Infrared Hole-Burning of Crystalline Ammonium Copper Tutton Salt: Tunneling Kinetics and Jahn−Teller Distortions

Yun-Hwan Cha and Herbert L. Strauss*

Department of Chemistry, University of California, Berkeley, California 94720-1460

Received: July 24, 2001; In Final Form: November 20, 2001

Irradiation of the N−D stretching band in crystalline deuterium-doped ammonium copper Tutton salt rotates the ammonium ion and changes the conformation of molecules about the copper. The crystal salt exists in at least two different crystal forms, each form containing a particular Jahn−Teller distorted copper conformation. We consider only the "A" form crystal. In this crystal, the minority conformation (B) appears with the majority conformation (A) as the temperature is raised. The spectral holes and antiholes produced by the changes in conformation occur in patterns that depend on the exact frequency of irradiation. Each pattern appears and eventually decays with different kinetics over a range of times. The variation of the hole widths, measured at different temperatures, reveals the presence of various conformations in the crystal lattice. This inhomogeneity is related to the statistical distribution of conformations A and B weighted by their thermal populations. The kinetics of the decay of the holes yields the rate constants of transformation from one conformation to the other. The numerical values and the kinetic model agree well with the experimental data.

I. Introduction

The Tutton salts form a series of isomorphous compounds containing a divalent metal cation. Typically, the metal exists in the form of a nearly octahedral complex ion formed with six water molecules. The divalent copper ion ($3d^9$: $t_{2g}{}^6$, $e_g{}^3$) is special, since its surroundings are subject to strong Jahn−Teller (J−T) distortions. The ammonium copper Tutton salt, AmCuTS, $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$, is particularly remarkable, because it can crystallize in at least two different crystal structures. Each of these is in the monoclinic space group, $P2_1/a$ (No. 14) ($Z = 2$), which characterizes the Tutton salts in general,[1] but each contains the $Cu(H_2O)_6{}^{2+}$ ion distorted in a different way. The components of the AmCuTS crystal form a complicated three-dimensional hydrogen-bonding network; the six water molecules around the Cu^{2+} ion are hydrogen bonded to the sulfate ions, which are in turn hydrogen bonded to the ammonium ions. In attempts to understand the behavior of these unique crystals, they have been extensively studied by crystallography (X-ray and neutron diffraction), infrared and visible spectroscopy, and electron paramagnetic resonance (EPR).[2−5] There are three CuO_6 possible J−T conformations in AmCuTS. The lowest energy one, conformation A, has a long Cu−O(7) distance with shorter Cu−O(8) and Cu−O(9) lengths. The conformation B is estimated to be 1.9 kJ/mol higher in energy.[6] Conformation B, has a long Cu−O(8) distance, and shorter Cu−O(7) and Cu−O(9) lengths. Conformation C, with Cu−O(9) the longest, is considerably higher in energy, and does not play a role at the temperatures we consider.

The different J−T conformations occur in two distinct circumstances. The first occurs at low temperatures where conformation A is in the "A" crystal and B is in the "B" crystal. In the second, some of the copper complex ions in the B conformation appear in the A crystal as the temperature is raised. The changing population of the A and B conformations then produce apparent A crystal structures and EPR spectra that change with temperature.

Small perturbations have pronounced effects on the conformation and the crystal structure. The deuterated crystal has a different crystal structure than the crystal containing only hydrogen with the relative energies for conformations A and B reversed. Applying small pressures to the crystal can also cause the J−T conformation and the crystal structure to switch. This pressure-induced switch involves an energy difference of less than 0.1 kJ per formula unit,[7] which is much less than the estimated difference between the conformations of the isolated ions. The discrepancies between the energy differences of the conformations of the individual copper complex ions (in solution, for example) and in the crystal have been suggested as arising from various cooperative and dynamic effects.[5,8,9] The diffraction studies[2,3,5] show that the switching of the J−T distortion in AmCuTS is associated with subtle changes in the rest of the crystal structure. The changes include a rotation of the ammonium ion with a concomitant change of the hydrogen-bonded sulfate group.

We have been investigating the effect of infrared hole burning of the N−D stretching bands of ammonium compounds containing a small amount of deuterium. Irradiating a single stretching band with a tunable infrared laser results in rotation of the ammonium ion.[10] For AmCuTS, the rotation changes the local structure and induces a transformation of the conformation of the complex copper ion.[11] The hole-burning produces two sets of conformations as evidenced by a series of double holes and antiholes. The components of the doubled bands relax at different rates and do so over a range of times from a fraction of a minute (or faster) to many hours.

We have recently been able to investigate hole-burning kinetics over a range of time scales by utilizing irradiations of 10 or 20 s (repeated many times and co-added) in one set of experiments and comparing the results to those from irradiations

10.1021/jp012848v CCC: $22.00

lasting many minutes.[12] Our initial experiments were on the ammonium nickel Tutton salt, which of course does not show double holes. The relaxation of the holes occurs in a range of times in this salt and two characteristic times are approximately 15 and 110 min.

In this paper, we apply short and long time irradiations to the ammonium copper Tutton salt and analyze the kinetics in order to obtain the rate of transformation from one J−T form to the other. It turns out that we can preferentially burn the molecules in either the A or the B conformation and thus obtain information on this transformation. We note that the change in the immediate surroundings of the copper must be accompanied by a rearrangement in some further parts of the crystal and so the rate of the transformation is entirely unknown a priori.

II. Experimental Section

The infrared spectra were taken using a Nicolet 850 FTIR equipped with an InSb detector. The long and short irradiation experiments were conducted as described previously using our difference frequency laser.[12] The long irradiation time was 5 min and the short time was 20 s. Twenty or more of the short irradiation spectra were averaged to produce the spectra shown here. The holes and antiholes decay with time, and series of spectra were taken after irradiation to follow these decays. After a 5 min irradiation, spectra were taken at intervals of about 5 min and then at progressively longer time intervals to about 20 h. After the 20 s irradiation, the spectra were first taken at intervals of about 20 s and then at longer intervals until the spectra could no longer be observed at about 1 h. The AmCuTS samples were prepared with about 5% deuterium. The deuterium substitutes for hydrogen atoms in both the ammonium ions and the water molecules.

III. Results and Discussion

The spectra of the Tutton salt were the same as those we have taken previously and show four N−D bands (from the four possible positions of the NH_3D^+ ion) and six O−D bands (from the six independent positions of the H atoms in the waters). The infrared spectra are shown in Figure 1 at a number of different temperatures. The bands are broadened and washed out at room temperature, but clear in the spectra at 100 K and at 10 K. The assignments of the four N−D and the six O−D bands are shown in Table 1. The crystal structure is that associated with the A conformation at low temperatures and the small amount of deuterium is not enough to switch either the J−T conformation or the crystal structure.[13]

As the temperature is increased, the diffraction studies show that the hydrogen-bond distances change; the distances between pairs of hydrogen-bonded heavy atoms become longer, except that between the sulfate group and the water, O(7), which gets shorter. The hydrogen stretching frequencies change with the hydrogen bond distances[14,15] and the observed changes of the frequencies are consistent with the changes in distances listed in Table 1. The ordering of the water to sulfate (O−O) bond distances switches with temperature, but the ordering of the ammonium to sulfate (N−O) bonds remains the same. The switching of O−O bond distances is related to the changes in the conformation of the $Cu(H_2O)_6^{2+}$ complex. Also, the relative intensities of N−D band I and II change with temperature; this occurs because the zero point energy of the system is different in each of the four possible orientations of the NH_3D^+ ion.

