuterium reveals new types of changes in the conformation in the crystals at low temperatures. Using X-ray diffraction, the crystal structure of the tosylate is determined and shows ammonium ions that are particularly strongly hydrogen bonded at one N−H. Upon hole burning, the ion pivots about this bond. The triflate forms a crystal with a number of low symmetry sites. Hole burning one type of ion causes changes in the bands that arise from the other type. The switch between different types is probably due to a reorientation of the CF_3 group of the triflate ion.

I. Introduction

We have found that the spectra of crystals of many ammonium salts can be hole burned at low temperatures;[1] the systematic study of the holes and antiholes reveals details of the local structure around the ammonium group, and study of the efficiency of the hole burning and the subsequent decay of the holes provides information on the energy flow in the crystal.[2] So far, most of our studies have been of inorganic compounds, such as ammonium sulfates, Tutton salts, and the like.[1] Spectral hole burning is particularly useful for studying disordered systems, which typically have broad, featureless bands. The hole burning process provides narrow spectral features characteristic of the various environments that give rise to each frequency interval in the broad band. We have previously used this technique in studying disordered mixed alkali-metal ammonium sulfates[3,4] and mixed Tutton salts.[5,6]

Many polymers form solid phases that are, at best, only partially crystallized, and hole burning shows promise of being able to elucidate their local structure.[7] In order to do so, however, we need information on the behavior of model constituents of the polymer. To this end, we have investigated two prototypical ionic monomers, monomers that are also of interest in their own right: the ammonium salt of *p*-toluenesulfonic acid ($CH_3C_6H_4SO_3$ NH_4, ammonium tosylate) and of trifluoro sulfonic acid (CF_3SO_3 NH_4, ammonium triflate). The toluenesulfonate is the repeating unit of the polymer poly(ammonium toluenesulfonate),[7] and the trifluoro compound is a model for fluoronated sulfonic acid polymers such as Nafion (copolymerized polytetrafluoroethylene and perfluorosulfonic acids).[8]

In this paper we elucidate, as completely as possible, the monomer crystal structures and their hole burning spectra, leaving comparison with the polymers for a later paper.

For most organic compounds, the crystal structures have not been determined, especially at the low temperatures at which we conduct the hole burning. When possible, we therefore start by determining the crystal structure and then go on to the hole burning. In some cases, the X-ray crystal structure does not match the hole burning results, and we conclude that a phase transition has occurred somewhere between the temperature of the crystal structure determination (either room temperature or 170 K) and the much lower temperatures of the hole burning. Here, we explore one example in which the crystal structure is well-characterized and one in which a phase transition has occurred to a new form.

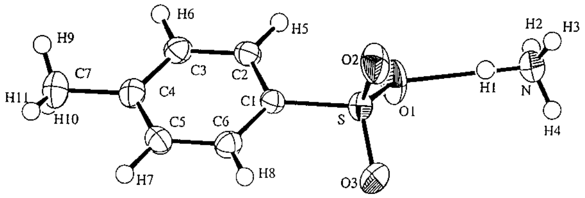

Figure 1. ORTEP plot of ammonium tosylate showing the arrangement of a single set of ions with their numbering. In Table 1, B_{eq} is the spherically arranged thermal parameter for the heavy atoms and simply the isotropic thermal parameter, B_{iso}, for the hydrogen atoms.

This paper presents the results of the first organic salts we have studied, and we find that the motions of the NH_3D^+ ions are quite different from those in the inorganic systems. The ammonium motions in the tosylate and in the triflate also differ strikingly from one another.

II. Ammonium *p*-Toluenesulfonate

A. Crystal Structure. Ammonium tosylate (ATS) easily forms crystals on evaporating an ammonia−water solution of the acid (Aldrich). The crystal structure was determined at 161 K.[9]

ATS forms an orthorhombic crystal of space group $P2_12_12_1$ or D_2^4 (No. 19) with unit cell dimensions $a = 6.189$ Å, $b = 7.034$ Å, and $c = 20.324$ Å and $Z = 4$. The numbering and the arrangement of the atoms in one molecule are shown in Figure 1, and the coordinates are given in Table 1, together with the values of the thermal factors.

As for many ionic crystals, the structure consists of the tosylate anions and the ammonium cations packed in alternating layers. The anion layers have alternating tosylates with their SO_3 groups pointing "up" and "down" along the *c* axis. We are particularly interested in the hydrogen bonds and these are listed in Table 2. The hydrogen bonds are between the NH_4 and the SO_3 oxygen atoms. Three of the hydrogen atoms participate in more or less linear H bonds. The remaining hydrogen (H_2) is in a bifurcated H bond. The ammonium ion is in a site of C_1 symmetry, and each of the H atoms is nonequivalent to the others.

