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Switching the Jahn−Teller Distortion in Crystalline Ammonium Hexaaquacopper Sulfate (Tutton Salt) with Infrared Radiation

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Abstract: The N−D and O−D stretching regions of the infrared spectrum of $(NH_4)_2[Cu(H_2O)_6]SO_4$ doped with a small amount of deuterium reflect the known structure of the crystals at 7 K. Irradiation at the wavenumber of any one of the N−D bands yields spectral holes and antiholes that are doubled, indicating the presence of two different conformations in the crystals. The infrared-induced changes in the N−D bands are coupled to the changes in the O−D bands, and these in turn are coupled to the Jahn−Teller distortions about the copper. The holes and antiholes decay back to equilibrium in a complicated nonmonotonic way. Irradiating the O−D bands also produces holes and antiholes in contrast to the situation for other Tutton salts.

Introduction

The copper(II) ion forms a large variety of six-coordinate complexes, and the symmetric octahedrally coordinated ion is subject to Jahn−Teller distortion. Even the nonsymmetrically substituted Cu ions can show the effects of Jahn−Teller-type interactions (pseudo-Jahn−Teller interactions). Since these ions are found in a wide variety of compounds and the magnitude of the J−T effects vary very widely, they have been extensively studied.[1,2] Typical properties studied have been the crystal structures (by both X-ray and neutron diffraction), the electronic spectra, and the magnetic properties, especially the electron spin resonance spectra.

The Cu Tutton salts A_2 $Cu(H_2O)_6(SO_4)_2$, where A is a monovalent metal ion or ammonium, contain the important ion $Cu(H_2O)_6$ in a particularly convenient form[2] and show "strong" J−T effects.[3] The Cu Tutton salts can be studied either neat or diluted in a non J−T active host such as a Zn Tutton salt. Indeed, this mixed crystal has been studied since the first days of electron spin resonance spectroscopy.[4,5] A strong J−T effect implies a J−T stabilization energy on the order of 1000 cm^{-1} and large nuclear distortions. The barriers between different distorted configurations are also large, perhaps a few hundred wavenumbers.

When crystallography is used to study the J−T effect, a number of possibilities arise.[2] The crystal can have each site locked into a distortion, and the distortions can be the same at each site, or they can be disordered. Another possibility is that the distortion at each site can move from one direction to another (dynamic J−T effect) or the various sites can move cooperatively. A formal theory of cooperative effects in crystals exists[6] but has not yet been applied to the type of molecule we consider here.

The ammonium copper Tutton salt,[7] $(NH_4)_2Cu(H_2O)_6(SO_4)_2$, shows a static distortion but differs from the related compounds with an alkali metal, $A_2Cu(H_2O)_6(SO_4)_2$ (A = K, Rb, Cu),[8] since the crystal structures of the alkali metal compounds have a different distortion. More remarkably, the *deuterated* ammonium Tutton salt has a structure similar to those of the alkali metal salts.[9] Clearly, the distortions in ammonium Tutton salts are delicately poised between different possibilities, and it is these possibilities that we explore further in this paper.

In previous work, we have investigated various Tutton salts containing the NH_3D^+ ion.[10−15] The Tutton salts are all isomorphic. The ammonium ions of a given compound are equivalent and sit in a site of low (C_1) symmetry. The barriers between different orientations of a labeled ammonium ion are on the order of 18 kJ/mol and thus, at low temperatures, each NH_3D^+ ion is localized in one of four possible inequivalent orientations. The hydrogen bonding of the deuterium is different in each one of the possible deuterium positions, and consequently, the infrared spectrum in the N−D stretching region consists of four bands. The intensities of the bands vary with temperature, and this reflects the small differences in energy between the four different orientations of the NH_3D^+ ion.[16]

When any one of the bands is irradiated by infrared radiation, those ammonium ions of the orientation to give rise to the irradiated band are rotated to another position. This produces a spectral "hole" at the irradiated band and "antiholes" at the other bands. We have studied the growth of the holes and antiholes in the light and their relaxation in the dark. The

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Table 1. Hydrogen Bonds X−H−O

	X−O distance^{a}	distance^{a}	X−H−O angle^{1}	wavenumber^{b}
I	N(10)−O(5**)	2.860 Å	176	2273 cm^{-1}
II	N(10)−O(6**)	2.899	164	2294
III	N(10)−O(3)	2.983	157	2330
IV	N(10)−O(3**)	3.007^{c}	159	2371
	O(4**)	3.121^{c}	135	
I	O(9)−O(3*)	2.683	171	2324
II	O(8)−O(4*)	2.707	178	2387
III	O(9)−O(5*)	2.732	170	2393
IV	O(8)−O(6**)	2.743	178	2426
V	O(7)−O(6*)	2.821	169	2520
VI	O(7)−O(5)	2.826	176	2535

[a] From ref 17, at room temperature. The asterisks identify bonds to various equivalent atoms. [b] This work, N−D and O−D stretches at 7 K. [c] Bifurcated hydrogen bond.

previous work has been of the Tutton salts in which the transition metal has been Co, Ni, or Mg.[11] The ammonium nickel chromate has also been studied.[11] The Co^{2+} ion is expected to show small Jahn−Teller distortions, while Cu^{2+} has large distortions. Ni^{2+} and Mg^{2+} do not have an orbital degeneracy and thus no J−T distortion. The Ni, Co, and Mg salts show very similar properties, although the mixed Ni−Co Tutton salt behaves differently.[13,14]

The Cu Tutton salts are distinctly different from the others we have studied, since the surroundings of the Cu ion show a considerable distortion from a regular octahedral geometry.[17] However, it is the variation of this distortion with temperature[8,9] and the sensitivity of the distortion about the Cu^{2+} and the accompanying change in crystal structure to small perturbations that mandates an interpretation in terms of Jahn−Teller forces. Examination of the infrared spectrum of the deuterium-doped ammonium Tutton salt does not reveal anything unusual. However, hole-burning immediately reveals multiple bands corresponding to multiple sites for the ammonium ion, and further investigation shows that the copper salt is indeed unique.

