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Assignment of Invisible Combination Bands in Ammonium Zinc Tutton Salt by Infrared Hole Burning

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A polycrystalline sample of the title compound containing a small fraction of deuterium was irradiated in an infrared region containing no apparent absorption bands. Holes and antiholes were produced in the N−D stretching bands. Each irradiation thus was at the wavenumber of a combination band involving a particular N−D stretch. Most of the combinations consist of the N−D stretch of the ammonium ion together with an internal mode of the zinc complex ion.

Introduction

A variety of ammonium-containing salts have been studied extensively via infrared-hole-burning spectroscopy.[1] In the majority of these studies, the samples were crystallized with a small amount of D_2O in order to form salts containing the NH_3D^+ ion. In crystal structures where the ammonium ion possesses low site symmetry, several distinct bands are observed in the N−D stretching region, reflecting the different possible orientations of the deuterium-containing ion. An infrared laser is used to irradiate one of the N−D stretches, and a typical result of this irradiation is for a fraction of the NH_3D^+ ions to rotate out of their initial configurations and into another. This process is monitored by infrared spectroscopy, and if the difference is taken between spectra of pre- and post-irradiated samples, negative differences (holes) are observed at the initial configuration, indicating a decrease in population, and positive differences (antiholes) are observed at the new configurations, indicating an increase in population. After the irradiation, these population differences eventually relax back to the original equilibrium distribution.

The precise details of the mechanism for the population reorientation differ from compound to compound depending on the exact nature of the combined vibrational−rotational potential energy surface of the NH_3D^+ ion.[2] The reorientation is thought to take place in the following manner for direct irradiation of an N−D stretch by an infrared laser. Initially, the stretching mode is excited and this populates the $n = 1$ vibrational surface without altering the orientation of the ion. In the excited vibrational state, some fraction of the ions then populate a high-lying level of the $n = 0$ vibrational surface (usually above the orientational barrier) through a process analogous to intersystem crossing. From there, the ammonium ions relax to a low-lying level with some going to the new orientation.[2] For the ammonium metal Tutton salts [$(NH_4)_2M(H_2O)_6(SO_4)_2$, where M is a bivalent metal cation], the energy barrier separating the different orientational positions of the NH_3D^+ ion in the crystal lattice is smaller than the energy separation between the ground and excited vibrational states of a given N−D stretch.[3]

In this study, we have induced orientational changes of the ammonium ion through a more indirect process, in which the infrared laser is not tuned to the frequency of a specific N−D stretch but instead to the frequency of an invisible combination band. The bands are invisible because they are broad and numerous and form an apparently featureless background with no distinct absorption features. The holes and antiholes appear at the positions of the N−D stretches, not at the burn frequencies. As will be examined in further detail below, we believe that the combination bands are modes localized to a relatively small region of space encompassing a few neighboring ions and that each component of the combination bands is an internal mode of a single ion (such as a breathing mode of an $M(H_2O)_6{}^{2+}$ ion or a stretch of an NH_3D^+ ion). It then seems reasonable that irradiation of the combination band reorients the NH_3D^+ ion by a similar mechanism as in the direct irradiation process.

We have previously seen this effect in the ammonium nickel Tutton salt,[4] but the irradiation frequencies used were in a region containing closely spaced combination bands, making definitive mode assignments difficult. Now we have found a less spectrally congested region and are able to assign the results of the irradiations to definite modes. The results of these experiments are presented below.

Experimental Section

The ammonium zinc Tutton salt, $(NH_4)_2[Zn(H_2O)_6](SO_4)_2$, was prepared by dissolving equimolar quantities of ammonium sulfate and zinc sulfate in an H_2O/D_2O mixture containing 5% D_2O. Samples were recrystallized and optically clear crystals used for this study. The crystals themselves were mulled with mineral oil and placed between two CaF_2 windows.

IR spectra were obtained from 2000 to 4000 cm^{-1} using a Nicolet 850 FTIR with a liquid-nitrogen-cooled InSb detector. The sample was held in a closed-cycle helium cryostat (CTI−Cryogenics SC 21), and the temperature was regulated to ±0.5 K through the use of a Lakeshore Cryotonics DTC 500-SP temperature controller. Each irradiation in this study was performed at 25 K and had a duration of 10 min.