The remaining bond distances and angles, as well as the nonbonded contact distances, seem to be normal. The space

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TABLE 1: Atomic Coordinates for $CH_3C_6H_4SO_3NH_4$ with Values of the Isotropic Temperature Factor

atom	*x*	*y*	*z*	B_{eq}
S	0.09876(6)	−0.00236(8)	0.101395(16)	2.27(2)
O1	−0.1343(2)	−0.0115(3)	0.10139(5)	3.80(6)
O2	0.1825(3)	0.1727(2)	0.07359(6)	3.87(7)
O3	0.2007(3)	−0.1644(2)	0.06922(6)	3.36(7)
N	−0.4212(2)	−0.0022(3)	−0.00272(7)	2.59(6)
C1	0.1809(2)	−0.0095(3)	0.18441(6)	1.97(6)
C2	0.0423(3)	0.0535(2)	0.23344(8)	2.21(7)
C3	0.1104(3)	0.0480(2)	0.29851(8)	2.42(7)
C4	0.3132(2)	−0.0193(3)	0.31559(7)	2.35(7)
C5	0.4492(3)	−0.0826(2)	0.26593(8)	2.46(7)
C6	0.3854(3)	−0.0778(2)	0.20042(8)	2.40(7)
C7	0.3846(4)	−0.0269(4)	0.38647(8)	3.4(1)
H1	−0.316(3)	0.004(4)	0.0310(9)	3.9(4)
H2	−0.561(4)	−0.010(4)	0.0199(10)	6.5(5)
H3	−0.421(5)	0.087(3)	−0.0242(11)	4.0(6)
H4	−0.391(4)	−0.106(3)	−0.0299(9)	3.3(5)
H5	−0.102(3)	0.104(2)	0.2217(7)	2.1(3)
H6	0.017(2)	0.102(2)	0.3324(7)	2.5(4)
H7	0.593(3)	−0.143(2)	0.2796(8)	3.1(4)
H8	0.478(2)	−0.122(2)	0.1678(7)	2.1(4)
H9	0.343(4)	0.080(3)	0.4082(10)	4.7(5)
H10	0.285(4)	−0.122(3)	0.4098(11)	5.9(6)
H11	0.531(5)	−0.042(4)	0.3901(12)	7.5(7)

TABLE 2: Hydrogen Bonds in Ammonium Tosylate[a]

atoms			distance/Å	angle/deg	B/Å$^{2\,b}$	ν/cm$^{-1\,c}$
O_1	H_1	N	2.758	172	3.9(4)	2229.5
O_2	H_2	N	3.144	151	6.5(5)	2312.7
O_2	H_3	N	2.801	162	4.0(6)	2273.0
O_3	H_4	N	2.807	168	3.3(5)	2288.8
O_3	H_2	N	2.978	142		
O_3[d]	H_4[d]	N[d]	2.88[d]	174		2236.9

[a] The hydrogen atoms are between the two heavy atoms; the distance is between the heavy atoms and the angle is the O−H−N angle. [b] The isotropic thermal factor of the H atom. [c] The frequency of the corresponding N−D stretching vibration measured at 7 K. [d] For ammonium sulfate by neutron scattering (ref 20).

group is noncentric, but refinement to either of the two enantiomorphic forms leads to identical *R* values, so we assume that the crystal examined was in fact an inversion twin.

More details are available as Supporting Information.

B. Infrared Spectra. Our hole burning technique has worked on the spectra of NH_3D^+ dilute in NH_4^+-containing crystals. The N−D stretches typically form a series of relatively sharp bands at about 2300 cm^{-1}, with patterns of bands characteristic of the various possible environments of the N−H bonds. A set of such spectra for ammonium tosylate is shown in Figure 2. The spectrum at 7 K shows the expected four bands and in Table 2, the frequencies of these bands are correlated to the crystallographic N−D−O (N−H−O) distances.

Returning to Figure 2, we see that the various changes with temperature are continuous, and so no phase transition is indicated. We can therefore assume that the structure we determined at 161 K is the structure over the entire temperature range. The four N−D change in different ways as a function of temperature. The highest frequency band (2313 cm^{-1}), which corresponds to the weak bifurcated H bond, broadens very rapidly as a function of temperature and disappears from the spectrum by about 30 K. The rapid change correlates with the exceptionally large thermal parameter for H_2 (Table 2). The next two bands, which arise from the two H bonds of about the same length, simply broaden and merge into a band which keeps its integrity up to room temperature. The lowest frequency band arising from the strongest H band remains relatively the same for the entire temperature range.