Structure

The structure of the ammonium copper Tutton salt has been extensively studied. The space group is ($P2_1/a$ #4) with $Z = 2$.[17−19] All of the atoms except the Cu are in general positions, while the Cu is in a position of inversion symmetry. The six water molecules coordinated to the Cu form three nonequivalent pairs. Each pair consists of water molecules related by the inversion. Similarly, the two ammonium ions are equivalent and are hydrogen bonded to the sulfate oxygen atoms. The hydrogen bonding is best characterized by neutron diffraction, since this accurately determines the position of the hydrogen atoms. In Table 1 we list the hydrogen bonds for the crystal at room temperature. The hydrogen bonds are listed in terms of heavy atom distances between pairs of water oxygens, sulfate oxygens, and nitrogen atoms. The hydrogen bonds are all in the expected range of distances and angles, except for the bifurcated bonds from the nitrogen to the sulfate oxygens 3 and 4. (The N−O (4) bond, as well as the N−O (3) one also have relatively bent hydrogen bonds.) The six oxygen atoms form a distorted octahedron about the Cu, with the Cu−O (7) bond exceptionally long at 2.2369 Å and the other two, Cu−O (8) at 2.0871 and Cu−0 (9) at 1.9710 Å (these values have been corrected using the riding model in which the oxygen atoms "ride" on the copper atom).[17]

The X-ray diffraction patterns and the electron spin resonance spectra have been redetermined at low temperature,[8] and it was found that the Cu−O distances change markedly to a more elongated tetragonal geometry as the temperature decreases. Similarly, the *g*-values along the directions of the Cu−O (7) and Cu−O (8) vectors diverge as the temperature decreases. The interpretation of both sets of measurements is that there are three CuO_6 conformations. The lowest energy one (A) has a long Cu−O (7) distance, with shorter, nearly equal Cu−O (9) and Cu−O (8) distances. About 1.9 kJ/mol higher in energy is a conformation (B) with a long Cu−O (8) and with Cu−O (7) and Cu−O (9) shorter. A conformation (C) with Cu−O (9) the longest is thought to be considerably higher in energy and does not affect the structure up to room temperature. In what follows, we will use the designations A, B, and C to identify the three possible CuO_6 octahedra. The notation is a problem because some methods, such as diffraction, measure a crystal structure, while others, such as our infrared methods, measure a *local* conformation. Our designation means a local conformation.

The neutron diffraction of the totally deuterated Tutton salt $(ND_4)_2\ Cu(D_2O)_6\ (SO_4)_2$ also shows temperature-dependent structures. However, at low temperatures, it is the Cu−O (8) distance that is the longest, that is a structure like conformation B for the hydrogen compound. This structure persists, albeit with changes, as the temperature is raised to room temperature.

The neutron diffraction-determined structure switches with pressure.[7] Simmons et al.[7] consider four structures D_L, D_H, H_L, and H_H. The D and H indicate deuterium and hydrogen, respectively, while the subscripts L and H indicate low and high pressure. The hydrogen compound does not change with pressure, i.e., $H_L \equiv H_H$. However, the deuterium compound changes. We have already noted that the D_L structure has a long Cu−O (8) distance. However, D_H is a switched structure similar to H_H. Diagrams of these distorted arrangements and of potential energy surfaces may be found in ref 7. Detailed analysis of the variation of bond lengths with temperature gives the energy difference between conformations A and B for the H_H structure as about 3 kJ/mol. For D_L, the energy difference is also about 3 kJ/mol but with the order of the two conformations reversed. The small pressure differences which accomplish the switch represent only about 0.2 kJ/mol, very significantly less than the estimated difference between the conformations of the individual ions.[20] The energy difference due to pressure is, of course, for a collective process of the crystal as a whole.

In addition to the switch of the CuO_6 octahedrons, there is a change in the hydrogen bonding around the ammonium ion at 15 K.[7] In D_L the weak hydrogen bond is from the nitrogen to sulfate oxygen (4), while in D_H it is to O (3). The room-temperature structure of the hydrogen compound[17] was interpreted to show a bifurcated hydrogen bond to both O (3) and O (4). Again, this is consistent with a number of conformations of the CuO_6 structure and the ions linked to it separated by small energy differences. The room-temperature structure is made up of a number of these conformations.

Infrared Spectra

The $(NH_4)_2\ Cu(H_2O)_6\ (SO_4)_2$ was lightly doped with deuterium (∼5% deuterium) and the crystals then mulled with mineral

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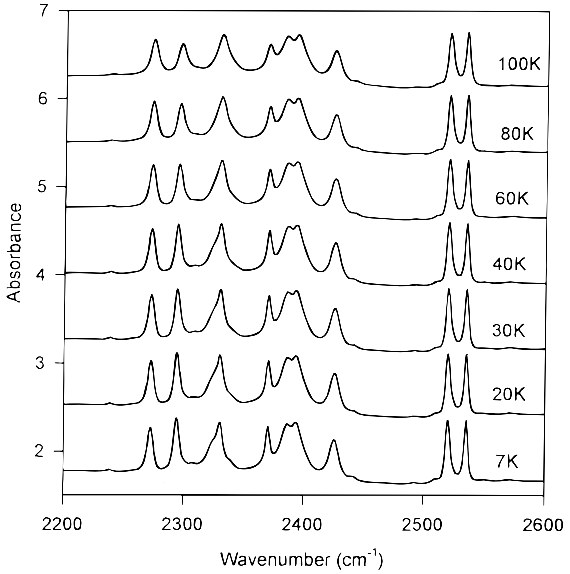

Figure 1. The infrared spectrum of ammonium copper Tutton salt doped with about 5% deuterium. The spectrum is of the region of the N−D and O−D stretches, and the assignments are listed in Table 1. The spectra change with temperature: the bands shift and become broader as the temperature is raised.

