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Burning Holes into the Spectrum of Ammonium Salts: Low-Temperature Transformations Initiated by Vibrational Excitation

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Introduction

At low temperatures (~10 K), the ammonium ion of many ionic salts can be rotated using the appropriate infrared irradiation. Subsequently in the dark, the ion will rotate back to its original position. Both the infrared-driven rotation and the dark return are characteristic of the ammonium ion and its surroundings and provide unique information on energy transfer, tunneling, and kinetics in crystals and glasses. For the ordered crystals, the positions of all the atoms are known in both the equilibrium system and the irradiated one, and so the path of the transformation can be visualized. For crystals that contain disorder and for amorphous solids, hole burning explores the inhomogeneous distribution of ammonium ion sites.

Our experiments are actually done on NH_3D^+ dilute in the solid. If the NH_3D^+ is in an asymmetric site, each NH_3D^+ can sit in one of the four distinguishable orientations. The infrared spectrum then shows four N−D bands, one for each orientation of the NH_3D^+. Irradiation of one of the N−D bands with an infrared laser rotates the ions that correspond to that band. This is indicated by a decrease in the absorption of the irradiated N−D band (a spectral hole) and an increase in the absorption of one or more of the other three N−D bands (antiholes).

The technique reviewed here provides (1) analytical information on the ammonium sites, (2) band assignments, (3) relaxation times for the N−D vibration under a variety of conditions, and (4) information on the kinetics of the various dark processes, especially tunneling.

The ammonium ions in ionic salts participate in a wide variety of motions in crystals, from simple reorientational motion to complex phase transitions. Such motion has been shown by many different methods: X-ray and neutron diffraction, heat capacity measurements, and magnetic resonance and other spectroscopies.[1,2] The ammonium ions—very often—occur in crystal structures in which all four of their hydrogen atoms participate in hydrogen bonds. The hydrogen bonds range from apparently straightforward linear bonds as in various cubic phases of the ammonium halides to hard-to-understand “bifurcated” hydrogen bonds. These latter are hydrogen bonds in which the N−H is close to *two* other electronegative atoms such as oxygen.[3] It is not surprising, then, that even a stoichiometrically simple ammonium salt such as NH_4NO_3 has as many as five solid phases that differ from one another by the relative orientation of the ammonium and nitrate ions.[1] The complex arrangements give rise to interesting properties; for example, ammonium sulfate has a phase transition from a paraelectric to a ferroelectric phase.[2]

The energy required to rotate an ammonium ion varies widely and depends on both the strength and arrangement of the hydrogen bonds holding the ion in place. The minimum barrier to rotation among the simple salts is probably for ammonium perchlorate (3 kJ/mol)[4] and among more complicated salts for ammonium tetraphenylborate (0.2 kJ/mol).[5,6] High barriers to reorientation exist for salts such as ammonium fluoride (39 kJ/mol).[4] Reorientation of the ions by laser irradiation has been successful with ions held with barriers of intermediate height—8−24 kJ/mol. Ions with lower barriers tunnel too rapidly to be observed,[7] and those with higher barriers cannot be moved with our 2300 cm^{-1} photons of energy 27 kJ/mol.

The rate of rotation or reorientation of ammonium ions can be investigated by NMR, typically by measuring the temperature dependence of a line width. Other possible measurements of the rate use dielectric relaxation[1] or the frequency-dependent acoustic response. Again, even such a simple salt as ammonium sulfate has a complex response, since there are two crystallographically distinct ammonium sites, each with a distinct set of orientational barriers and consequent time response.[2,8]

At the temperatures typical for our experiments (4−50 K), kT is about 0.02−0.4 kJ/mol, a range of about a factor of 10. The Boltzmann factor for activated processes, $\Delta E/kT$, is then on the order of 10−1000. This says that the over-the-barrier rates are negligible at the lower temperatures and that the holes must refill by *tunneling* through the barrier.

Herbert L. Strauss was born in Aachen Germany, March 26, 1936. He attended Columbia University (New York), earning an A.B. in 1957, an M.A. in 1958, and a Ph.D in 1960. His Ph.D. research was in magnetic resonance with George K. Fraenkel. He then studied with Charles A. Coulson at Oxford and came to Berkeley in 1961. He is now a Professor of Chemistry as well as the Associate Dean for Undergraduate Affairs for the College of Chemistry. At Berkeley his research has been in the vibrational spectroscopy of molecules undergoing fluxional or conformational motion.