The difference-frequency laser system has been described previously[5] but, briefly, is capable of generating 8 ns tunable pulses of IR radiation from 2200 to 2600 cm^{-1} at a repetition rate of 30 Hz. The system generates approximately 750 μJ per pulse over the range 2460−2580 cm^{-1}. The wavenumber of the laser radiation is set by a grating in the dye laser and was

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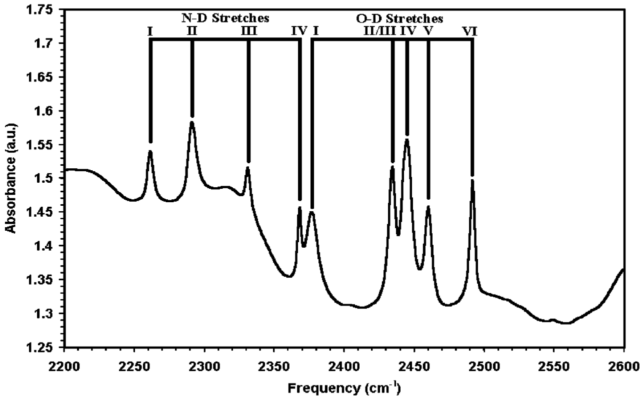

Figure 1. Infrared spectrum at 25 K of crystalline ammonium zinc Tutton salt grown in a 5% H2O/D2O mixture. The N−D and O−D stretching bands are labeled. The band positions are listed in Table 1.

TABLE 1: Fundamental Band Positions

fundamental band	wavenumber
N−D I	2261.2
N−D II	2291.1
N−D III	2330.8
N−D IV	2368.0
O−D I	2376.6
O−D II/III	2434.2
O−D IV	2444.6
O−D V	2459.8
O−D VI	2491.6

checked as in ref 5 by measuring the apparent position of the carbon dioxide Q branch. The small correction (2 cm^{-1}) from this calibration was applied to determine the frequency of the infrared beam. A parabolic mirror immediately prior to the sample focuses the pulses to a spot size somewhat larger than the 1.5 mm diameter hole in the mask placed over the sample. The mask ensures that the IR pulses pass through the same sample area as the broadband IR beam from the FTIR spectrometer.

Prior to performing any irradiations, samples were verified to be thermally equilibrated on the time scale of the experiment by acquiring spectra every 30 min, until no change was apparent on the order of several hours. Equilibration typically required 2 $^1/_2$ days when initially cooling from room temperature and 4−5 h between irradiations at 25 K.

Results and Discussion

I. Overview. The IR spectrum of the partially deuterated ammonium zinc Tutton salt is similar to that of the other Tutton salts.[1,3,4] In a Tutton salt, the introduction of small amounts of deuterium results in the formation of NH_3D^+ ions as well as some HDO molecules. The crystal belongs to space group $P2_1/a$, #14. Because of the low site symmetry of the NH_4^+ ion in the crystal, 4 N−D bands are observed (one for each orientation of the NH_3D^+) along with 6 O−D bands. For the $Zn(H_2O)_6{}^{2+}$ ion, there are 12 possible O−D positions, but only 6 are distinguishable because of the presence of an inversion center, and therefore, a total of 10 bands are present in the O−D and N−D stretching region. Only 9 of these bands are apparent as O-Ds II and III have very similar stretching frequencies. A typical spectrum of an equilibrated sample at 25 K is shown in Figure 1, and the wavenumbers of the assigned bands are listed in Table 1.

In this study, irradiations were performed every 5 cm^{-1} from 2473 to 2578 cm^{-1}, a region above that of any of the N−D stretch bands (Table 1). This wavenumber range includes the area near the O−D VI as well as what was previously thought to be a nonresonant background region. Irradiation at any of the above wavenumbers reveals a distinct pattern of holes and antiholes in the N−D stretching region.

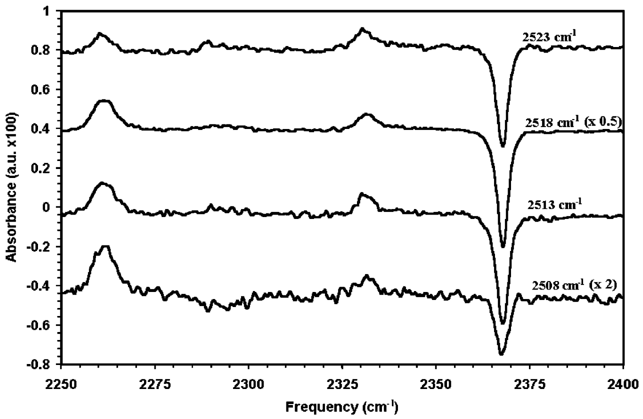

Figure 2. Differences between the spectra of samples irradiated in intervals from 2508 to 2523 cm^{-1} and the original spectrum. Each spectrum is labeled with the irradiating wavenumber. The holes and antiholes are at the positions of the N−D bands. Note only the intensities of the holes change in going from spectrum to spectrum in this region.