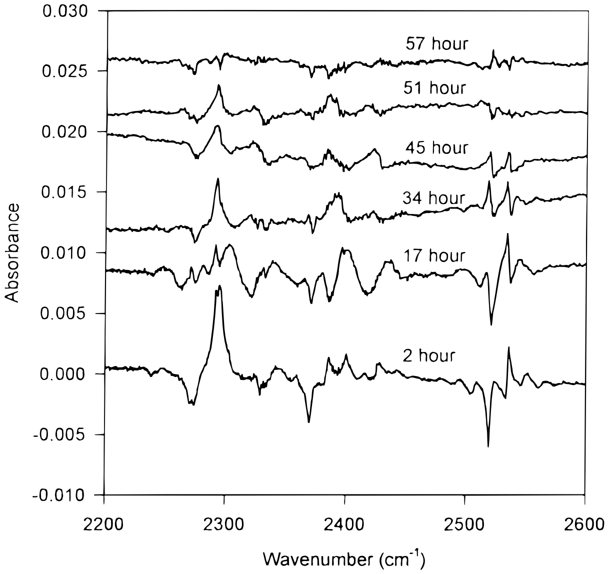

Figure 2. Equilibration of the ammonium copper Tutton salt at 7 K. The spectra are differences between spectra taken at time T and $T - 1$ h. The sample is cooled from room temperature in a closed-cycle He refrigerator, a process that takes about an hour. This constitutes a (slow) T-jump. The sample equilibrates in about 2 days. Note the split bands at 2273 and 2294 cm^{-1}.

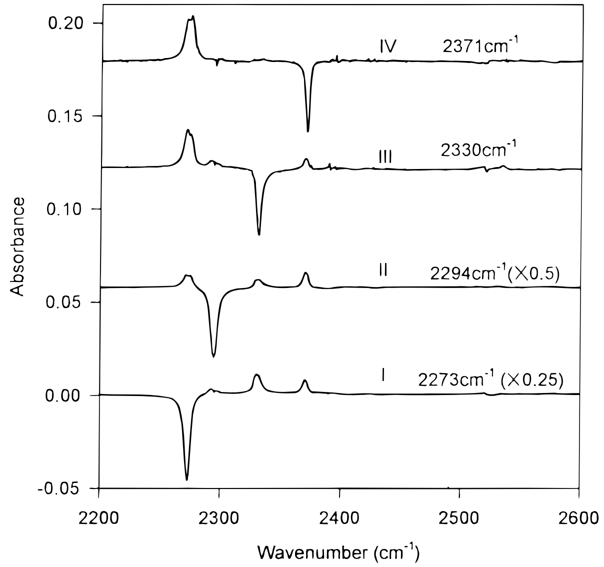

Figure 3. Difference spectra from hole burning of the N−D bands at 7 K. The sample was irradiated at the frequency indicated for about 5 min. The curves shown are the differences between the spectra after irradiation and those before. Note the scale of these differences (∼0.1 abs) compared to the spectra (∼1 abs). Difference spectrum II has been multiplied by 0.5, and spectrum I by 0.25.

oil and put into a cryostat as in our previous work. The spectra were taken at about 7 K and show notable differences from the spectra of the other Tutton salts. The spectra we consider are all of the N−D and O−D stretching regions. There are four different types of N−D bonds and six different types of O−D bonds, so that 10 bands are expected altogether. In the other Tutton salts we have examined, the six O−D stretches are tightly bunched between 2380 and 2500 cm^{-1}. For the Cu Tutton salt, they cover the much wider range 2324−2535 (Figure 1 and Table 1). Particularly notable are the two high-frequency bands above 2500 cm^{-1}. The detailed assignment of these bands is determined as outlined below.

We identify each band as belonging to either an N−D stretch or to an O−D stretch by hole burning. This allows the assignment of bands at 2272, 2294, 2330, and 2371 cm^{-1} to the N−D stretches (Table 1) and the remaining bands to the O−D stretches. The O−D band at 2324 cm^{-1} is below the frequency of the highest N−D stretch, again in contrast to the situation for other Tutton salts.[16] The detailed assignment uses the structure as reported in ref 17 and follows Oxton and Knop.[21]

The relative intensities of the bands change with temperature much as those of the Ni and Co Tutton salts.[10,11] The spectra of the Cu Tutton salt taken at various temperatures are displayed in Figure 1. The changes are difficult to observe on the scale of the figure, and thus, in Figure 2 we display difference spectra at 7 K. These show the differences observed after dropping the temperature to 7 K from room temperature. The difference spectra are from spectra taken 1 h apart; for example, the spectrum labeled 34 hrs is the difference between the 33 h and the 34 h spectra. Both the intensities and the positions of the N−D stretches and the O−D stretches change, and these changes have a time constant on the order of a day (see further discussion below).

Each of the N−D stretching bands can be burned with different results at different temperatures. We start with spectra at 7 K. The difference between the spectrum after irradiation at the indicated frequency and the equilibrated unirradiated sample is shown in Figure 3. Irradiation of any one of the N−D bands moves intensity into the other three bands. Band II behaves a little differently than the other three bands, just as in the Co Tutton salt.[12] The interchange among the four bands identifies them as N−D stretching bands and identifies the remaining six bands as O−D stretching bands. The unique feature of the Cu difference spectra is the doublets that appear in the difference spectra at 2273 and 2294 cm^{-1}.

At 20 K, the hole-burning experiment gives different results, as shown in Figure 4. The 20-K spectra show the doublet nature of hole II clearly.