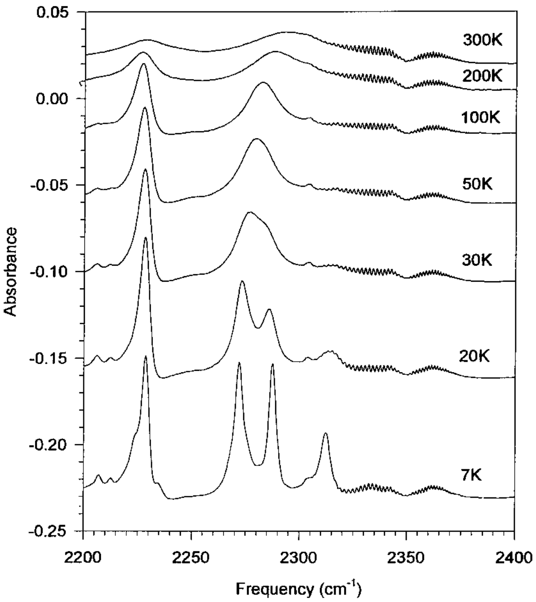

Figure 2. Infrared spectra of ammonium tosylate, which was doped with 5% deuterium to form some NH_3D^+. The spectral region is of the N−D stretches, and the four bands expected appear at low temperature. Note the rapid changes with temperature. (The structure centered at about 2350 cm^{-1} is uncompensated absorption by CO_2 in the optical path.)

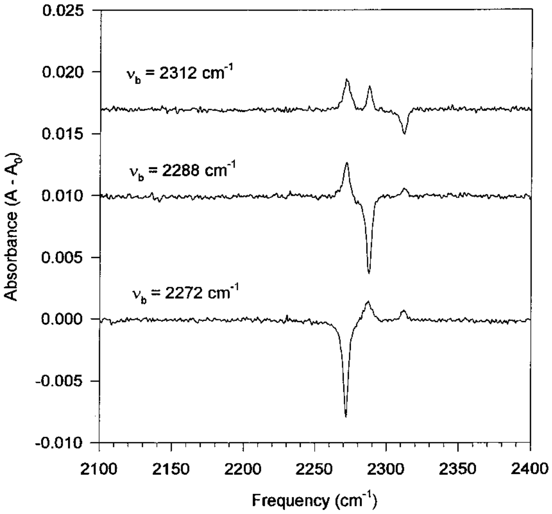

Figure 3. Hole-burning spectra of ammonium tosylate doped with NH_3D^+ ions at 7 K. Irradiating the bands indicated results in a hole at the position of the irradiation and in antiholes in the other two higher frequency bands. The lowest frequency N−D band at 2229.5 cm^{-1} shows neither a hole on irradiation nor an antihole on irradiation of one of the other bands.

The hole burning was done as in our previous experiments using our difference-frequency laser.[10] Trying to burn each of the four bands in turn, we obtain the results summarized in Figure 3. Irradiating any one of the three higher frequency bands causes a hole in that band and antiholes in the other two. All attempts to burn the lowest frequency band (2230 cm^{-1}) were unsuccessful. Some properties of the three holes are listed in Table 3.

The relaxation times were estimated at 40 K, a temperature at which the holes decayed with half-times of a few days. The decays do return the bands towards their original intensities, but only partway. In other words, the decay occurs on at least two time scales, with the first on the order of days at 40 K and the second too slow to determine at this temperature. (We do not list the times since we do not understand the kinetics.)

TABLE 3: Properties of the Spectral Holes in ATS

N−D band	ν_{N-D}/cm^{-1}	width/cm$^{-1\,a}$	area (%)^{b}
II	2272.0	4.24	1.45
III	2288.8	4.88	1.35
IV	2312.7	4.85	1.44

[a] fwhh at 7 K. [b] As a percentage of the original area of the band at 7 K.

The data are consistent with a hole burning process in which the NH_3D^+ rotates away from the position of the irradiated N−D. The rotation occurs about the 3-fold axis of the ammonium—the 3-fold axis that goes through N−H bond 1. This N−H is held in a H bond considerably stronger than the other H bonds, and it neither hole burns nor forms antiholes after hole burning of other bands. The variation observed in the relaxation rates in the dark for the three holes is presumably due to the differences in energy among the different orientations of the NH_3D^+ ions and to differences in the coupling of the orientational coordinates to the lattice.