In most cases, irradiation produces a fairly simple difference spectrum, with one hole and three antiholes in the N−D region and little or no change in the O−D region. We have previously attributed this type of pattern to the rotation of an NH_3D^+ out of one of the four possible configurations and into one of the other three. It therefore appears reasonable that the difference spectra we have observed are due to the irradiation of a combination band of which one component is an N−D stretch. A few of the irradiations at the higher frequencies produced difference spectra containing multiple holes; these are thought to be due to the effects of burning overlapping bands, each of which arises from a combination based on a different N−D stretch.

II. Combination Band Locations. Systematic irradiation has revealed that from 2473 to 2498 cm^{-1} and 2508−2523 cm^{-1}, the same basic pattern of holes and antiholes can be observed and only the intensities of the bands vary throughout each of the two ranges (Figure 2 shows the higher of these wavenumber ranges). Specifically, the most intense burns in these ranges occur at 2488 and 2518 cm^{-1}, suggesting that these positions are close to the center of two distinct combination bands and that the combination bands are relatively broad with homogeneous widths of approximately 20 cm^{-1}.

For the irradiations from 2538 to 2578 cm^{-1}, the pattern of holes and antiholes changes almost every 5 cm^{-1} (Figure 3). These changes include changes in the number of holes and antiholes as well as in their positions. For example, the difference spectrum resulting from irradiation at 2543 cm^{-1} shows two holes and two antiholes. The primary hole in this spectrum is located at the position of the N−D IV band, and there is a shallow hole at the position of the N−D II band. Two antiholes are also present: a strong anti-hole at N−D I and a weak anti-hole at N−D III. The difference spectrum due to irradiation at 2548 cm^{-1} is markedly changed. There are still two holes and two antiholes, but their positions are different. The weak hole at N−D II has now become the primary hole in this spectrum, the weak antihole from N−D III has become a weak hole, and the strong hole at N−D IV has become a strong antihole. A further shift of the irradiation frequency to 2553 cm^{-1} again changes the spectrum: the primary hole is now at N−D III, N−D I and N−D IV both remain anti-holes, and the

TABLE 2: Spectral−Hole Positions and Assignments

irradiation position (cm^{-1})	hole position (cm^{-1})	difference (cm^{-1})	N−D component	assignment	literature value (cm^{-1})
2483	2291.1[a]	191.9	N−D II	T_{2g}	193
2518	2367.7	150.3	N−D IV	T_{2u}/SO_4^{2-} libration	146/159
2543	2368.0	175.0	N−D IV	T_{2g}/T_{1u}	180/181
2548	2291.1[a]	256.9	N−D II	E_g	256
2553	2331.1	221.9	N−D III	T_{2g}	217
2563	2367.7	195.3	N−D IV	T_{2g}	193
2573	2330.6	242.4	N−D III	E_g	243
2578	2261.4	316.6	N−D I	?	?

[a] Wide holes; the position listed is that of the fundamental band, see text.

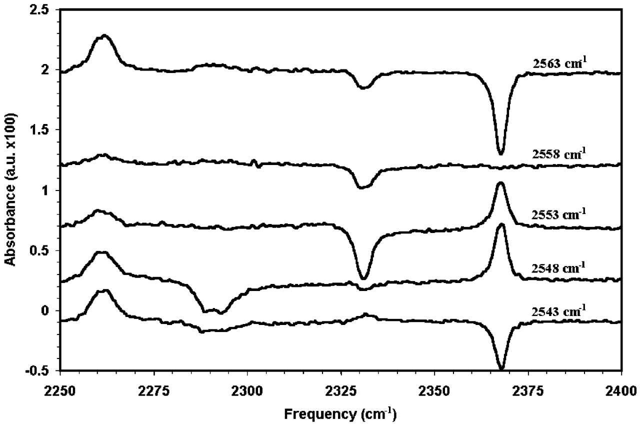

Figure 3. Difference spectra arising from irradiations from 2543 to 2563 cm^{-1}, which show changes in both the intensity and in the basic pattern of holes and antiholes in going from spectrum to spectrum. Table 2 lists the wavenumbers of the holes and their assignments.

difference spectrum appears to be relatively flat at the N−D II position, showing no clear evidence of a hole or an antihole.

We interpret the complicated changes from one irradiation to the next in the following manner. It would appear that there are a large number of possible combination bands present in this region, and these are based upon the various different N−D stretching bands. The bands are relatively broad and may overlap, resulting in difference spectra showing more than one hole.

III. Combination Band Assignments. To ascertain the identity of the smaller wavenumber component in these combination bands, the position of the primary hole in each difference spectrum was recorded, along with the difference of the hole position and the irradiation frequency. Table 2 shows the wavenumbers of the laser and then that of the observed hole and the appropriate differences. The hole position listed is that actually observed and in most cases is within 0.2 cm^{-1} of the absorption band maximum (compare Tables 1 and 2). The exceptions are the holes at position N−D II. These are broad and we list the position of the absorption band, a value close to the center of the broad hole. The differences between the hole and the irradiation positions range from approximately 150 to 320 cm^{-1}. In the cases where successive difference spectra yield qualitatively similar hole and antihole patterns, the irradiation frequency that resulted in the most intense difference spectrum is taken as the center of the broad combination band. Table 2 presents a listing of the observed combination bands along with our proposed assignments.