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(1) Parsonnage, N. G.; Staveley, L. A. K. *Disorder in Crystals*; Oxford: Oxford, 1978; 926 pp.

(2) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; Benjamin: New York, 1968; 284 pp.

(3) Templeton, D. Private communication. I once asked D. Templeton what crystals would have bifurcated bonds. He answered (by way of saying that no principles are known), “Just try crystals that are likely to have hydrogen bonds, and every tenth hydrogen bond will be bifurcated”.

(4) Smith, D. *Chem. Rev.* **1994**, *94*, 1567−1584.

(5) Roberts, M. P.; Clavell-Grunbaum, D.; Strauss, H. L. *J. Chem. Phys.* **1987**, *87*, 6393−6405.

(6) Roberts, M. P.; Cavagnat, R. M.; Lucazeau, G.; Boquet, J. F.; Strauss, H. L. *J. Chem. Phys.* **1990**, *93*, 7632−7638.

(7) For example, we have not been able to detect a hole on irradiating NH_4ClO_4 (barrier of about 3 kJ/mol). The hole—if one is produced—probably refills rapidly by tunneling. Faster detection schemes might see such a hole.

(8) Burrows, W.; Strauss, H. L. *J. Chem. Phys.* **1990**, *93*, 7510−7512.

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Spectroscopy

The spectroscopy of hydrogen-bonded systems has been investigated, especially by vibrational spectroscopy, since the 1940s. The standard summary of the information known in 1960 is in the book of Pimentel and McClellan.[9] The hydrogen bonds are often pictured as X−H···Y, where X and Y are heavy atoms, typically O, N, and S. In a series of hydrogen bonds formed by water with other molecules, as the strength of the hydrogen bond goes up, the X−H bond length increases, the frequency of the X−H stretch goes down, the intensity goes up, and the width increases. The correlations involving water are mostly monotonic;[9] those involving the ammonium ion are well characterized, but more complicated.[10] The use of deuterium substitution to provide spectra of isotopically isolated species such as HDO (for H and D), NH_3D^+ (for D), and ND_3H^+ (for H) minimizes the effect of both intramolecular and intermolecular couplings and leads to more direct information on an individual hydrogen bond.[11,12] Isotopic substitution was exploited as a systematic method for the exploration of hydrogen bonding by M. Falk and his co-workers, and it was the discovery of the temperature dependence of the spectra of HDO and NH_3D^+ (as well as our own observations on other molecules) that made us try the hole-burning experiments.[13]

In the compounds we have hole-burned, the ammonium ion occupies a locally asymmetric site (C_1), and so an NH_3D^+ ion can sit in one of four distinguishable orientations. The N−D region of the spectrum then shows up to four N−D stretching bands at low temperatures. Figure 1 shows the spectra of NH_3D^+ dilute in ammonium nitrate[14] at a number of temperatures. Below 100 K, the expected four lines appear. At 150 K, the bands are already merged in pairs, and at room temperature the bands are further broadened. The changes, which are typical, are due partly to phase transitions and partly to other mechanisms.

On lowering the temperature, the four N−D bands appear with different intensities due to two quite different factors. The first—already mentioned—is that the intrinsic intensity varies with hydrogen bond strength. The second factor is more subtle; the energy of the NH_3D^+ ion is slightly different in the different orientations. Consider a hypothetical molecule HXD with two possible orientations and two D−X stretching bands, one for each orientation, 10 wavenumbers apart. A calculation shows that the HXD and DXH molecules will then differ in energy in the crystal by about 2 cm^{-1} due to the differences in the zero point energy.[15] This small energy difference has a substantial effect at low temperatures. There is, of course, no assurance that a system disturbed by either a temperature jump or laser excitation will return to its equilibrium configuration at low temperatures. If it does not, the variation of intensity in the N−D stretches may be the result of the thermal history of the sample.