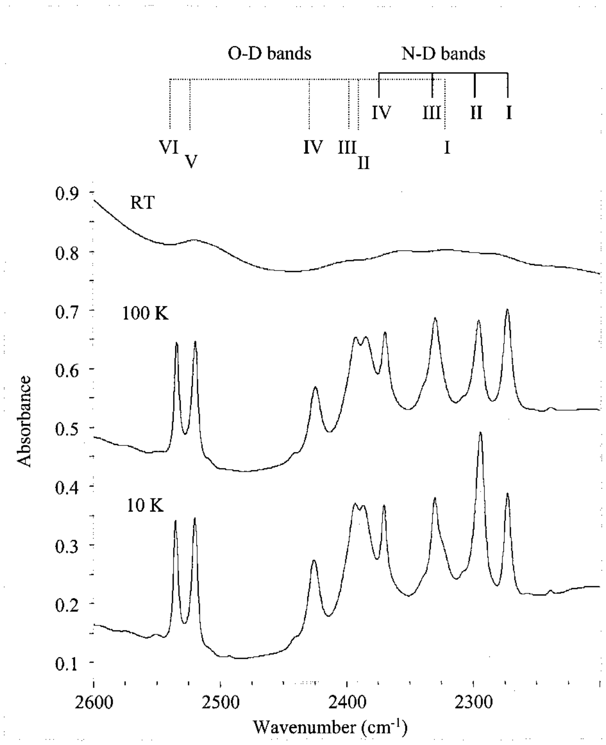

Figure 1. Infrared absorption spectra of ammonium copper Tutton salt with about 5% deuterium. The assignments of the bands are given in Table 1.

TABLE 1: Assignment of Hydrogen Bonds X−H−O in Ammonium Copper Tutton Salt

band no.	peak[a] (cm^{-1}) 10 K	peak[a] (cm^{-1}) 100 K	14 K[b] X−O	14 K[b] distance (Å)	293 K[c] X−O	293 K[c] distance (Å)
I	2273	2273	N(10)−O(5)	2.846	N(10)−O(5)	2.869
II	2294	2296	N(10)−O(6)	2.872	N(10)−O(6)	2.901
III	2330	2330	N(10)−O(3)	2.971	N(10)−O(3)	2.979
IV	2370	2370	N(10)−O(3)[d] N(10) −O(4)[d]	3.047[e]	N(10)−O(3)[d] N(10)−O(4)[d]	3.065[e]
I	2322		O(8)−O(4)	2.658	O(9)−O(3)	2.682
II	2387	2384	O(9)−O(3)	2.690	O(8)−O(4)	2.708
III	2393	2393	O(8)−O(6)	2.722	O(9)−O(5)	2.734
IV	2426	2425	O(9)−O(5)	2.727	O(8)−O(6)	2.744
V	2520	2520	O(7)−O(6)	2.827	O(7)−O(6)	2.820
VI	2535	2534	O(7)−O(5)	2.831	O(7)−O(5)	2.821

[a] From this work. [b] Neutron data from ref 3. [c] Neutron data from ref 4. [d] Bifurcated hydrogen bond. [e] The average of two bifurcated bonds.

A. Temperature Dependence. As the temperature changes, the proportion of each copper conformation is altered, which without inducing a phase transition, results in the subtle structural changes, as we have already noted. In Figure 2, the infrared hole-burning spectra of AmCuTS at 10 and 35 K are displayed. Parts a and b of Figure 2 present the difference spectra (the spectrum after irradiation minus the original spectrum) for 5 min irradiation at the peak maximum of N−D band I for each temperature, and Figure 2c depicts the original spectrum of AmCuTS at 10 K.

The positions of the holes and the antiholes are at 2272, 2292, 2331, and 2370 cm^{-1} in Figure 2a and at 2272, 2296, 2332, and 2370 cm^{-1} in Figure 2b. Although the holes are on the low frequency (LF) sides of the maximum of the corresponding peaks, the positions of the antiholes vary. The weak N−D II antihole in Figure 2a is LF, but as the temperature is increased, it moves to the high frequency (HF) side and becomes stronger. This nonmonotonic change is indicative of the complicated hole-burning and kinetics that we discuss below. The positions of the antiholes in N−D III and IV are HF and LF, respectively, at both 10 and 35 K.

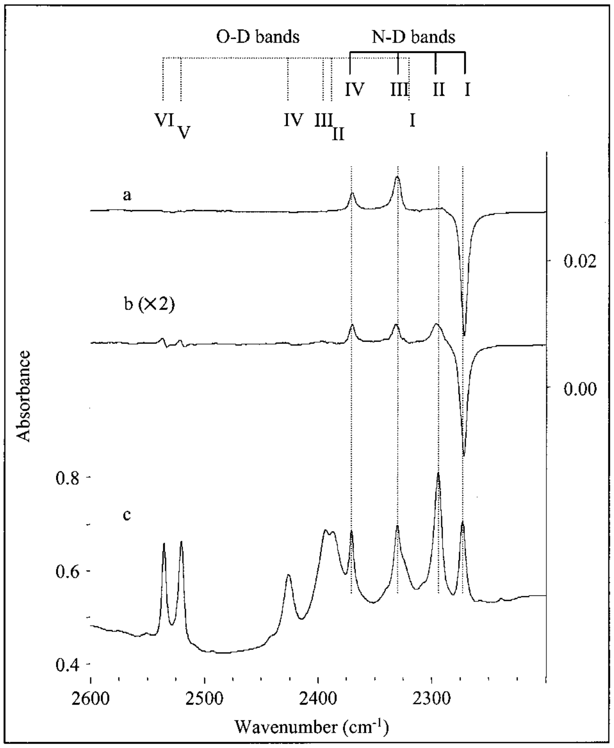

Figure 2. Infrared hole-burning spectra of ammonium copper Tutton salt: (a) the difference between the spectrum after 5 min irradiation and that before at 10 K; (b) the difference spectrum at 35 K; (c) the original spectrum at 10 K. The laser frequency was set to the position of N–D band I. Difference spectrum (b) has been multiplied by 2. Note that the different absorption scale for the original spectrum and the difference spectra.