The frequencies resulting from this analysis were compared to previous vibrational studies of the ammonium zinc Tutton salt. The assignments of the combination bands are primarily based on the newer and more complete work of Barashkov et al.[6] rather than the older work of Sekar et al.[7,8] Barashkov et al. compared the IR and the polarized Raman spectra of several Tutton salts to each other and to the results of normal mode calculations for the metal complex.

The majority of our assignments are of combinations of a specific N−D stretch with a mode of the $Zn(H_2O)_6^{2+}$ complex and are given here with symmetry labels corresponding to the internal modes of an octahedral molecule. The metal complex is only approximately octahedral, because it occupies a site of C_i symmetry. The nonoctahedral distortions are relatively small (on the order of 0.05 Å),[9] so the use of octahedral labels is retained. However, the distortions are large enough to split the degenerate fundamental bands by up to 50 cm^{-1}. Factor group splittings appear to be negligible for this compound and so are ignored. Most of the observed combination bands detailed in Table 2 appear to be made up of one of the N−D stretches and one of the E_g or T_{2g} octahedral modes of the metal complex. The modes at 151 and 175 cm^{-1} could be due to one of a number of modes, but most of the possibilities are also modes of the metal complex (see Table 2). The assignment for the mode at 317 cm^{-1} is uncertain, but this mode is already at a higher frequency and may itself be a combination. The agreement of better than a few wavenumbers between our combination frequencies and those of the assigned fundamentals is excellent. Two sources of error are the 5 cm^{-1} spacing of our hole-burning positions and the fact that these studies were performed at 25 K, whereas the assignments come from data taken at 93 K. The spectra shift by up to 10 cm^{-1} on going from room temperature to 93 K and will shift further on going to 25 K.[6] Combinations involving lattice modes are a possibility. We did one check, studying the hole depth from irradiation at 2518 cm^{-1} as a function of temperature. This showed no obvious temperature dependence from 17.5 to 35 K, contrary to what might be expected for phonon-related bands.

It is not possible to make a quantitative comparison of the hole-burning efficiencies between direct irradiation of an N−D stretch and irradiation of a combination band from these results. This is because it is extremely difficult to compare the absorbance of the combination bands with the absorbance of the N−D stretches because of the difficulty of separating the contributions of the combination bands and the background in our spectra. The holes produced by indirect irradiation are about the same depth as those resulting from the direct process. However, the combination bands are far less intense than the N−D stretches, and our laser produces about five times more power in the combination band region than in the N−D stretching region. There are two possibilities: The combination bands may be just five times weaker than the fundamental absorption bands, or the efficiency of the interwell crossing may be much more efficient for irradiation of the combination bands. The latter seems more likely and may be due to the indirect process populating higher orientational energy levels.

Discussion

The existence of relatively strong combinations bands between internal modes of the ammonium ion on one hand and modes of the metal complex ion on the other and, a fortiori, the production of holes at the bands of the ammonium ion after irradiation at the combination bands implies the existence of substantial and specific interactions among these ions. The ammonium ions and the metal complex ions are not even neighbors in the crystal structure but are separated by sulfate ions. However, all of the ions are connected by a hydrogen bond network and this must account for a substantial part of the interaction. Detailed analysis of the correlation between the mean amplitudes of thermal motion of the atoms in some ruthenium Tutton salts as revealed by X-ray diffraction has shown that the Ru−O stretch motion is coupled to the translation of the O−Ru−O moiety.[10] The large coupling is explained qualitatively by the effect of the hydrogen bonds. Hydrogen bonding (A−H−B) profoundly affects the A−H bond.[11] The resulting anharmonicity of the hydrogen bond is nicely illustrated by recent measurements of the hydrogen atom transfer in excited vibrational states in liquid water.[12]

Are there approximate rules that can be used to provide a prediction of the relative size of the couplings? The symmetry of the full unit cell is so low that almost everything is allowed. We can take the metal ion as octahedral as above. However, the symmetry at the other ions, both the sulfate and the ammonium is C_1. The formal symmetry of the unit cell is reduced to C_1 by the presence of the deuterium. Because this is in low concentration, there is usually only one deuterium per ammonium ion and only one per unit cell and so no approximate symmetry on which to base a propensity rule is apparent. A quantitative explanation of the effects of coupling among the many components of the Tutton salt that leads to coupling among the vibrations will have to wait for a detailed many-molecule model of the crystal.

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