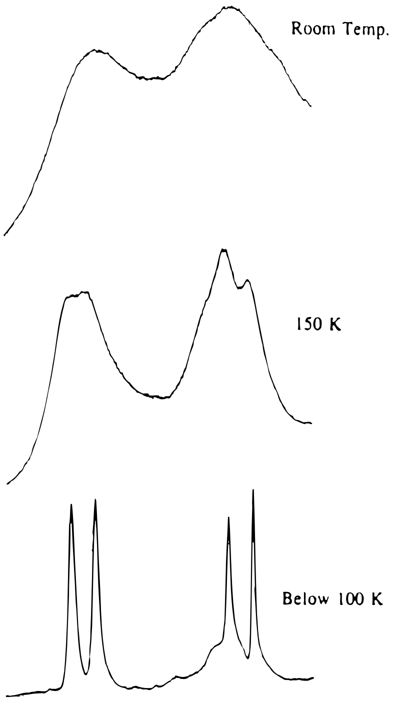

FIGURE 1. Infrared spectral N−D stretching region as a function of temperature of NH_3D^+ dilute in ammonium nitrate. At low temperature, the four bands are at 2282, 2294, 2359, and 2371 cm^{-1}, respectively. The broadening with temperature is due to thermal motion and, perhaps, to the solid−solid phase transition near or somewhat below room temperature. Reprinted with permission from ref 14. Copyright 1992 American Institute of Physics.

Hole Burning

Hole-burning spectroscopy is a technique that has advanced with the improvement of excitation sources. Most optical hole-burning spectroscopy is done in the visible, taking advantage of the widely available and powerful visible lasers. These experiments typically burn holes in the spectral band of a dye molecule and provide information on properties of the vibronic levels of the molecule.[16,17] Visible hole burning has interesting potential applications, for example, as the basis for data storage technology.[18]

Infrared hole burning started with the availability of first laser diode sources[19] and advanced with improvements of these and other tunable infrared sources. The various X−D stretches occur at about 2000−2500 cm^{-1} and are within the range of both the diodes and of difference frequency generation done by taking the difference between two visible or near-infrared lasers in a nonlinear crystal.[20]

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(9) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, 1960; 475 pp.

(10) Kearly, G. J.; Oxton, I. A. *Adv. Infrared Raman Spectrosc.* **1983**, *10*, 111−143.

(11) Hrostowski, H. J.; Pimentel, G. C. *J. Chem. Phys.* **1951**, *19*, 661−662.

(12) Hiebert, G. L.; Hornig, D. F. *J. Chem. Phys.* **1952**, *20*, 918−919.

(13) Brink, G.; Falk, M. *Can. J. Chem.* **1970**, *48*, 2096−2103. See also: Brink, G.; Falk, M. Private communication.

(14) Weier, J.; Strauss, H. L. *J. Chem. Phys.* **1992**, *96*, 8799−8805.

(15) If the difference between the X−D stretches in the two possible orientations is 10 cm^{-1}, the difference between the two X−H stretches will be 14 cm^{-1}. The difference between the zero point energies will be half that of the difference in energy between HXD and DXH, so it will be 2 cm^{-1}.

(16) Moerner, W. E., Ed. *Persistent Hole-burning: Science and Applications*; Springer: NY, 1988; 315 pp.

(17) *Persistent Spectral Hole Burning*; Moerner, W. E., Small, G. J., Eds. *J. Opt. Soc. Am.* **1992**, *9* (5) (entire issue). Jankowiak, R.; Hayes, J. M.; Small, G. J. *Chem. Rev.* **1993**, *93*, 1471−1502.

(18) Maniloff, E. S.; Altner, S. B.; Bernet, S.; Graf, F. R.; Wild, U. P. *Appl. Opt.* **1995**, *34*, 4140−4148.

(19) Dubs, M.; Gunthard, H. H. *Chem. Phys. Lett.* **1979**, *64*, 105−107.

(20) Kung, A.; Fei, S.; Strauss, H. L. *Appl. Spectrosc.*, **1996**, *50*, 790−794.