The irradiation of the various N−D bands shows small but reproducible changes in the O−D bands, changes too small to see on the scale of Figures 3 and 4. Burning the O−D bands

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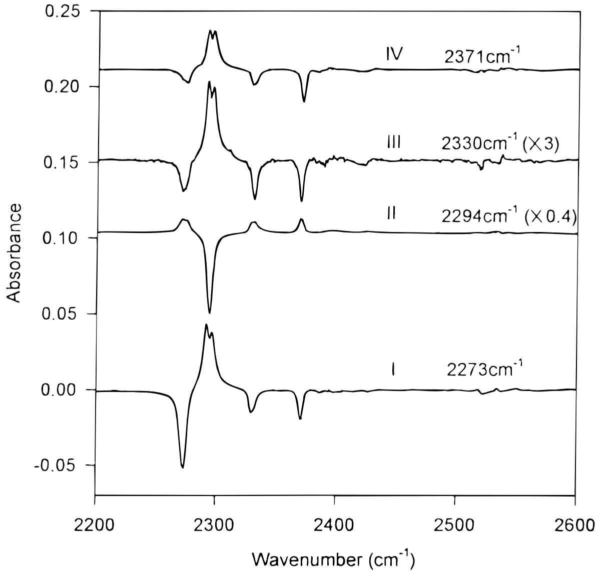

Figure 4. Difference spectra from hole burning at 20 K. The spectra of II and III have been multiplied by the factors indicated to get them on the same diagram. Note the clear doubling of the band at 2294 cm^{-1}.

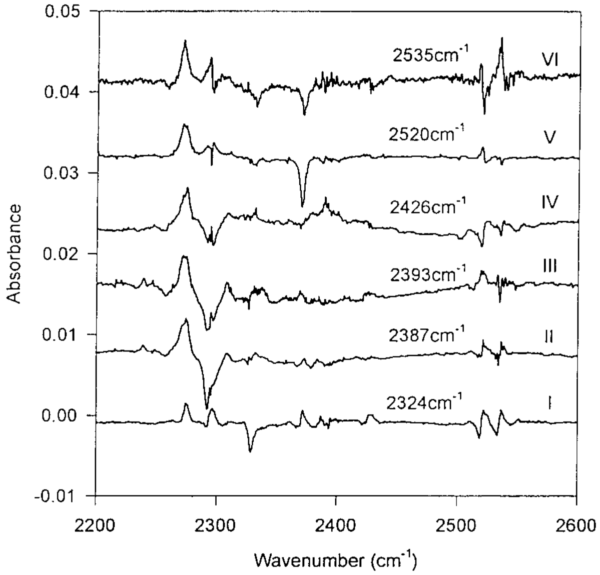

Figure 5. Difference spectra from burning the O−D bands at 7 K for about 20 min. These spectra have much smaller features than those of Figures 3 and 4.

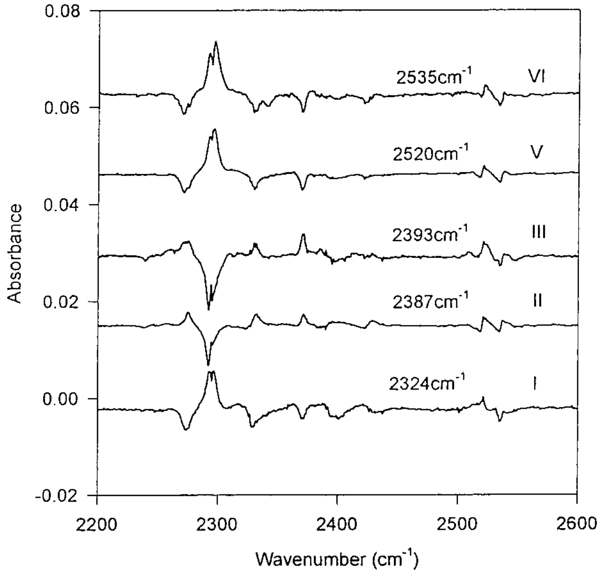

Figure 6. Difference spectra from burning the O−D bands at 20 K.

directly produces the spectra of Figures 5 (7 K) and 6 (20 K). These spectra show that both the N−D bands and the O−D bands are affected by irradiation of the O−D bands in a complicated pattern. We have not been able to observe hole burning due to irradiation of the O−D bands in any of the other pure Tutton salts and have seen changes in the O−D bands on irradiating the N−D bands only in the mixed Ni−Co Tutton salts.

A reasonable hypothesis is that the difference in the behavior of the Cu salt is due to the presence of the two conformations A and B of the distorted CuO_6 octahedra. Both diffraction and ESR studies show that the structure about the Cu atom shifts with temperature as conformation B becomes populated. Careful examination of the spectra of Figure 1 shows that both the N−D and the O−D bands shift with temperature (difficult to see on the scale of Figure 1). We compare the shifts in the structural parameters to the shifts in the infrared frequencies in Table 2. Since an increased distance means a weaker hydrogen bond and a higher infrared frequency, the data for N−D bands I and II and for O−D VI are consistent. For other bands, such as N−D III and IV, the shifts are too small to measure accurately, especially since the bands are overlapped. Also, the shift of the hydrogen bond for the two conformations of N−D IV makes it difficult to predict the infrared shift.

The doubled holes/antiholes I and II each consist of the hole from the original conformation and a new hole/antihole from the new conformation. For both bands, the new conformation shows up as a hole/antihole to higher frequency, in agreement with the shifts of bands I and II.

The shift of the bands occurs because conformation B is gradually populated with an increase in temperature. We have analyzed the shift of the three clear bands (N−D I, N−D II and O−D VI), and although the shifts are small, they are reproducible. The shift of band II between 7 and 100 K is +2 cm^{-1}. The shift of band I is only +0.5 cm^{-1} and that for O−D VI is −1.2 cm^{-1}. If the shifts are due to the gradual population of a second conformation, B, then ΔE_{BA} is about 1.1 ± 0.4 kJ/mol. This is of the same order of magnitude as the previous estimates of the conformational energy differences. However, the band shifts must be due to two different mechanisms, the change of conformation and the asymmetric thermal expansion of the lattice. The latter is often modeled by a Gruneisen formula,[22] but we do not have enough information to estimate the Gruneisen parameters.

For N−D I, the holes/antiholes (Figure 3) are at 2271.3 and 2274.5 cm^{-1}, while the absorption peak is at 2273 cm^{-1}. For N−D II, the absorption peak center is at 2294 cm^{-1}, while the peaks of the antiholes are at 2292.24 and 2296.53 cm^{-1}. For each, the maxima of the antiholes are on either side of the absorption maximum.The holes and antiholes are on a flat baseline (Figure 3), and thus their positions can be determined with more accuracy than the position of the absorption peaks. The absorption peaks are relatively close (Figure 1) and could be deconvoluted from each other in order to obtain better peak positions. However, we will use the observed maxima without correction.