III. Ammonium Triflate (ATF)

A. Crystal Structure. The crystal structure of ATF at 20 °C has been previously determined.[11] The crystal has space group *P*4/*nmm* or D_{4h}^{7} (No. 129) with $Z = 2$. The unit cell dimensions are $a = 7.7176(3)$ and $c = 6.052(3)$ Å. The crystallographic data refined to a highly-symmetric disordered structure with the layers of the triflate ions alternating with the ammonium cations in planes normal to the *c* axis. The triflate ions are alternatively "up" and "down" along the *c* axis, a bit like the tosylate ions discussed above. The C and S atoms each occupy *c* positions, and the F and O atoms are arranged around these. The six F atoms for the two molecules occupy 8 i and 16 h positions, and so each crystallographic position has an occupancy of $^1/_4$. The O atoms occupy another set of i and h positions. The ammonium groups occupy the a positions of D_{2d} symmetry, and all the N−H bonds are equivalent. The hydrogen bonds are from the nitrogen to the disordered oxygen atoms, with an O−H−N distance of 2.49 Å to the oxygen in the i position and a distance of 2.78 Å to the two nearest oxygen sites in the general h position. Comparison to the tosylate (Table 2) suggests that these are strong hydrogen bonds, but each oxygen site has only a fractional occupation and so the average hydrogen bond is much longer and weaker. (See further discussion of "average" below.)

As is typical of many disordered crystals, ammonium triflate apparently undergoes a phase transition to a lower-temperature, less symmetric form.[12] When crystallized at 173 K, the structure is reported to be $P4_12_12$, D_4^{4} (No. 92), or $P4_32_12$, D_4^{8} (No. 96), with $Z = 8$. Only the unit cell dimensions are known, with $a = 7.16$ and $c = 24.08$ Å. The unit cell is thus 4 times that of the room temperature structure with four different pairs of molecules along the *c* axis. The possible sites for the ammonium groups are two nonequivalent sets of four a sites of C_2 symmetry or one set of eight equivalent b sites of C_1 symmetry. The a sites would give two N−D stretching lines for each type of ammonium or four lines altogether; the b sites would give one set of four N−D stretching lines.

Since we do not have a complete structure for the ammonium triflate, we briefly review the structure of some crystals made of similar molecules. The crystal structure of oxonium triflate (H_3O^+ $CH_3SO_3^-$) has been measured at a number of temperatures by X-ray and neutron diffraction. The H-bond stoichiometry is different than that of the ammonium compound since the oxonium ion has three hydrogen atoms to H bond with the three oxygen atoms of the triflate. The oxonium and the triflate form alternating layers and the three O−H−O distances are about 2.55, 2.58, and 2.67 Å, respectively.[13,14] Ammonium methylsulfonate is similar to the triflate except that the methyl group is substantially smaller than the trifluoromethyl group.[15] The C, S, and N atoms are in a line, and the three hydrogen bonds have one O−H−N distance of 2.8 Å and two symmetry-related distances of 2.9 Å. The remaining hydrogen has no close hydrogen-bonding contacts. This would lead to a N−D stretching spectrum of three bands, two close together and the third at a considerable distance to higher frequency.

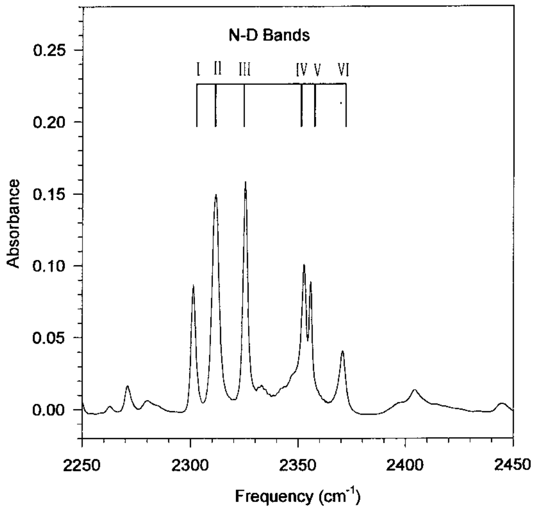

Figure 4. Spectrum of NH_3D^+-doped ammonium triflate at 7 K. The N−D stretching region of the infrared spectrum is shown. The existence of at least six N−D bands shows that there must be at least two nonequivalent ammonium sites. The unlabeled bands in the spectrum are also present in the nondeuterated spectrum and are not N−D stretching bands.

In thinking about the crystal structure of the triflate, the question of possible hydrogen bonding of the ammonium to the CF_3 group arises. The available evidence is not clear. The highly symmetric molecules ammonium silicon hexafluoride and ammonium phosphorus hexafluoride form a number of crystal structures.[16,17] Both of the compounds have cubic crystal structures at room temperature that change into more asymmetric forms at low temperatures. The N−H bonds apparently point to the center of the figure formed by a number of Si−F or P−F bonds, for example, the triangle formed by three F atoms. This arrangement could be due to either dynamic effects or static disorder. In any case, there is no evidence for a simple classical hydrogen bond. On the other hand, studies of the ionic fluoride $KF\cdot 2H_2O$ show clear evidence of hydrogen bonding from both the OD infrared spectrum and neutron diffraction.[18]

The molecule 2-fluoroethanol (CH_2FCH_2OH), which is perhaps closer to the triflate ions, has been studied extensively by both infrared and NMR spectroscopies.[19] The most recent study, which included comparison with model compounds and with ab initio calculations, concluded intramolecular hydrogen bonding was *not* important in determining the observed conformer distribution of fluoroethanol in solution.