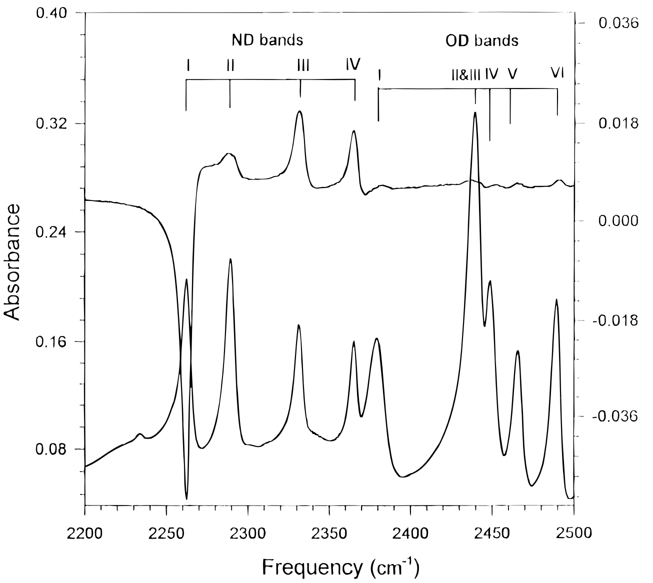

FIGURE 2. Hole burning of the 2262 cm^{-1} band of NH_3D^+ in $(NH_4)_2Co(H_2O)_6(SO_4)_2$. The lower spectrum is the original spectrum at 7 K; the upper spectrum is the difference between the sample after 30 min of laser irradiation at the position of ND band I and the original. Reprinted with permission from ref 21. Copyright 1995 American Chemical Society.

The N−D stretches of NH_3D^+ have proved remarkably easy to hole burn. Irradiating one of the stretches of a Tutton salt, ammonium cobalt hexahydrate sulfate [$(NH_4)_2Co(H_2O)_6(SO_4)_2$], for example, burns the band, as shown in Figure 2.[21] The other three N−D bands *increase* in intensity as the first N−D band decreases. The NH_3D^+ ions that are irradiated are those with an orientation that puts the N−D in a position to give rise to band I. These ions then rotate to positions II, III, and IV. The spectrum also shows the six OD stretching bands that are produced since the deuterium substitutes for the hydrogen in the water as well as in the ammonium ions. The O−D bands do not change, ruling out such conceivable processes as N−D dissociation.

The hole-burning process thus requires the conversion of energy from the N−D stretch into libration/rotation. The ammonium ions are in asymmetric sites with hydrogen bonds that are often not linear, and a simple mechanical picture gives a qualitative model of the conversion process. Figure 3 shows such a picture for one of the sites of ammonium sulfate and makes it obvious that stretching an N−D band can provide a torque.[22] Switching to a quantum mechanical picture, the process looks more like that in Figure 4, in which excitation of the N−D stretch is followed by tunneling either in the vibrationally excited manifold or in the ground state manifold. We have found that the hole-burning efficiency, that is, the probability of having a conformational change once the N−D stretch is excited, is relatively unaffected by changes in either temperature or librational barrier height, and this allows us to conclude that the librational change occurs as tunneling in the vibrationally excited state.[22]

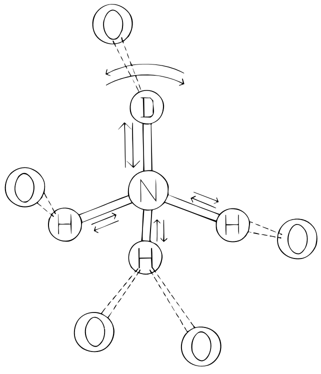

FIGURE 3. The surroundings of the ammonium ion in site 1 of ammonium sulfate. The N−D−O hydrogen bond pictured is nonlinear, and excitation of the N−D stretch produces a torque. Reprinted with permission from ref 22. Copyright 1993 American Institute of Physics.

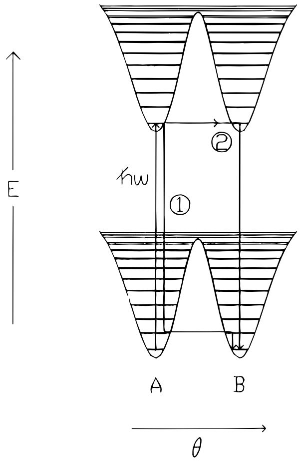

FIGURE 4. Schematic diagram of the energy levels and energy transfer involved in the hole-burning process. θ is a rotation angle for the ammonium ion, and only two of the four possible positions of an NH_3D^+ ion are shown. The vibrational quantum $\hbar\omega$ is about 2300 cm^{-1} and excites the system to another manifold of libration/rotation states. The excited molecules probably fall rapidly to the lowest librational level and then tunnel before the vibrational energy decays (path 2). One of the alternate paths, 1, is also shown; here the molecule decays to an excited libration of the ground vibrational state and then tunnels. Reprinted with permission from ref 22. Copyright 1993 American Institute of Physics.