The split antiholes are unexpected. A possible mechanism is that the newly formed orientation of the NH_3D^+ is formed in either of two orientations (presumably A and B), while the

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Table 2. Shifts in Hydrogen Bonding Parameters

	band	Distance (Å) 14 K[b]	295 K[a]	Δ[c]	IR shift with T	hole splitting
I	N−H(14)−O(5)	2.846	2.860	0.014	(+)	+3.2 cm^{-1}
II	N−H(11)−O(6)	2.872	2.899	0.027	(+)	+4.3
III	N−H(12)−O(3)	2.971	2.983	0.012	small	none
IV	N−H(13)−O(3*)	2.885	see text		small	none
O−DV1	O(7)−H(15)−O(5)	2.831	2.826	−0.005	(−)	

[a] From ref 17. [b] From ref 7. [c] Δ is the distance at 298 K minus that at 14 K.

absorption peaks are made up of conformations that have had time to anneal. Note that the holes/antiholes are doubled on burning of the O−D bands (Figure 6), as well as on burning of the N−D bands (Figure 3).

Relaxation of the Holes and Antiholes

In the dark, the holes and antiholes decay. As a starting model for the decay, we recall our results for the Co Tutton salt. For that salt, the decay kinetics can be described by three elementary rate constants. The first is for the interchange among I, III, and IV (called k_{around} in ref 12). The other two are for II → I, III, IV (k_{out}) and I, III, IV → II (k_{in}). The rate k_{around} is about 3 times k_{in} and k_{out} at 7 K. The rate equations are

$$A_{\text{II}}(t) = \Delta A_{\text{II}}\, e^{-\lambda_1 t} + A_{\text{II}}{}^{\text{eq}}$$

$$A_n(t) = -{}^1/_3 \Delta A_{\text{II}}\, e^{-\lambda_1 t} + [\Delta A_n + {}^1/_3 \Delta A_{\text{II}}]\, e^{-\lambda_2 t} + A_n{}^{\text{eq}}$$

n = N−D I, N−D III, or N−D IV

$$\Delta A_i = A_i{}^{\text{o}} - A_i{}^{\text{eq}}$$

$$A_i{}^{\text{o}} = A_i(t = 0) \qquad \text{A}_i{}^{\text{eq}} = A_{\text{i}}(t = \infty)$$

The A's are the occupancy of the four different N−D sites, which are in turn proportional to the absorbance of the respective bands. The four sites give rise to four possible rates λ_i which are $\lambda_1 = k_{\text{o}} + 3k_{\text{i}}$ and $\lambda_2 = \lambda_3 = k_{\text{o}} + 3k_{\text{a}}$. The fourth possible rate constant, λ_4, is zero, since it represents the rate of decay of the total N−D population.

Note that the decay kinetics depend on the initial values of ΔA_i; these are produced by the excitation process. [Longer burning of band I does not increase the size of the antihole II (Figure 7).] At 7 K (Figure 3), ΔA_{II} is small and it also turns out that $k_{\text{a}} \gg k_{\text{i}}$, k_{o}, so that the decay is dominated by the rate k_{a}. The decay was observed in the range of 7 to 16 K, with the results shown in Table 3. The rate constant k_{a} increases rapidly with temperature. In contrast, the constants k_{i} and k_{o} are much smaller but can be estimated from the results of burning band II. By 20 K, the rates k_{a} are too fast to measure, that is the bands I, III, and IV equilibrate in the burn time. This results in much simplified difference spectra as in Figure 4, in which burning band I, for example, results in holes at I, III, and IV and only one antihole, that at II. The decay of band I is shown in Figure 8 and shows two time constants. The fast process (k_{a}) occurs instantaneously on the time scale shown, while the second, the combination of k_{i} and k_{o} occurs in about 1000 min (Figure 8, Table 3). These constants, k_{i} and k_{o}, could be determined up to about 39 K. The temperature dependence of all three constants is shown in Figure 9 as Arrhenius plots. The rates are due to tunneling and show the characteristic two processes,[16] phonon-assisted tunneling at low temperature and quantum transition-state tunneling at higher temperature. Figure 9 shows apparent activation energies of about 0.13 kJ/mol for the first and 4.1 kJ/mol for the second process (Table 3).

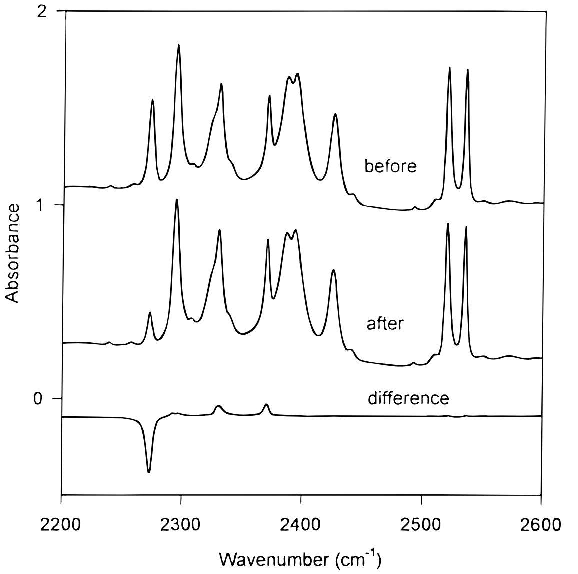

Figure 7. Results of irradiation at N−D I for 20 min. The irradiation of N−D bands I, III, or IV gives only a small antihole at position II. Note the large hole at N−D I.

Table 3.