TABLE 2: Lengths of the Hydrogen Bonds in the Crystals Containing the Two Conformations

	X–O distance[a] (Å)				
	conformation A 14 K		conformation B 15 K		
band no.					10 K[b]
N–D I	N(10)–O(5)	2.846	N(10)–O(5)	2.865	LF
N–D II	N(10)–O(6)	2.872	N(10)–O(3)	2.882	LF
N–D III	N(10)–O(3)	2.971	N(10)–O(6)	2.907	HF
N–D IV	N(10)–O(3) N(10)–O(4)	2.885[c]	N(10)–O(3) N(10)–O(4)	2.911[c]	LF
O–D I	O(8)–O(4)	2.658	O(9)–O(3)	2.690	LF
O–D II	O(9)–O(3)	2.690	O(9)–O(5)	2.736	LF
O–D III	O(8)–O(6)	2.722	O(7)–O(5)	2.754	LF
O–D IV	O(9)–O(5)	2.727	O(7)–O(6)	2.791	LF
O–D V	O(7)–O(6)	2.827	O(8)–O(4)	2.791	HF
O–D VI	O(7)–O(5)	2.831	O(8)–O(6)	2.839	LF

[a] Neutron data from ref 3. The distance of conformation A is based on the nondeuterated AmCuTS at 14 K, 1.4 bar, and that of B on the fully deuterated one at 15 K, 1 bar. [b] These are the expected relative peak locations for conformation A as compared to conformation B. [c] The distance corresponding to N–D IV from conformation A is N(10)–O(3), and that from conformation B is N(10)–O(4).

We assume that the local structure changes with the conformation of the copper ion. That is a copper ion with a B conformation in an A crystal is surrounded by a local structure that is close to that of a B ion in a pure B crystal. The lengths of the hydrogen bonds in the two pure crystals with conformations A and B, respectively, are listed in Table 2. Since the infrared band positions change with these lengths, the bands should shift with a change in conformation. The hydrogen bonds for A are shorter than those for B, except N–D III and O–D V, which are longer. Thus all peak locations for A are expected to be LF in the difference spectrum at 10 K compared to those for B, which are HF, except for N–D III and O–D V. When the system is irradiated at 2273 cm^{-1} (the center of the N–D I band) at 10 K, the holes and antiholes for the N–D bands correspond to conformation A. The positions and intensities of the bands in the O–D band region do not change and no holes or antiholes appear in this region. However at 35 K, the N–D holes/antiholes correspond to both A and B conformations and holes/antiholes appear in the O–D band region. When an ammonium ion in a B-like conformation is hole burned, the strain induced in the crystal must force more of the surroundings of a B copper conformation into a B-like crystal structure. The concomitant changes in the O–D stretching bands lead to holes and antiholes in the O–D region of the spectrum. Note that a B-hole is always accompanied by a B-pattern in the O–D band region. As we will see below, this pattern changes if the B-hole transforms to an A-hole.

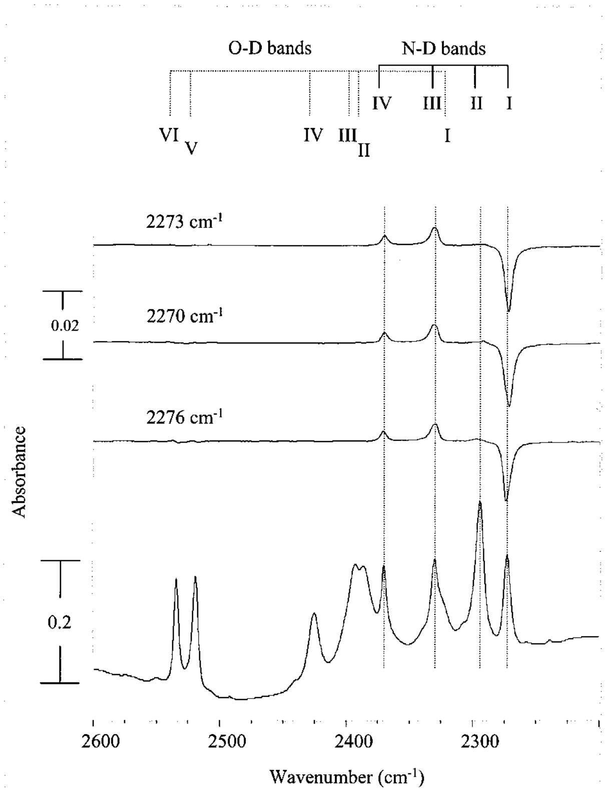

Figure 3. Infrared hole-burning difference spectra of ammonium copper Tutton salt after 5 min irradiation with various frequencies together with the absorption spectrum at 10 K. Irradiation at 2270 cm^{-1} excites *A* sites while that at 2276 cm^{-1} excites B-like sites.

B. Excitation-Frequency Dependence. B-1. Long Irradiation Time. Since the frequencies of the holes and antiholes depend on conformation, it is possible to excite either conformation A or B. The infrared spectra at 10 K with excitation at different parts of band N–D I are displayed in Figure 3. The lowest spectrum in Figure 3 depicts the absorption spectrum of AmCuTS at 10 K. The excitation frequencies were chosen as the location at half-height of each side in the N–D band I.

The positions of the hole and antiholes are at 2272 (LF), 2292 (LF), 2331 (HF), and 2370 (LF) cm^{-1} after excitation at 2270 cm^{-1}, corresponding to change of the NH_3D^+ ion within conformation A. The positions of the hole and antiholes are 2274 (HF), 2297 (HF), 2329 (LF), and 2371 (HF) cm^{-1} after excitation at 2276 cm^{-1}, corresponding to the changes in conformation B. Holes/antiholes appear in O–D V and VI upon 2276 cm^{-1} excitation. The positions of the hole and antiholes

TABLE 3: Original Conformation of the Holes and Antiholes of Each Band upon Irradiation in Ammonium Copper Tutton Salt

	hole/antihole (cm^{-1})					
	10 K			35 K		
band no.	2273	2270	2276	2273	2270	2276
N−D I	H_A[a]	H_A	H_B[a]	H_A	H_A	H_B
N−D II	AH_A[a]	AH_A	AH_B[a]	AH	AH_A	AH_A AH_B
N−D III	AH_A	AH_A	AH_B	AH	AH	AH
N−D IV	AH_A	AH_A	AH_B	AH	AH	AH
O−D V			AH_A H_B	AH_A H_B		AH_A H_B
O−D VI			H_A AH_B	H_A AH_B		H_A AH_B

[a] H, AH, A, and B represent the hole, the antihole, conformation A, and conformation B, respectively.