The ammonium ion motion can be pumped by irradiating combination bands; for example, the N−D stretch can be burned and the ammonium ion can be rotated by irradiation of the combination band, $\nu_L{}^I + \nu_S{}^I$ ($\nu_L{}^I$ is a librational mode of the NH_3D^+ with the D in orientation I and $\nu_S{}^I$ is the corresponding N−D stretch).[23] The combination band can be weak; in the case of the Tutton salts it need not even be detectable in the absorption spectrum (Figures 5 and 6).[23] In small gas-phase molecules, it is known that energy can transfer from vibrations in a mode selective way.[24] The same is true for small molecules in a matrix that has no modes that can easily accept the energy.[25] It is, however, surprising that, in a complex ionic hydrogen-bonded crystal, the energy can still propagate efficiently and selectively.

The N−D bands burn homogeneously; that is, they burn over their entire width, at least on our time scale on

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(21) Fei, S.; Strauss, H. L. *J. Phys. Chem.* **1995**, *99*, 2256−2261.

(22) Cho, H.-G.; Strauss, H. L. *J. Chem. Phys.* **1993**, *98*, 2774−2782.

(23) Fei, S.; Yu, G. S.; Li, H. W.; Strauss, H. L. *J. Chem. Phys.* **1996**, *104*, 6398−6400.

(24) Green, W. H.; Moore, C. B.; Polk, W. F. *Annu. Rev. Phys. Chem.* **1992**, *43*, 591−626.

(25) Shirk, J. S.; Marquardt, C. L. *J. Chem. Phys.* **1990**, *92*, 7234−7240.

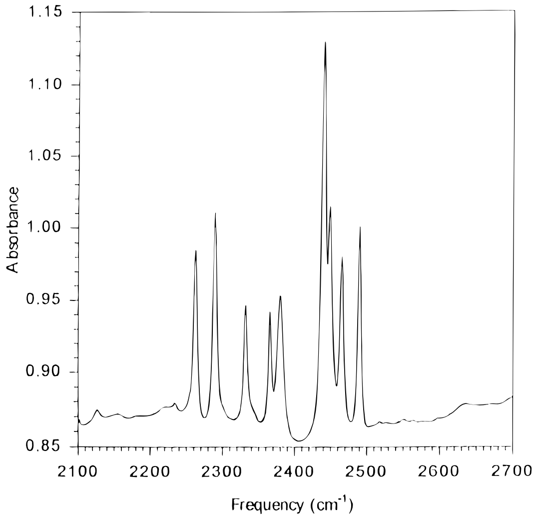

FIGURE 5. N−D and O−D stretching region of the deuterium-doped ammonium nickel Tutton salt, showing more of the baseline than Figure 2. The bands are assigned as in Figure 2. Reprinted with permission from ref 23. Copyright 1996 American Institute of Physics.

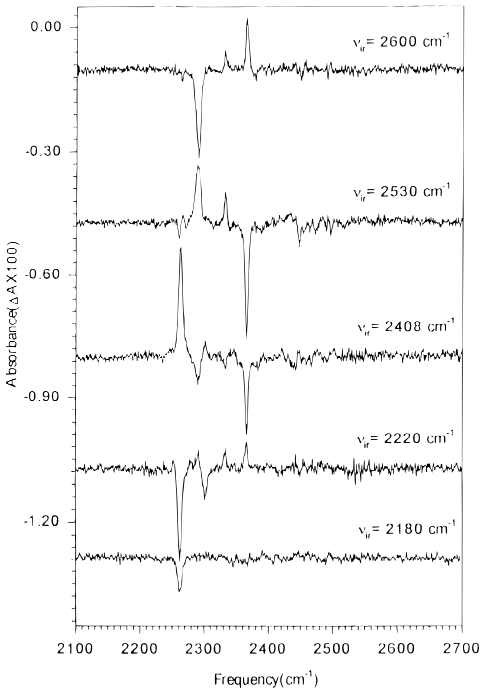

FIGURE 6. Difference spectra resulting from irradiating *away* from the fundamental absorption bands in the ammonium nickel Tutton salt. For example, irradiating at 2600 cm^{-1} (see Figure 5) results in burning the N−D band at about 2260 cm^{-1}. Note that the effects of irradiation are specific; each irradiation frequency produces a different result. Reprinted with permission from ref 23. Copyright 1996 American Institute of Physics.