B. Infrared Spectra. The N−D stretching region of ammonium triflate containing some NH_3D^+ is shown in Figure 4. This spectrum is taken at about 7 K and shows six N−D stretching bands. These must come from at least two inequivalent ammonium sites. The variation of the spectrum with temperature is shown in Figure 5. The six bands broaden and come together, and the spectrum collapses substantially between 75 K and 100 K. This change corresponds to a phase transition from the *P*4/*nmm* structure at room temperature to the one of the more asymmetric structures at low temperature.

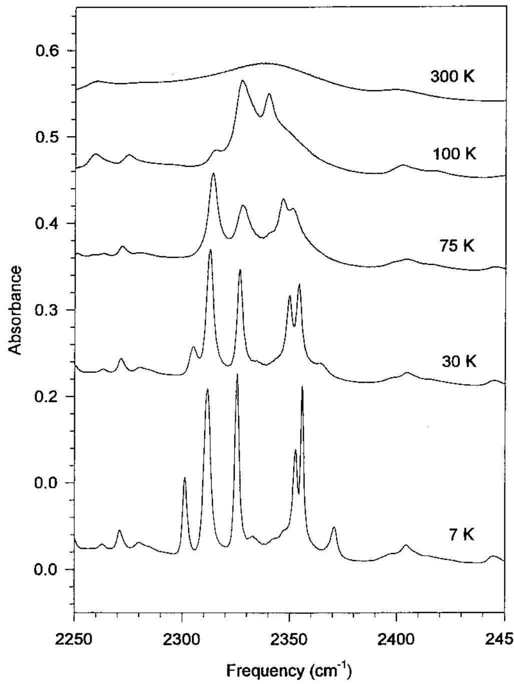

Figure 5. Spectrum of the NH_3D^+-doped ammonium triflate as a function of temperature. A phase transition probably occurs near 100 K.

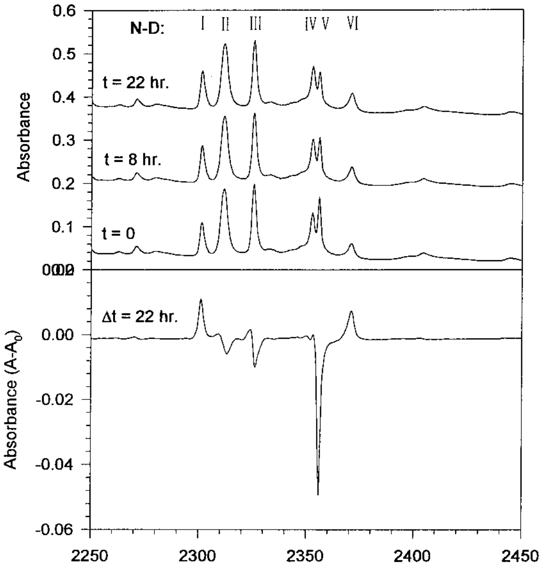

Figure 6. Variation of the spectrum of ammonium triflate with time at 7 K. The sample is cooled to 7 K in a closed cycle refrigerator over a period of about 2 h and then the spectrum is followed as a function of time. The cooling amounts to a temperature jump and the ammonium groups slowly tunnel toward equilibrium. The bottom panel shows a difference between the spectrum at $t = 0$ and $t = 22$ h.

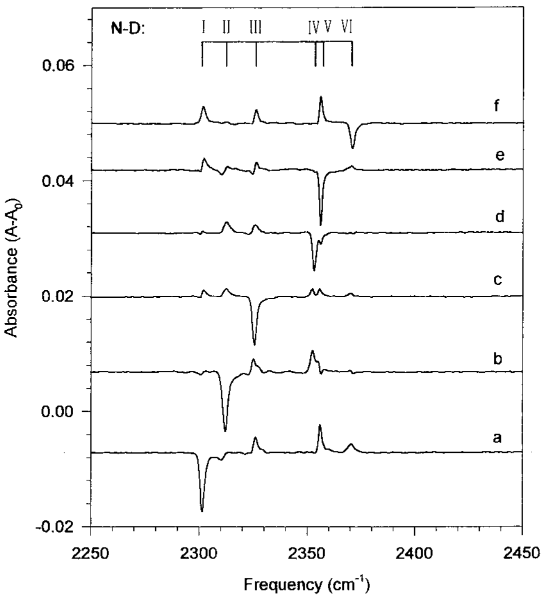

Figure 7. Results of irradiating each band in turn. Panels a−f correspond to burning bands I to VI, respectively. The bands form two overlapping sets I, III, V, and VI and II, III, and IV. The clearest is panel f, which shows the antiholes at I, III, and V on burning band VI. For further discussion, see the text. The spectra are at 7 K and each irradiation was for 3 min.