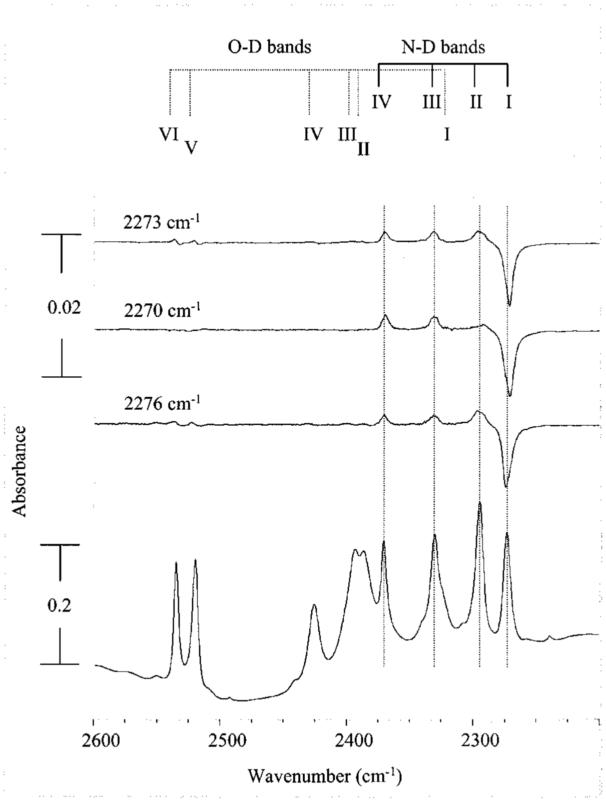

Figure 4. Infrared hole-burning spectra of ammonium copper Tutton salt at 35 K. Compare to Figure 3.

in the difference spectrum after 5 min irradiation at 2273 cm^{-1} are the same as those after excitation at 2270 cm^{-1}, which result from the change of the NH_3D^+ ion within conformation A. The assignment of the hole/antiholes is listed in Table 3.

The crystals contain mainly conformation A at 10 K and on hole-burning of the A conformation, the intensities change immediately only in the N−D band region and not in the O−D band region. However, the structural change upon the excitation of conformation B induced by the J−T distortion in a majority A crystal is accompanied by the change of the hydrogen bond distances between the sulfate groups and the waters. This leads to changes in the O−D stretching region of the spectrum and these changes are larger at 35 K, a temperature at which there is a larger proportion of B.

The difference spectra at 35 K with different excitation frequencies are displayed in Figure 4. The difference spectrum upon the excitation at 2270 cm^{-1} is similar to that at 10 K with the same excitation frequency. On the other hand, the spectral changes upon excitation at the maximum peak position at 35 K are different from those at 10 K, but are similar to those with the excitation of conformation B at the same temperature, except for the position of the primary hole. The relative intensities of the antiholes change with increasing temperature upon irradiation at 2273 and 2276 cm^{-1}, especially the intensity of the N−D II antihole, which becomes stronger, but they do not change upon irradiation at 2270 cm^{-1}. Note that the position of the antihole in N−D II goes to HF in the spectrum after excitation at 2273 cm^{-1}, just as in the spectrum after excitation at 2276 cm^{-1}. Furthermore, the spectrum with 2273 cm^{-1} excitation shows changes in the O−D band region, while there still is no change in the O−D bands with excitation at 2270 cm^{-1}. We conclude that the excitation at the maximum peak position mostly induces the structural change in B at 35 K.

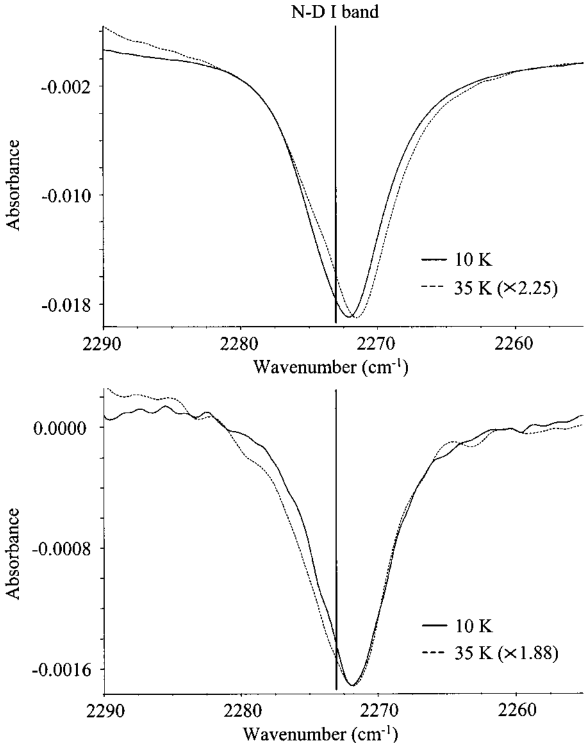

Figure 5. Comparison between the holes in the spectrum at 10 K (solid line) and at 35 K (dotted line) with irradiation at 2273 cm^{-1}. The upper panel is for 5 min irradiation, and the lower is for 20 s irradiation. The dotted line spectra are expanded by 2.25 (upper) and 1.88 (lower). The line in the center of each panel indicates the original position of the peak of the ND I absorption band.

Conformation B becomes gradually populated as the temperature goes up, and the peak position of each band in conformation B shifts. To compare the holes in the difference spectra (Figures 3 and 4), in the upper panel of Figure 5 we plot the spectra with excitation at 2273 cm^{-1}. The width of the N−D I hole, 6.75 cm^{-1} at lower temperature is narrower than that at higher temperature, 6.99 cm^{-1}. The hole position shifts with temperature from 2272.3 cm^{-1} at 10 K to 2271.5 cm^{-1} at 35 K.

B-2. Short Irradiation Time. It is clear that the AmCuTS holes/antiholes relax in a complex way and in an attempt to catch the process of converting between conformations A and B, we reduced the irradiation time to 20 s.

Figure 6 presents a series of difference spectra for 20 s irradiation at 10 K. We comment only on the differences between the 20 s and the 5 min spectra. Excitation at 2270 cm^{-1} produces the expected changes within conformation A, except

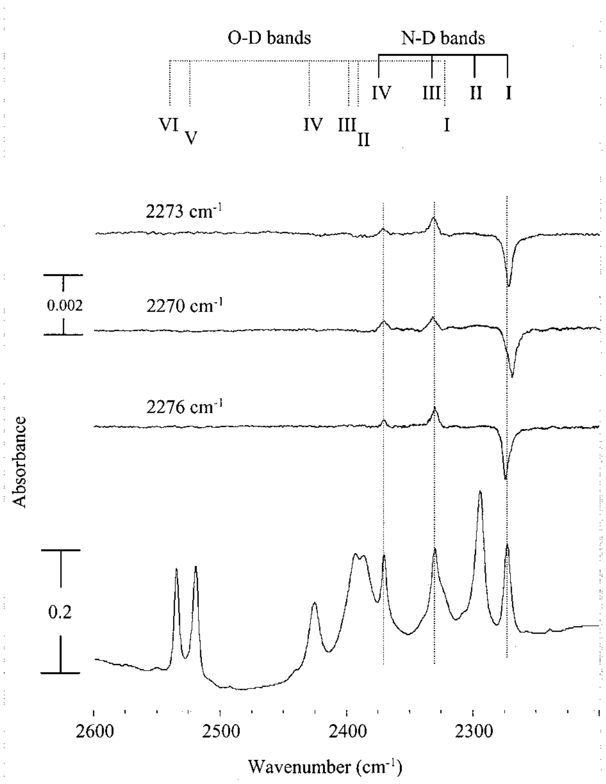

Figure 6. Infrared hole-burning difference spectra of ammonium copper Tutton salt after 20 s irradiation at 10 K.

for the absence of an antihole at N−D II, which is apparently too small to show up. Excitation at 2276 cm^{-1} yields the changes within conformation B. The holes and antiholes in the difference spectrum after 20 s irradiation at 2273 cm^{-1} are again the same as those in the spectrum with 2270 cm^{-1} excitation that result from the change within conformation A.