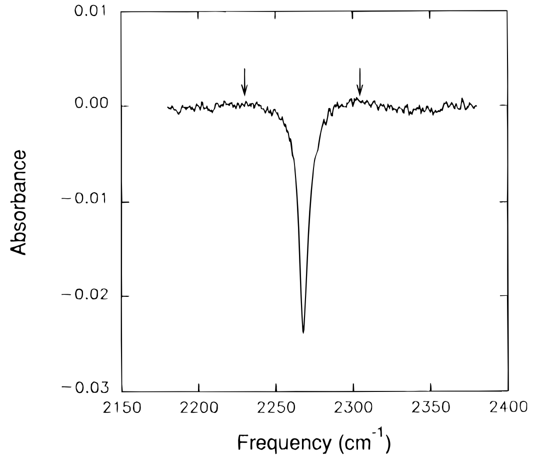

FIGURE 7. A spectral hole of $[(NH_4)_xRb_{(1-x)}]_2SO_4$ ($x = 0.52$) shown as an infrared difference spectrum. The arrows show the weak antiholes produced together with the hole. Reprinted with permission from ref 26. Copyright 1993 American Institute of Physics.

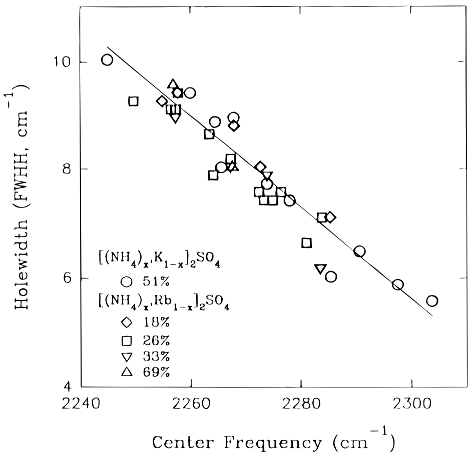

FIGURE 8. Hole width (FWHH) vs the center frequency of holes such as that in Figure 7. The holes were all burned at 7.5 K at less than 5 min of irradiation with a diode laser. The different crystals are indicated by different symbols, labeled by the fraction of cations that are ammonium ions. Reprinted with permission from ref 26. Copyright 1993 American Institute of Physics.

the order of minutes. The intrinsic widths of the bands can be obtained by hole burning in samples with very broad N−D absorption features, such as crystals with disorder. We digress to describe one such set of crystals, the ammonium alkali-metal sulfates.[22,26] Ammonium sulfate and alkali-metal sulfates form mixed crystals, all of the same structure. However, these mixed crystals have ammonium sites with various alkali-metal or ammonium ion neighbors. The corresponding N−D stretches form a continuous distribution. Holes can be burned into the continuous band (Figure 7). The width of such a band in the limit of weak hole burning is twice the *homogeneous* width of the line.[27,28] Remarkably, the width of these bands is a linear function of the frequency (Figure 8) and is the same over a considerable range of different systems. This linear dependence is similar to that of the width of absorption lines in classical hydrogen-bonded systems at room temperature—systems such as phenol in a variety of solvents.[9] I suggest that the stretching vibrational absorption bands for the classical systems are also homogeneous and that their line width and that of the low temperature holes are determined by interaction with modes local to the hydrogen bond, perhaps the D−Y stretch or the X−D···Y bend.

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(26) Cho, H. G.; Strauss, H. L. *J. Chem. Phys.* **1993**, *99*, 5661−5667.

(27) Friedrich, J.; Swalen, J. D.; Harrer, D. *J. Chem. Phys.* **1980**, *73*, 705−711.

(28) The usual distinction between homogeneous and inhomogeneous effects assumes considerable separation of time scales with respect to the time scale of the experiment. Situations in which such a separation is not possible must be discussed in a more sophisticated manner: Mukamel, S. *Principles of Nonlinear Optical Spectroscopy*; Oxford: New York, 1995; 543 pp.