TABLE 4: N−D Stretching Bands of Ammonium Triflate at 7 K

N−D band	ν/cm^{-1}	identification	
I	2301.5	A_1	
II	2311.5		B_1, B_2
III	2325.3	A_2	B_3
IV	2352.7		B_4
V	2355.8	A_3	
VI	2370.8	A_4	

We have often found that freshly prepared samples of ammonium salts are not at equilibrium with respect to the distribution of the N−D in the four possible positions about each ammonium ion and that the spectrum changes with time. This is the situation with ammonium triflate, as shown by a sequence of spectra at 7 K in Figure 6. Both the spectra and a difference spectrum are shown. On irradiating each of the bands, we see the various holes and antiholes as shown in Figure 7. Comparing Figures 6 and 7, we see that the bands are connected in two sets, “A” and “B”. In set A are bands I, III, V, and VI; in set B are II, III, and IV. Note this assignment suggests that band III has both A and B components. The relatively large area of band II suggests that it is a double consisting of the superposition of two B bands. The notation and position of the various bands is summarized in Table 4.

Burning band I(A_1) produces antiholes at A_2, A_3 or A_4 (Figure 7a), thus clearly identifying these bands. Similarly burning A_2, A_3, or A_4 produces antiholes at the other three positions (Figure 7c,e,f). Burning band A_4 gives a clean result, as does burning A_1, but the other burns give more complicated results. Burning B_1 and B_2 (Figure 7b) gives the expected antiholes at B_3 and B_4. Spectrum d shows the result of burning B_4.

The burns that result in many antiholes, such as that in panel c, affect both the A and B sites, and this provides evidence for the assignment of band III as consisting of A_2 and B_3. Similarly, bands IV and V are a closely spaced pair, and exciting one of the pair (spectrum d) tends to affect both the A and the B sites. Returning to Figure 6, we see that, as a function of time, band V goes down while I and VI go up; this is the rotation of ammonium A ($A_3 \rightarrow A_1, A_4$). The B site shows small changes, and the shape of the change in band III makes it clear that it consists of at least two components. The hole burning shown in Figure 7 can be repeated at temperatures up to about 30 K. However, by 50 K, only band II can be burned.

Figure 8 shows that the N−D holes are narrower in triflate than in the tosylate (Table 3) and approach that of the narrowest N−D bands we have seen.[3] However, the widths hardly change with frequency or with temperature (7−30 K), in marked contrast to the ammonium sulfate systems.[3]

After a hole is burned, more information often results from studying the hole decay. We carried out such studies at 30 K,

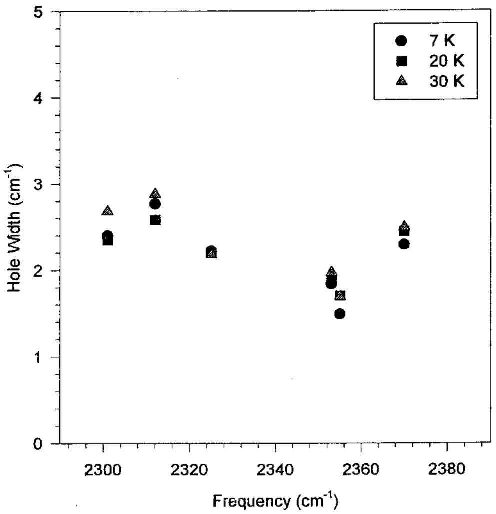

Figure 8. Width of the holes (fwhh) as a function of frequency and temperature. The holes are narrow and have a very weak dependence on the frequency.