The difference spectra at 35 K for 20 s irradiation are displayed in Figure 1S (Supporting Information). The pattern of holes/antiholes upon excitation at 2270 cm^{-1} is similar to that at 10 K. On the other hand, the spectral changes upon excitation with the maximum peak position (2273 cm^{-1}) and 2276 cm^{-1} at 35 K are different from those at 10 K and correspond to conformation B. The relative intensities of the antiholes change with increasing temperature upon irradiation at 2273 and 2276 cm^{-1}, while they do not change upon irradiation at 2270 cm^{-1}.

To compare the holes in the difference spectra in more detail, we expand the scale of the spectra with excitation at 2273 cm^{-1} at the two temperatures (Figures 6 and 1S) in the lower panel in Figure 5. The hole positions are the same, while those with for long irradiation are different (the upper panel of Figure 5). Since there is a distribution of NH_3D^+ ions at various distances from A and B centers, there is a statistical distribution of N−D bands near the center frequency of the hole. At longer times, N−D stretches with spectral positions further and further away from the original hole center are burned. At 35 K, there is more B and so the spectral bands are more inhomogeneous. Consequently, the broadening and shift of the hole is seen at longer times and higher temperatures.

C. Kinetics. C-1. Decay Processes after Long Irradiation. The kinetics of the production and decay of the holes/antiholes involve at least eight different sites: four orientations for the NH_3D^+ in each of the two conformations A and B. Perusal of the spectra presented so far makes it clear that the spectra are qualitatively different for short and long irradiation times. Furthermore, as might be expected, the spectra and the decay of the holes change with temperature. The decay, e.g., hole filling, of each of the holes/antiholes occurring after 5 min of irradiation at the excitation frequencies of 2270, 2276, and 2273 cm^{-1} of the difference spectra of AmCuTS at 10 K are shown in Figures 7, 8, and 2S, respectively. We designate the holes at LF as H_A and those at HF as H_B, and the antiholes at LF as AH_A and at HF as AH_B. For N−D III and O−D IV, the assignments are switched as previously mentioned.

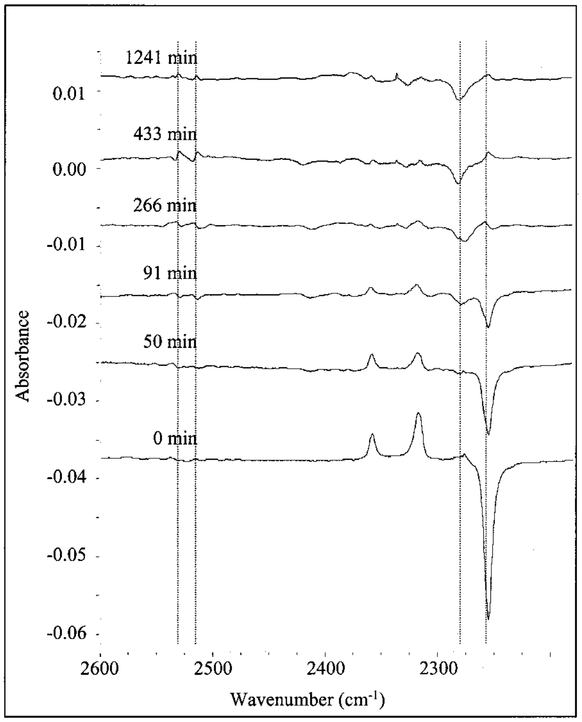

Figure 7. Decay of the infrared difference spectra with time after 5 min irradiation at 2270 cm^{-1} in ammonium copper Tutton salt at 10 K.

After 5 min irradiation at 2270 cm^{-1} at 10 K (Figure 7), the hole, H_A, at N−D I that appears immediately on excitation, decays monotonically for about 300 min and turns into AH_A at about 400 min. The antihole decays in turn after a few days. AH_A (N−D II) decays with time, and becomes H_A about 90 min after irradiation. This hole becomes H_B (HF) at later times. The antiholes, AH_A's, in N−D III and IV decay monotonically. Although there is no initial change in the O−D band region, the O−D bands change later in the decay process. The relative intensities of the holes and antiholes in O−D V and VI switch by about 400 min, which is on the same time scale as the hole/antihole reversal in N−D I and II. These observations imply that transfer from site A to site B takes between 300 and 400 min. We do not see changes in all the bands; for example O−D I, II, and III. Since O−D I is located on the shoulder of N−D III, and the O−D II and III bands are not separated from each other, it is hard to detect the spectral changes in these three bands.

The decay of AmCuTS with excitation at 2276 cm^{-1}, the frequency that can excite conformation B directly, is shown in Figure 8. Until about 200 min, the spectral changes of the N−D bands are in the opposite sense to those in Figure 7; H_B in N−D I becomes AH_B, and AH_B in N−D II becomes H_A with time. However, the intensities of the O−D bands change differently from the case of conformation A. This time, the intensities

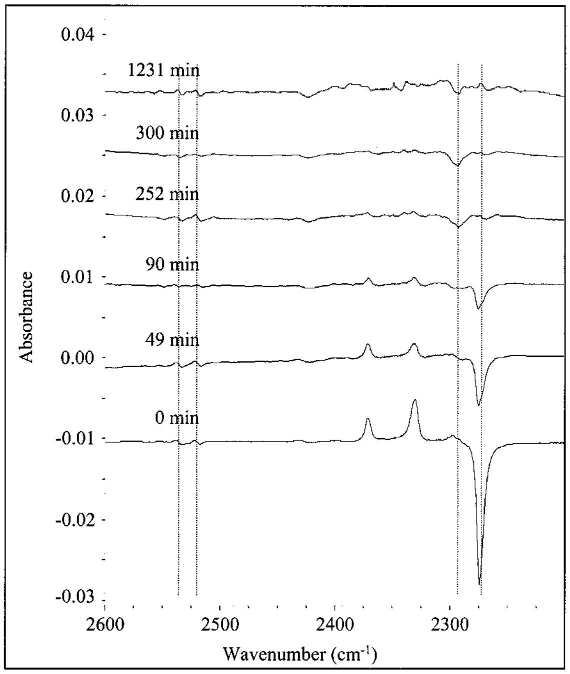

Figure 8. Decay of the infrared difference spectra with time after 5 min irradiation at 2276 cm^{-1} in ammonium copper Tutton salt at 10 K.

change immediately after irradiation of conformation B, and they do not switch throughout the decay process.