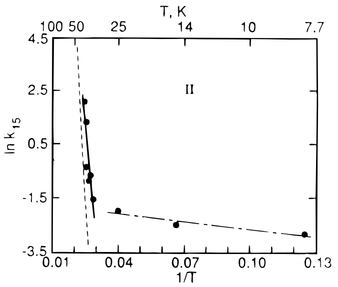

FIGURE 9. One of the rate constants for reorientation in ammonium sulfate. The data are plotted as ln *k* vs 1/*T* and fit to straight lines. The low-temperature data have an apparent activation energy, E_a/hc, of 6.4 cm^{-1}; the temperature dependence is due to phonon-assisted tunneling. The high-temperature data have an apparent activation energy of 571 cm^{-1}. The classical over-the-barrier rate is shown as the dashed line with an activation energy of 1026 cm^{-1}. The observed rate conforms to quantum mechanical transition-state theory. The classical and quantum mechanical curves must merge at still higher temperatures. Reprinted with permission from ref 8. Copyright 1990 American Institute of Physics.

Dark Kinetics Hole Filling

The hole-burning process prepares the system in a state characterized by ammonium ions in a nonequilibrium distribution. This distribution will eventually decay back to equilibrium. As discussed above, the temperature is too low to allow the ions to reorient by over-the-barrier processes in a reasonable time and the reorientation observed occurs by tunneling. There are four N−D orientations, each one of which can reorient to one of three others. The 12 possible transitions obey first-order kinetics, and such a system of interconnected rates can be solved.[29] By studying the decay of the NH_3D^+ orientations in a Tutton salt after burning each of the N−D bands in turn, we have determined the rate constants.[30] As in many complicated rate problems, it is difficult to obtain enough data to determine all possible rates independently, and we have used a kinetic model in which some of the rate constants are set equal. For the Tutton salt at 7 K, we find tunneling constants of 1/60 to 1/20 h^{-1}.[31]

The rate constants increase with temperature, first slowly and then more rapidly. At the lowest temperatures, the tunneling is phonon-assisted; that is, the tunneling system exchanges energy with the phonon bath.[32,33] For the ammonium ion in ammonium sulfate, we have been able to follow the recovery process from about 7 to 60 K (Figure 9).[8] The barrier to ammonium reorientation[34] is known from NMR and is about 1000 cm^{-1}. The tunneling kinetics at temperature above about 30 K follows a "quantum-mechanical-transition-state" model.[35] This model makes many of the same assumptions as traditional over-the-barrier theory[36] and adds up the tunneling contributions from each librational level. As the temperature is raised, successively higher librational levels are populated, leading to kinetics with an apparent activation energy of about 570 cm^{-1} instead of the expected 1000 cm^{-1}.

In ordinary chemical kinetics, both electron and nuclear transfer, there is typically a temperature range in which the kinetics is activated and one in which the kinetics is temperature independent.[37,38] Here we see an activated region essentially due to tunneling. The low-temperature, "temperature-independent" region is not quite temperature-independent either, although it must become so in the limit as $T \rightarrow 0$.

Disorder

New phenomena appear as we introduce disorder into the crystals. The most delicate disruption of the crystal structure is found in mixed Tutton salts $(NH_4)_2Co_x$-$Ni_{1-x}(H_2O)_6(SO_4)_2$. These mixed salts have the same structure for all values of x with just slight variations in the average unit cell dimension.[39] $Co(H_2O)_6^{2+}$ and Ni-$(H_2O)_6^{2+}$ occur randomly in the crystal, but the local variation in their distribution leads to strain. The N−D stretches look similar to those for the pure Tutton salts, but the strain lowers the average barrier to rotation and leads to considerably faster relaxation times.[21] The N−D bands can be burned as in the pure salt and then relax back to equilibrium. Now this is accompanied by a much slower relaxation of the HOD molecules on the metal hexaaquo ions.[21,40,41] How is this possible? The NH_4^+ (or NH_3D^+) ions and the water molecules are not even in direct contact; they are separated by sulfate ions. The original reorientation of the ammonium ion by hole burning must create additional strain in the crystal, strain which propagates and eventually allows the water to reorient as well. The reorientation of both the ammonium and the water occurs by tunneling, resulting in the long times—hours or days—required to observe the reorientation. A nice picture is provided by Trommsdorff et al.[42] Imagine the potential energy surface as a dimpled pool-table surface. The configuration of the crystal system is represented by the position of a pool ball. The ball starts at a local equilibrium position—a pocket. It is raised to the surface of the table by the infrared radiation and then tunnels from depression to depression, eventually falling into another pocket, which is, perhaps, far in configuration space from the first one.