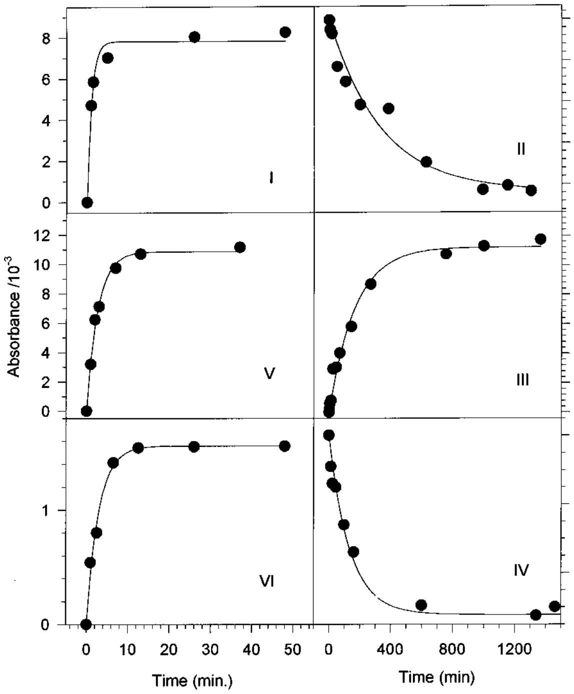

Figure 9. Recovery of the holes as a function of time at 30 K. Note the order of magnitude difference in the time scales with I, V, and VI relaxing much faster than II, III, and IV. Also note that holes II and IV *grow* as a function of time.

since the decays at 7 K took unreasonably long times. As we have mentioned above, we were still able to burn holes at 30 K. It turns out that the decay occurs on two quite different time scales. The faster set of relaxation times belong to the A ammonium group. Figure 9 shows the recovery of the holes after burning. In Figure 9, panels labeled I, V, and VI show the decay of the holes that result from the A group. These take a few minutes. The A antiholes decay with comparable rates.

The B holes behave very differently. The band II hole increases in depth (the hole gets bigger) as time goes on. The time scale is also much longer—hours instead of minutes. The band IV hole also grows with time, while the band III hole decays slowly. The kinetics are more complicated than implied by Figure 9. Figure 10 shows that irradiating band I initially causes antiholes at III, V, and VI, as we have already noted. The holes and the antiholes all decay. But simultaneously bands II, III, and IV, that is, the B bands, develop holes which subsequently decay on the longer time scale. The second series of spectra show the results of irradiating band II, causing antiholes at III and IV. Now we see the slow growth of the A antiholes (for example, band I). We conclude that the perturbation caused by the various irradiations tends to force the change of ammonium ions from B sites to A sites.

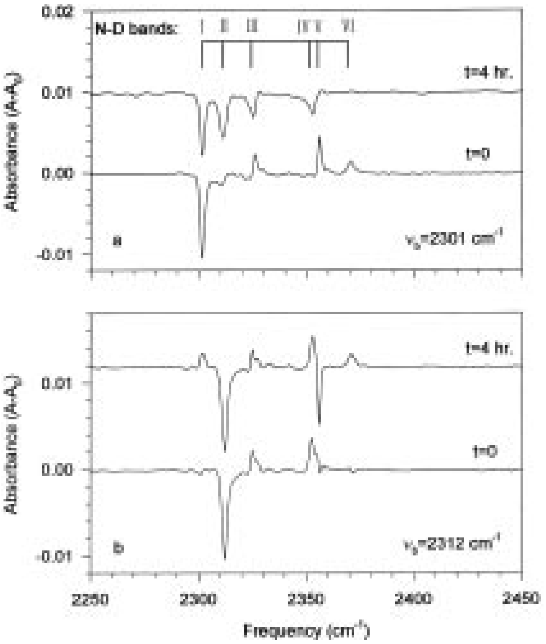

Figure 10. Time-dependent decay of the burned spectra. The spectra illustrated are the difference between the burned spectrum and the original. In panel a, the decay of the burned band I is shown at $t = 0$ and $t = 4$ h. In panel b, the decay of the burned band II is shown.

TABLE 5: Kinetics of the Reorientation of NH_3D^+ Ion in Ammonium Triflate after Laser Irradiation

band	freq/ (cm^{-1})	10^3 min^{-1} ($T = 20$ K)	hole filling[a]	10^3 min^{-1} ($T = 30$ K)	hole filling[a]
I	2302	8.3	89.6	90.5	71.9
II	2312	3.5	82.2	3.2	27.6
III	2326	3.4	52.9	6.0	90.9
IV	2352	4.2	66.7	7.4	38.8
V	2356	9.6	89.6	37.3	89.0
VI	2370	17.0	85.2	33.5	70.9

[a] The hole filling is given as the ratio of the hole and the initial absorbance, i.e., $(A - A_{ir})/(A_0 - A_{ir}) \times 100$, where A, A_{ir}, and A_0 are the band absorbance after reequilibration, after laser irradiation, and before irradiation, respectively.

There is another attribute that distinguishes between the A and B sites. The rate of relaxation of the faster A bands increases a factor of 2−10 between 20 and 30 K (Table 5). In contrast, the rate for the B bands increases by a factor of less than 2.