The decay of AmCuTS after irradiation at 2273 cm^{-1} is shown in Figure 2S. The overall decay of each N−D and O−D band is very similar to that in conformation A. This suggests that excitation at the peak maximum induces structural changes only within conformation A.

The decay in the dark after irradiation at each excitation frequency is different at 35 K than at 10 K. The decay of A after irradiation at 2270 cm^{-1} is shown in Figure 9. Although the difference spectrum immediately after irradiation shows the same spectral changes as those at 10 K, the decay process is different. A single H_A appears in the initial spectrum, which doubles as a HF component, corresponding to B, grows in. The antihole in N−D II, AH_A, doubles as well. The antiholes in N−D III and IV become holes in the decay process, and the intensities of O−D bands change with time. The decay of the B spectrum after irradiation at 2276 cm^{-1} is shown in Figure 3S. The spectral changes in B are similar to those in A, but the positions of the holes/antiholes are reversed.

The decay process after excitation at the maximum peak position, 2273 cm^{-1}, is shown in Figure 4S. The initial spectral changes are the same as those in B, except for the position of the primary hole. The holes/antiholes at each N−D and O−D band switch from one side to the other at about 500 min, and then switch back as time goes on.

C-2. Decay Processes after Short Irradiation. The decays occurring after 20 s of irradiation at the excitation frequencies of 2270, 2276, and 2273 cm^{-1} at 10 K are shown in Figures 5S, 6S, and 7S, respectively. The overall decays after 20 s irradiation are very similar to those with 5 min irradiation. However, we can follow them only over much shorter times (less than 1 h in contrast to 20 h).

In Figure 5S, H_A appears in the position of N−D I immediately after excitation at 2270 cm^{-1}, decays monotonically within 20 min, and then becomes AH_A after about 30 min (it eventually decays). A hole appears at N−D II within 7 min, even though there is no hole/antihole immediately after irradiation. The position of the hole in N−D II goes to HF as time goes on. Although there is no immediate change in the O−D band region, the intensities of the O−D bands do change during the decay process. The relative intensities of the holes and antiholes at O−D V and VI switch at about 20 min, which is at about the same time at which H_B appears at N−D II.

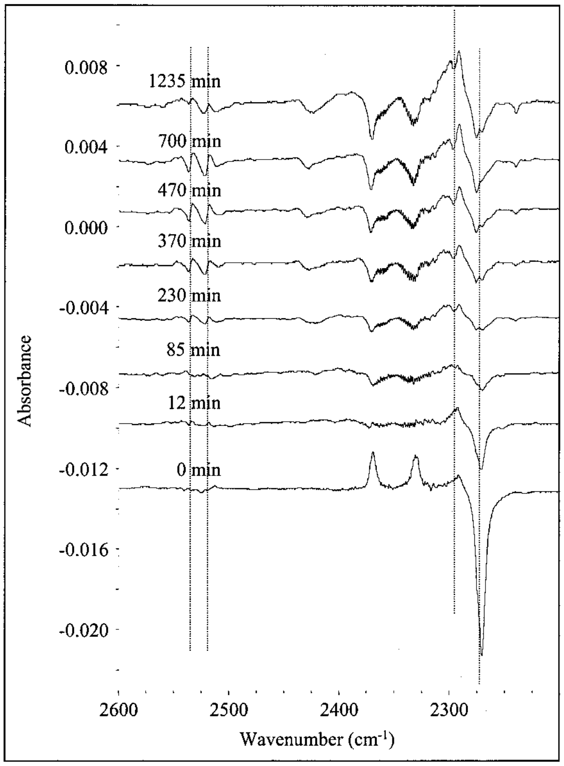

Figure 9. Decay of the infrared difference spectra with time after 5 min irradiation at 2270 cm^{-1} in ammonium copper Tutton salt at 35 K. Note the doubling of the hole at N−D I.

The decay process of AmCuTS with excitation at 2276 cm^{-1}, the frequency that can excite conformation B directly, is shown in Figure 6S. Until about 20 min, the spectral change of each N−D band decays in the opposite sense to that in Figure 5S; thereafter, H_B in N−D I becomes AH_B, and H_A appears in N−D II. However, the intensities of the O−D bands change differently from the decay following irradiation at 2270 cm^{-1}. The intensities change immediately after irradiation of conformation B (even though the holes/antiholes are very weak), and they do not switch throughout the decay process.

The decay of AmCuTS after irradiation at 2273 cm^{-1} is shown in Figure 7S. The overall decay process is very similar to that for 2270 cm^{-1}. This suggests that excitation at the peak maximum induces structural changes only to conformation A at 10 K.

The decay processes with 20 s irradiation at 35 K are very different from those with 5 min irradiation, while those with 20 s and 5 min irradiations at 10 K are very similar to each other.

The decay process in A after irradiation at 2270 cm^{-1} at 35 K is shown in Figure 8S. Although the difference spectrum immediately after irradiation shows the same spectral changes as that at 10 K, the decay is different. H_A appears in the position of N−D I in the 0 min spectrum and decays monotonically until 3 min. H_A/AH_B appear at the same position about 40 min after excitation. The antihole in N−D II, AH_B, appears at about 0.3 min, decays with time, and then becomes H_A in N−D II at about 40 min. The intensities of O−D bands also change, even though they do not change immediately after irradiation.