Rates for Reorientation of the NH_3D^+

temperature (K)	k_{around} (min^{-1})	k_{in} (min^{-1})	k_{out} (min^{-1})
7	0.037	0.00020	0.00049
13	0.063		
16	0.16		
20		0.0011	0.0017
33		0.044	0.058
39		0.45	0.58

Apparent Activation Energies (kJ/mol)

Around		0.13		
In	(low T)		(high T)	4.1
Out	(low T)		(high T)	

The O−D Bands

We have already noted that small changes in the O−D bands show up when burning the N−D bands, for example on the difference spectra resulting from burning N−D III (Figure 3). The O−D bands also burn directly (Figures 5 and 6). When the O−D bands are burned, the N−D bands change markedly, and we did most of our experiments at 20 K, a temperature at which the relaxation of the N−D bands is relatively simple. The O−D bands do not burn as easily as do the N−D bands, and we irradiated the O−D bands for 20 min or more, while the N−D bands were irradiated for about 5 min.

Some of the results may occur because of the severe overlap of the various bands, for example the 2330 cm^{-1} N−D III band overlaps with the O−D I band at 2324 cm^{-1}, and the results of

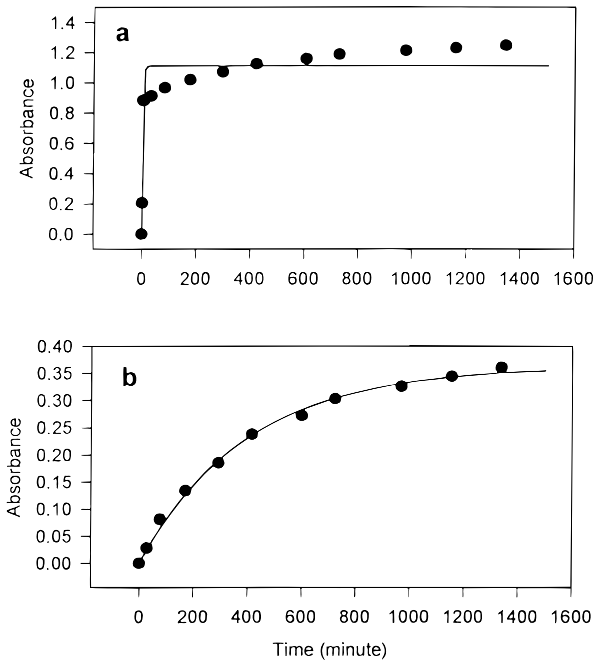

Figure 8. Decay of hole at 2273 cm^{-1} in the dark. The sample was irradiated at 2273 cm^{-1} for 5 min. Panel a shows that the decay occurs on two time scales. Panel b shows the same data as Panel a, with the first few points removed. The points in b fit well to a simple exponential $A = A_\infty (1 - e^{-kt})$ with $k = 0.0029$ min^{-}1.

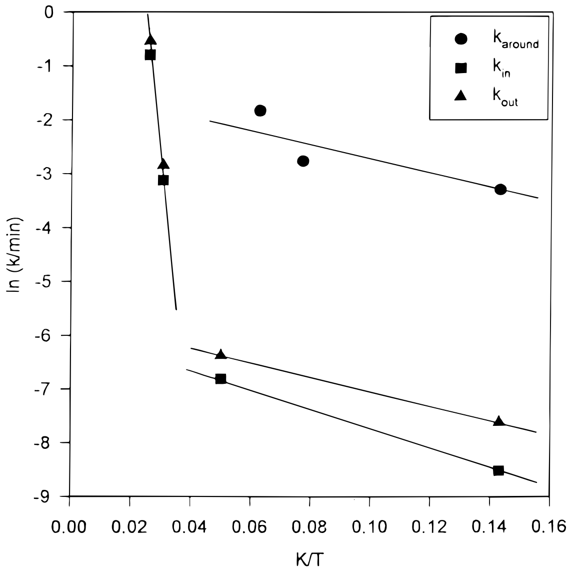

Figure 9. The rate constants for the various rates for relaxation in the dark of the N−D bands. The curves are characterized by apparent activation energies of about 0.13 kJ/mol at low temperature and about 4.1 kJ/mol at high temperature. The rate constants k_a, k_o, and k_i are for processes described in the text.

burning at either wavenumber are similar. Even irradiating at positions at which there is no obvious band can change the N−D bands.[15] It is important to note that irradiating at different wavenumbers results in different N−D patterns, both for irradiating the O−D bands (Figures 5 and 6) and for irradiating elsewhere. This shows that the holeburning process is specific and not just a process that heats the system.

The O−D bands are coupled to the doubling of N−D II in an unexpected way. The decay of the irradiation at N−D I is shown in Figure 10. The hole at I decays, together with the accompanying holes III and IV. The antihole II is doubled. The spectrum at 605 min shows that the two parts of antihole II decay at different rates. When they become significantly different in depth, the hole/antiholes at 2520 and 2535 appear. All the bands then decay.

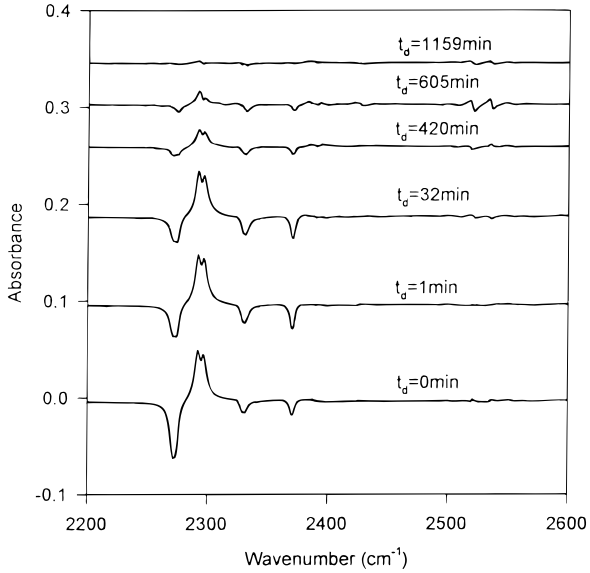

Figure 10. Decay of the difference spectra following irradiation at N−D I at 20 K. Note the split N−D II band and the nonmonotonic behavior of O−D bands V and IV.