As the amount of disorder in a sample increases, the N−D bands broaden into a featureless band. This is what happens to the mixed salts $[NH_4Rb_{1-x}]_2SO_4$, discussed

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(29) Matson, F. A.; Franklin, J. L. *J. Am. Chem. Soc.* **1950**, *72*, 3337−3341.

(30) Only 6 of the 12 rate constants are independent since the 12 constants obey 6 conditions of equilibrium.

(31) Trapani, A. P.; Strauss, H. L. *J. Am. Chem. Soc.* **1989**, *111*, 910−917.

(32) Phonon-assisted processes were first extensively studied in magnetic systems, and a good discussion is in the following: Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Oxford: Oxford, 1970; pp 541−583.

(33) Sussman, J. A. *Phys. Condens. Matter* **1964**, *2*, 146−160.

(34) There are two different (distinguishable) ammonium sites in $(NH_4)_2$-SO_4. The parameters we quote are for the ion with the faster relaxation time. We also need to account for the zero point energies in discussing barriers; see ref 8.

(35) Hanggi, P.; Talkner, P.; Borkovic, M. *Rev. Mod. Phys.* **1990**, *62*, 251−341.

(36) Johnston, H. S. *Gas Phase Reaction-Rate Theory;* Ronald Press: New York, 1966; 362 pp.

(37) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; Wiley: New York, 1981; pp 370−372.

(38) Benderskii, V. A.; Makarov, D. E.; Wight, C. A. *Chemical Dynamics at Low Temperatures*; Wiley: New York, 1994; 385 pp.

(39) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Quesada, J. E. *Inorg. Chem.* **1993**, *32*, 4861−4867.

(40) Fei, S.; Strauss, H. L. *J. Phys. Chem.* **1996**, *100*, 3414−3417.

(41) Adding a small amount of D_2O to the solution from which we crystallize the salt forms some HOD as well as some NH_3D^+.

(42) Trommsdorff, H. P.; Corval, A.; von Laue, L. *Pure Appl. Chem.* **1995**, *67*, 191−198.

above. It is also the situation for the ammonium salts of ionic polymers, such as poly(ammonium styrenesulfonate). Such polymers form amorphous solids, and so little is known about their structure. Holes can be burned into such a band; they look just like the holes in the mixed sulfates (Figure 7).[43] The holes do vary in their properties—depth, width, rate of relaxation, temperature coefficients, etc.—and we have found that these changes can be correlated to the properties of the salts of simple monomers.[44] The monomers can in some cases be crystallized, and so the properties of the holes can be used to deduce the local structure in the polymer. Different polymers show quite different hole properties[44] and interesting relaxation kinetics, which promise to reveal much new information.

Conclusion

Infrared irradiation puts a relatively small amount of energy into a molecule, and in a low-temperature solid often results in a spectral hole. Both the production of the hole and its subsequent decay in the dark provide a new tool with which to elucidate the local properties of the probe molecule. In this Account, I have discussed hole burning of ammonium ions in both single crystals and in crystals and amorphous systems with progressively more disorder.

Some of the phenomena that have been considered are vibrational energy transfer from vibrations to specific librations—even from combination bands, the relaxation of vibrational states as a function of hydrogen bond strength, introduction of strain in a mixed crystal leading to reorientation of water molecules many angstroms away from the ammonium ions, the variation in tunneling rates with temperature, and the variation of sites within disordered systems.

In the near future, I expect that we will be able to obtain much more information on ammonium sites in polymers. Still to come are hole-burning experiments on other infrared chromophores, experiments that will open up new types of solids to investigation.

I thank R. G. Snyder for his encouragement and continuing good advice. I thank him and J. R. Scherer, who remembered literature reports of temperature-dependent splittings of bands in crystals, and M. Falk, who suggested the Tutton salts. I am indebted to my co-workers who pioneered in carrying out the hole-burning spectroscopy and who are acknowledged indirectly in the footnotes. I acknowledge continuing support from the National Science Foundation (Grant No. CHE-9526754).

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(43) Cho, H-G.; Strauss, H. L. *J. Chem. Phys.* **1993**, *99*, 10068−10069.
(44) Chen, Z.; Fei, S.; Strauss, H. L. To be published.