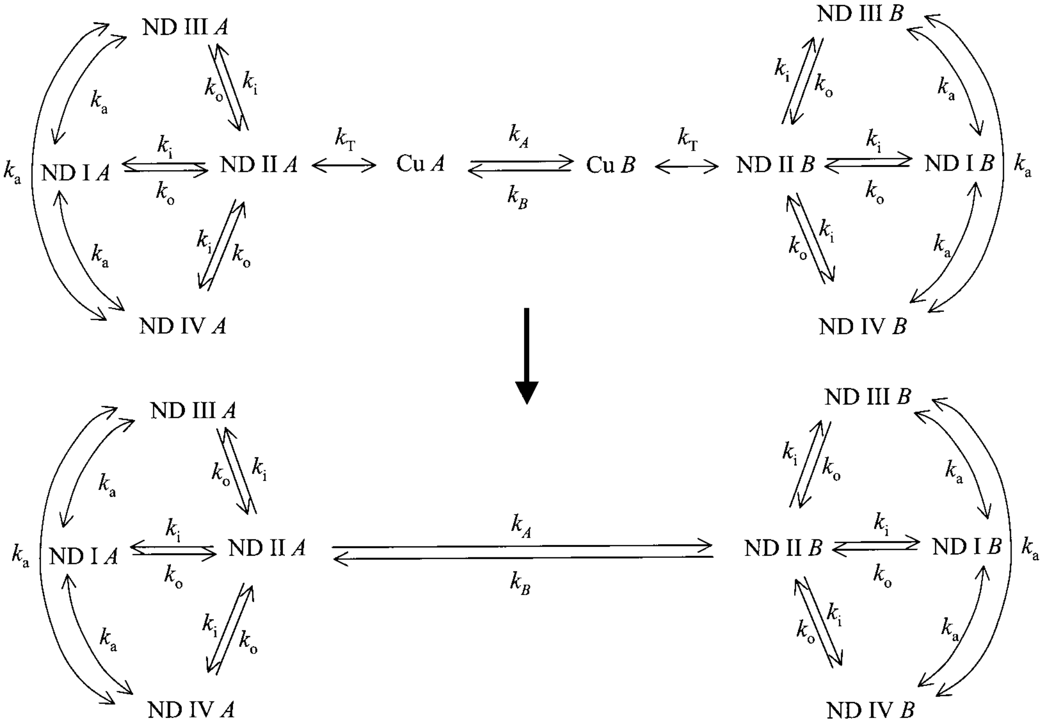

Figure 10. Kinetic scheme: $k_a = k_{around}$, $k_i = k_{in \rightarrow out}$, $k_o = k_{out \rightarrow in}$, $k_T = k_{Transfer}$, $k_A = k_{A \rightarrow B}$, and $k_B = k_{B \rightarrow A}$.

The decay process of B after irradiation at 2276 cm^{-1} is shown in Figure 9S. The spectral changes after 20 s irradiation show a pattern similar to those with 5 min irradiation. The position of the hole is HF, H_B, in N−D I, which goes to LF with time, H_A.

The decay process after excitation at the maximum peak position, 2273 cm^{-1}, is shown in Figure 10S. The immediate spectral changes in the difference spectra are the same as those in B, except for the position of the hole. Surprisingly, the position of the hole in N−D I switches from one side to the other without becoming doubled; H_A becomes H_B in N−D I within 1 min, and then decays immediately, and appears again at about 2 min and decays gradually.

C-3. Analysis. Previously, we have analyzed the decay of the holes/antiholes in the ammonium cobalt Tutton salt.[1] The analysis proceeded as follows. There are four possible orientations of the NH_3D^+ ion. The decay proceeds by a series of first-order kinetic steps between pairs of sites (orientations). Such a series of first-order kinetic steps lead to a set of first-order differential equations that can be solved.[16] We used the results for the cobalt salt as a starting point for analyzing the copper salt.

The situation for the copper salt is more complicated, since there are two copper conformations and four ammonium orientations for each. The water O−D sites also change and they must enter the kinetic scheme as well. If just the eight possible N−D sites are considered, there can be 56 rate constants and 28 equilibria. They are not all independent, but the number of independent constants is still far too many to evaluate from our data. We consider the simplified kinetic scheme of Figure 10. We imagine two sets of the four orientations each containing sites I, III, and IV interchanging with a rate constant k_a, where *a* standing for "around". They are connected to the unique site II by rate constants k_{in} and k_{out}. The copper conformations change in what is certainly a complex multistep process, but here we simplify it assuming a set of copper constants connected to N−D II (top diagram in Figure 10). This is simplified even further in the bottom half of the figure as a direct interchange between N−D II in A to N−D II in B with rate constants k_A and k_B. The rate constants we can determine directly are the weighed rates, *c*, that enter the symmetrized rate matrix for a set of first-order rates. These weighted rates are c_a, c_i, and c_A. For example, for A to B, $c_A = k_A (\sqrt{A_{eq}}/\sqrt{B_{eq}})$, where k_A is the ordinary rate constant and c_A is the weighted rate constant. We estimated the three weighted rate constants and then solved the resulting equations as in ref 16. The results are listed in Table 4. This table also gives the unnormalized eigenvectors, which relate the rate processes characterized by the eigenvalues to the elementary processes of Figure 10.

Now, let us assume that the proportion of the B conformation is 1% at 10 K. Then the weighting factor is 0.1 and k_A is 0.007/min. k_B would have the weight reversed and becomes 0.7/min. The 1% concentration would imply an energy difference of 46 K between the conformations. At 35 K the ratio B/A would be 21% and we have seen that we can burn the B conformation at this temperature by irradiating at either the band center or the B side of the band. The rate constants k_A and k_B would differ by a factor of about 2.

The first four eigenrates in Table 4 are for the interchanges among sites I, III, and IV, two for each copper conformation. The fifth is the rate of decay of the N−D II within a conformation. The more interesting rates, six and seven relate the two sites II via interchanging conformations. Rate six is for the A ↔ B transformation and seven is a mixed rate. The "α" in the eigenvalues for λ_6 and λ_7 is a parameter that we can evaluate and is 0.84 in this case. Finally eight is the zero eigenrate that comes from the requirement that the overall number of N−D bonds does not change. The rate expressions are complicated and we do not reproduce them here. However it turns out that the data fits well to the largest terms in each of these rate expressions. The fit of the data for the decay of each of the holes of the N−D band I upon long and short irradiation with different excitation frequencies at the different temperatures are shown in Figures 11, 12, and 11S. Figure 11 represents the filling of the hole occurring in after long irradiation at 10 K, while Figures 11S and 12 are for short irradiation time at 10

TABLE 4: Rate Constants (min^{-1}) of Ammonium Copper Tutton Salt[a]

λ_{1-4}	1.16	c_a	0.37
λ_5	0.2	$c_i{}^a$	0.05
λ_6	0.022	$c_A{}^a$	0.07
λ_7	0.318		
λ_8	0		

[a] $c_i = c_o$ and $c_A = c_B$.

$$\lambda_{1-4} = 3c_a + c_i \qquad \text{eigenvectors:} \begin{bmatrix} 0 \\ -^1/_2 \\ 1 \\ -^1/_2 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \begin{bmatrix} 0 \\ -^1/_2 \\ -^1/_2 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -^1/_2 \\ 1 \\ -^1/_2 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -^1/_2 \\ -^1/_2 \\ 1 \end{bmatrix}$$

$$\lambda_5 = 4c_i \qquad \text{eigenvector:} \begin{bmatrix} 1 \\ -^1/_3 \\ -^1/_3 \\ -^1/_3 \\ 1 \\ -^1/_3 \\ -^1/_3 \\ -^1/_3 \end{bmatrix}$$

$$\left.\begin{aligned} \lambda_6 &= 0.16(2c_A) \\ \lambda_7 &= \lambda_5 + 0.84(2c_A) \end{aligned}\right\} \qquad \text{eigenvector:} \quad \text{mixed}$$

$$\lambda_8 = 0 \qquad \text{eigenvector:} \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{bmatrix}$$

and 35 K, respectively. Although the model we used here is a complex kinetic scheme including initial, transition, and steady-state regimes, we only fit the experimental data from the steady-state conditions. Two terms fit all the data in Figures 11, 12, and 11S reasonably well. One of the rates that fits is 0.022/min, the rate due to the A ↔ B transformation, and the other is 1.16/min, the rate for the intraconformation transfer. Since the intraconformation transfer is much faster than the interconformation transfer, all the decays from the initial burn to fairly long times fit with the latter. Only the short initial decays fit with the intraconformational rate and this is shown in Figure 12 for the 20 s irradiation at 2273 cm^{-1} at 35 K. Here the first minute approximately fits the faster rate and from four to six minutes, the slower rate. More typical is the decay of all the holes at 10 K, which fit the slower rate out to about 250 min as shown in Figure 11.