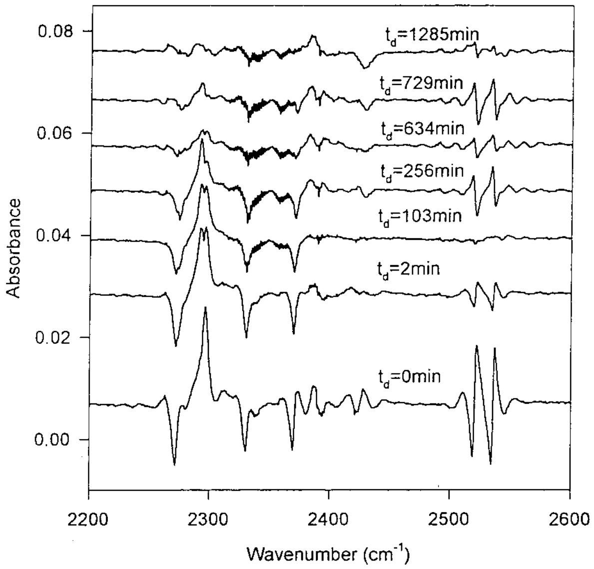

Figure 11. As in Figure 10, but following irradiation at N−D III. The O−D bands change shape, see Figure 12.

Perhaps a clearer example is shown in Figure 11. This shows the result of irradiating N−D III at 20 K (although this band, of course, is overlapped with O−D I). The burning produces a single antihole at N−D II and an intense set of holes and antiholes at O−D V and VI. The antihole at II starts at high wavenumbers, and the low wavenumber partner grows in (103 min), while the O−D holes/antiholes disappear and the N−D I also doubles. At 250 min, N−D II has changed, with the low wavenumber feature more intense, and the O−D V and VI are again prominent. However, now the O−D V and VI combination have the reversed holes and antiholes compared to the 0 min spectra, as shown on an expanded scale in Figure 12.

The O−D V and O−D VI bands must have two components A and B, just as the two components of N−D I and N−D II. From Figure 11, it is clear that the higher wavenumber part of

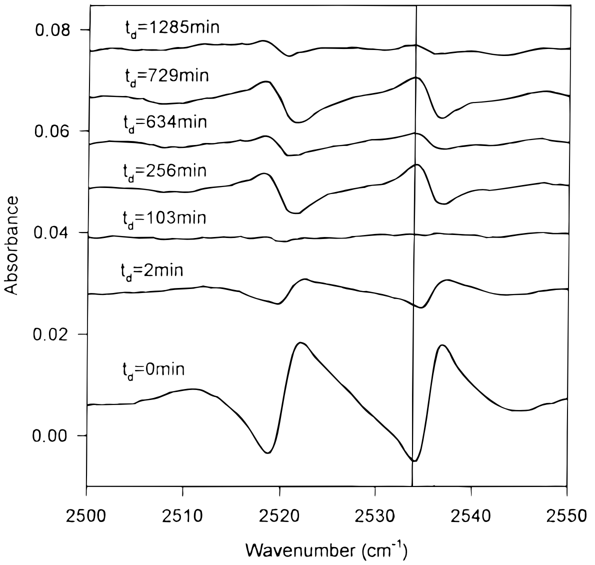

Figure 12. The O−D V, O−D VI part of the spectra of Figure 11 on an expanded wavenumber scale. In this figure, it is clear that the bands change with time, with the holes and antiholes changing into antiholes and holes, respectively. The absorption bands are at 2520 and 2535 cm^{-1}, approximately at the point of inflection in each pair of bands. The vertical line shows that, although the spectrum changes, the major features remain at the same positions.

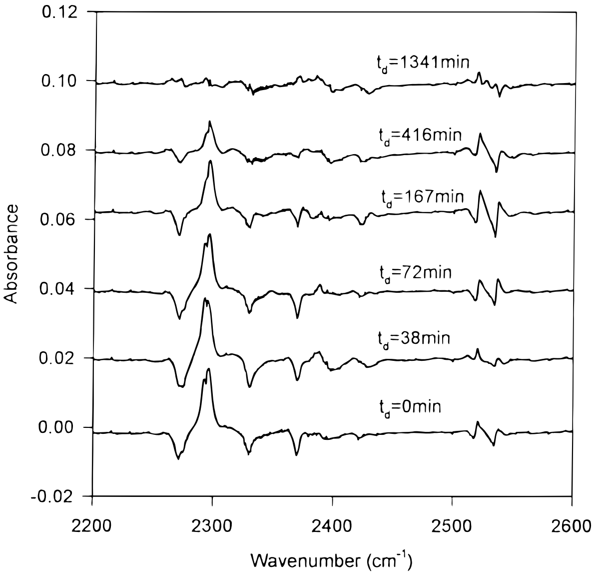

Figure 13. As for Figure 10, but for irradiation at O−D V. The results are qualitatively similar whether the N−D or the O−D bands are irradiated.

N−D II (conformation B) goes with the high wavenumber components of both O−D V and O−D VI.

N−D I shows a hole in these spectra. At 0 min, this is a single hole, which doubles as time goes on. The hole, of course, represents a depletion of a conformation/orientation. The hole I starts at the lower wavenumber of the doublet, and so again it is the higher wavenumber feature of the band that arises from conformation B.

Figure 13 reinforces this assignment. It shows the results of irradiating at O−D V. At zero time, the high-frequency components of N−D II, O−D V, and O−D VI antiholes and the low wavenumber component of the N−D I hole are prominent and then change *together* in a complicated time sequence. It is evident that the decay of the holes and antiholes proceeds by a set of coupled steps. These steps for the NH_3D^+ alone qualitatively follow the pattern we have observed in other Tutton salts. However, the O−D bands and the *individual* components of the split components of N−D I and N−D II clearly involve additional steps. We suggest that hole burning gives rise to some ratio of A and B conformations; these then equilibrate by rearrangement of the CuO_6 octrahedra, together with concomitant changes around the NH_3D^+ ions as well as of the other surrounding ions.