We have seen indirect motion induced by hole burning in only one other experiment. In the mixed Tutton salt $(NH_4)_2(Co_x,Ni_{1-x})(H_2O)_6(SO_4)_2$, the hole burning and rapid relaxation of the N−D bands are followed by much slower motion of the HDO molecules on the metal. The motion of the ammonium and water molecules must be coupled through a complex multidimensional potential energy.

In ammonium triflate, the various possible positions of the F atoms and the O atoms provide the likely source of disorder. At room temperature, the relatively symmetric crystal has a range of possibilities. At one extreme, we picture the CF_3 and SO_3 groups rotating rapidly and providing an average structure with the $^1/_4$ atom occupancy that is observed. At the other extreme, we envision a crystal made up of a disordered arrangement of ammonium ions, each stuck in a different configuration of the CF_3 and SO_3 groups. A possible arrangement of this sort is shown in Figure 2 of ref 11. The real situation is undoubtedly in between these two extremes. At low temperatures, the crystal becomes more asymmetric, but little is known about the ammonium sites and the possible disorder. Our infrared results suggest that there are two sites, A and B. The A site behaves as expected at short times, but at longer times or burning the B site leads to continued depletion of the B bands. Thus, burning either the A or B bands leads to a transformation of B into something else, probably A sites. Rotation of the surrounding CF_3 groups would accomplish this. The behavior of the A bands at long times is complicated and must involve rates of tunneling of the ion from A to different A positions, rates for the transformation of B to A, and rates for the interchange of the B positions. Our data are insufficient to allow determination of all these rates. We note that heating the crystals to 60 K and recooling to 7 K restores the original spectrum and thus the A/B distribution.

IV. Discussion

The simplest model of the motion of the NH_3D^+ is of an ion held in an asymmetric site and thus giving rise to four distinct N−D stretching bands. Irradiating one band rotates the ions that give rise to that band into the three other positions. Irradiating a second band rotates the ion out of the second position and so on for irradiating each of the bands. The decay of both the holes and the antiholes reverses this, with each hole decaying by transfer of intensity from the other three bands (the ammonium ion rotating to put the N−D bands into the position of the hole). This model accounts for our results in inorganic ammonium salts including the sulfate, nitrate, and the Tutton salts (ammonium hexaaquo metal sulfates). The salts of the organic acids studied here give distinctly different results.

The ammonium ion of the ammonium tosylate sits in a site with a number of distinctly different hydrogen bonds and moves as if attached around hydrogen bond $N-H_1-O_1$. Only the other three bands can be burned and produce both holes and antiholes. The three bands relax among themselves. Although the pivot hydrogen bond is strong, it is of about the same strength as others that behaved in the expected manner and that can be burned. An example is the shortest bond in ammonium sulfate, which gives rise to a relatively high-frequency band with parameters that are listed in Table 2 for comparison. The H---O distance for the sulfate and that for our tosylate are nominally the same (1.82 Å), and the N−D frequencies are very close: 2236.9 cm^{-1} for the sulfate and 2229.5 cm^{-1} for the sulfonate.

The behavior of the ammonium ion in the triflate is also unexpected. One problem with our analysis is that we do not know the detailed structure of the crystal. The high-temperature form is well characterized by X-ray analysis and shows disorder. A phase transition occurs at about 100 K, leading to a crystal that is presumably similar to the high-temperature one. The low-temperature crystal probably has the disorder seen in the high-temperature form frozen in—leading to a variety of fixed ammonium sites. The frozen-in disorder likely freezes to discrete positions, i.e., a complicated crystal rather than a glass, as evidenced by our observation of discrete, sharp N−D stretching bands.

The ammonium bands arise from two types of sites, A and B. The A site initially behaves as expected—burning any of the four bands produces holes and antiholes that decay in the normal way. However, after a period of time, the A holes transfer to B holes. If the B sites are first disturbed by irradiation, the holes grow from the beginning. The A and B sites must differ by some relatively small rearrangement of the molecules of the crystal. We suggest that these sites differ by the arrangement of the CF_3 groups and that to transfer ammonium from B to A requires only a subtle rearrangement (reorientation) of the neighboring CF_3 groups.

In the mixed Tutton salts referred to above, the HDO molecules move after burning the NH_3D^+ ions. This shows explicitly that it is possible to propagate a disturbance through the crystal and end up in a configuration not originally present. For the triflate, our evidence is indirect since we see only a change among various ammonium bands. However, a reorientation of the CF_3 is the motion we think takes the least energy. Note that the motion induced is still local in the sense that burning only a single ammonium ion can induce a change—the hole burning does not induce crystallization or other massive change in the sample.

Organic compounds provide an endless variety of conformations. We have just begun to elucidate the motions possible in some of them.

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Supporting Information Available: Details of the X-ray diffraction analysis of ammonium tosylate (14 pages). See any current masthead page for ordering information.

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