There are various estimates of the energy difference between conformation A and conformation B derived from the temperature dependence of the crystal structures. If we accept these estimates, which are in the range of 200 cm^{-1} or 288 K,[3,6,17] we would have almost no conformation B at10 K. There are two possibilities: either the energy differences are much smaller than those estimates from the variation observed by the diffraction studies, or the radiation and consequent strain induces the B conformation when irradiating in the “B side” of the band. We envision an inhomogeneous distribution of A copper ions. Some of these copper ions are frozen in surroundings that are relatively “B-like” and have B-like N−D spectral positions. Such copper ions might be more susceptible to transformation to a B conformation.

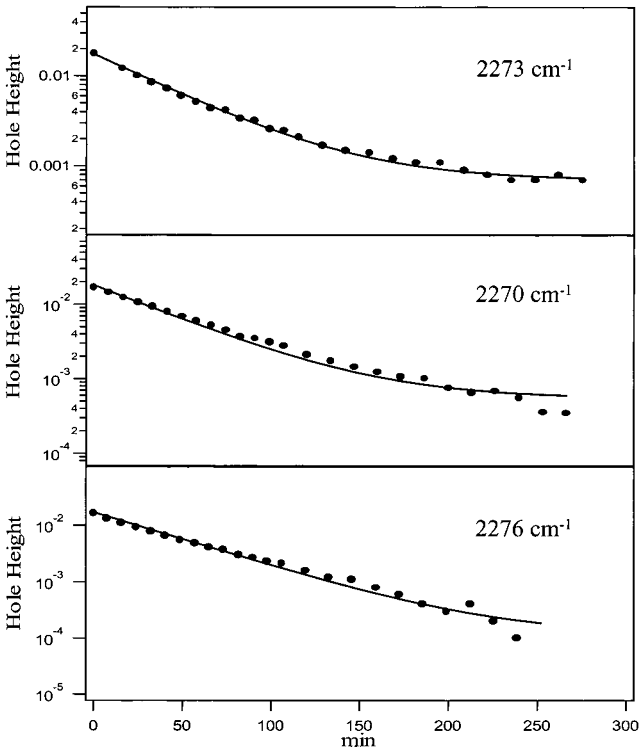

Figure 11. Comparison between the calculated relaxation curves (solid lines) and the experimental data (dots) after 5 min irradiation with various excitation frequencies at 10 K.

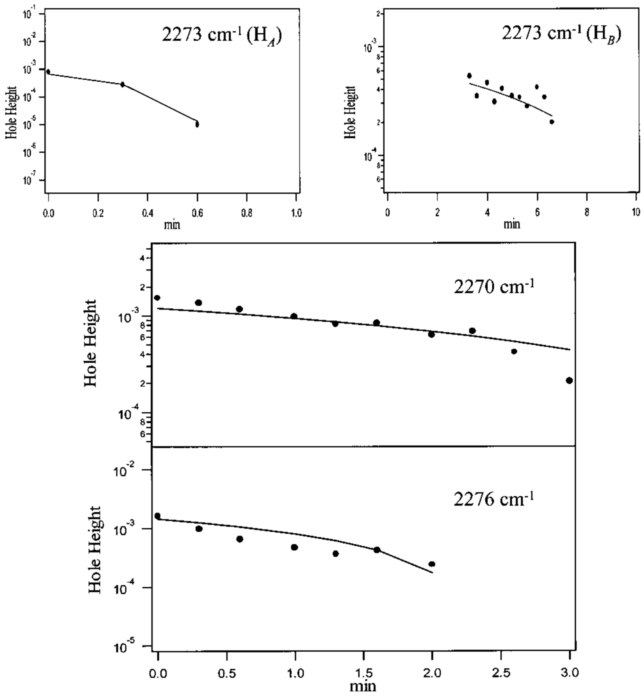

Figure 12. Comparison between the calculated relaxation curves (solid lines) and the experimental data (dots) after 20 s irradiation with various excitation frequencies at 35 K.

IV. Summary and Conclusions

The AmCuTS forms two crystal structures that differ in energy by a very small amount. At low temperatures the lower energy crystal structure contains the A copper complex conformation. Substituting a few percent of deuterium does not change the crystal structure. Irradiating one of the N−D stretching bands of the ammonium ion rotates the ion causing a small amount of strain in the crystal structure. This is sufficient to induce some of the copper ions to transform to the B conformation. The weighted rate for this transformation is about 0.022/min (see discussion above) which leads to a rate constant for the A → B of about 0.07/min at 10 K. We have been able to preferentially excite ammonium ions associated with either the A or the B conformation by burning different parts of the N−D I band. For the longer 5 min irradiation, conformation A starts to change to B during the irradiation. For the shorter time irradiation, the A and B conformers remain distinct for the 20 s of the irradiation, if we irradiate on one or another side of the N−D band. When the temperature is increased, the hydrogen bond distances change, which results in conformation changes and thermal expansion of the crystal lattice. Therefore, the decay processes in the dark after irradiation at each excitation frequency are different at 35 K and at 10 K. The kinetic model of Figure 10 nicely fits our results with drastically simplified assumptions about the relative rates.

A major challenge which remains is to determine how much of the crystal transforms around an isolated B conformation in an A crystal. The B holes we produce all eventually decay away, back to their A counterparts. The N−D holes and antiholes and the O−D holes and antiholes decay together showing that at least some of the surroundings of the copper ion transform together.

Acknowledgment. Y.-H.C. is grateful for the guidance and support that Prof. Tasumi showed during her graduate career at the University of Tokyo. His enthusiasm for science will forever be a model for her to pursue. H.L.S. celebrates many years of spectroscopy and friendship with Prof. Tasumi. We are pleased to acknowledge support by the National Science Foundation, Grant CHE 98-15945.

Supporting Information Available: Eleven figures: infrared absorption difference spectra of ammonium copper Tutton salt, and the decay of the holes and antiholes. This material is available free of charge via the Internet at http://pubs.acs.org.

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