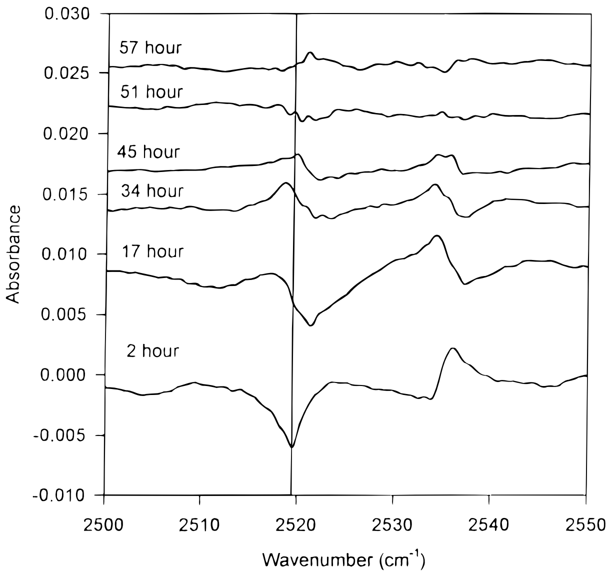

Figure 14. The O−D V, O−D VI part of Figure 2 on an expanded wavenumber scale. Note the change in shape of the bands near 2535 cm^{-1} and the shifts near 2520 cm^{-1}.

Similar changes occur on changing the thermal equilibrium between conformations A and B on a T-jump. Figure 2 shows such a jump in which the T is decreased from room temperature to 7 K in the course of an hour. Equilibration then proceeds over the course of many hours. Bands N−D I and II are split, and both they and the O−D bands change with time in a complex way. This figure, which represents the time-dependent changes with successive spectra representing successive changes, is different from our other figures which display the changes accumulated since time zero. Figure 14 shows the O−D V and VI regions of the spectra of Figure 2 on an expanded scale. The results are similar to those shown in Figure 12, for example the double hole/antihole at about 2535 cm^{-1} (O−D VI) switches between 2 h and 17 h. However, the bands near 2520 change in an apparently different fashion, with the change of 2 h peaked at the position of the absorption band rather than at the position of the one of the doublet components, as in the 17 h spectrum.

Finally, we have examined the widths of the N−D holes as a function of temperature and irradiation wavenumber. We have found no systematic variation with temperature over our 7−39 K range.

Summary and Conclusions

The Tutton salt, ammonium hexaaquacopper sulfate, is well-known to exist in two crystal structures. These two structures differ in the direction of the J−T distortion of the CuO_6 octahedron accompanied by small changes in the other features of the crystal. Which crystal structure is the lowest in energy is determined by very small changes, deuterium vs hydrogen, alkali metals vs ammonium, and pressure on the order of 0.2 kbar vs atmospheric pressure at room temperature.[23] That these

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(23) Schultz, A. J.; Hitchman, M. A.; Jorgensen, J. D.; Lujkin S.; Radaelli, P. G.; Simmons, C. J.; Stratemeier, H. *Inorg. Chem.* **1997**, *36*, 3382−3385.

small perturbations make a difference implies that the energy difference between the two major CuO_6 conformations A and B is small, and it has been estimated as 0.2 kJ/mol or less.[20]

We study the ammonium Tutton salt containing about 5% deuterium. Because of the sensitivity of the crystal structure to deuterium, it is possible that the crystals contain the CuO_6 in a distorted crystal, although studies in progress suggest no effect at this level of deuteration.[24] However, the absorption spectrum looks normal with single bands for each of the expected N−D and O−D bands. The large wavenumber range of the various O−D stretches reflects the large range of O−D hydrogen bond strengths that in turn results from the range of Cu−O distances.[21]

On hole burning, the bands N−D I, N−D II, O−D V, and O−D VI split into doublets. The lower wavenumber part of each doublet is associated with conformation A, and the higher wavenumber part with B. The relative contributions of the A and B parts to the N−D holes (here we do not distinguish between holes and antiholes but call them both "holes") vary with time, but in a number of hours, all the bands decay back to the equilibrium distribution. The O−D holes are coupled to the two parts of the N−D I and II holes. When the A and B parts of N−D I and II are of equal intensity, the O−D holes vanish only to reappear at later times! The method by which the nonequilibrium distribution is produced, by irradiation at a given band or by temperature jump, does not affect the relaxation process. The fact that O−D bands can be burned is in contrast to our results on other pure Tutton salts. The only Tutton salt that has shown any change in the O−D region at all is the *mixed* ammonium Ni−Co salt. In this, the O−D bands change upon burning the N−D bands. For the Cu salt, the O−D bands form holes and antiholes, both on irradiation of the N−D bands and on irradiation of the O−D bands. The Cu salt may act as does the mixed crystal because a variety of conformations are accessible to the perturbed molecules.

The crystal structures change continuously with temperature. This change has been interpreted in terms of continuous changes in the occurrence of the A and B conformations. Of course, the crystal lattice must also expand as the temperature is increased, and the changes observed must result from both effects. Both the N−D infrared and the O−D bands shift consistent with the observed changes in the length of the hydrogen bonds. The N−D shifts are consistent with the observed A and B parts of N−D I and N−D II, but the O−D shifts are not consistent with the parts of the O−D bands. The differences between the center of the absorption bands and the center of the component bands suggest the existence of slow "annealing" processes in the lattice. The time scale is hours, as shown in Figure 14, which compares the 2-hour spectrum to a 17-hour one.

The crystal structures show that the details of the hydrogen bonding of the ammonium ions is coupled to the change in J−T distortion about the Cu. We envision the infrared hole-burning process as rotating the NH_3D^+ ions, a process discussed, for example, in ref 25. This rotation perturbs the Cu environment enough to produce a nonequilibrium distribution of A and B conformers. These conformers slowly relax back to equilibrium. Further work on a faster time scale might be expected to show that the various absorption bands are inhomogeneous and made up of components of a number of possible conformations. It will probably be possible to manufacture either conformation at will for at least a short time at low temperature with the proper irradiation.

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JA980782K

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