

LETTERS TO THE EDITOR

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COMMUNICATIONS

Rotation of ammonium groups by infrared irradiation far from obvious absorption bands

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Direct irradiation of any of the four distinct N–D stretching bands of the ammonium nickel Tutton salt $[(\text{NH}_4)_2\text{Ni}(\text{H}_2\text{O})_6(\text{SO}_4)_2]$ that has been doped with a few percent deuterium, produces a persistent hole in that band. The hole and the accompanying antiholes indicate rotation of the ammonium ion. Indirect irradiation at up to a few hundred wave numbers away from the stretching bands—in a region of the spectrum that appears to be featureless background—also rotates the ion, although this requires considerably more power. The most effective indirect irradiation takes place at the positions of the combination bands between the stretches and the librations of the ammonium ions. Other effective irradiation positions are in the tails of the stretching bands or in combinations with other unassigned modes. Sufficient energy is transferred through the vibrational degrees of freedom to the librations without being dissipated to drive the rotation of the ammonium ion. © 1996 American Institute of Physics. [S0021-9606(96)03416-5]

INTRODUCTION

The change in the infrared bands concomitant with persistent spectral hole-burning provides an indicator of the structural changes that produce the hole. A variety of ammonium salts—doped with a small amount of deuterium—that have low enough symmetry show four distinct N–D stretching bands. There is one N–D band for each distinct D site and, in many cases, any of the N–D bands can be burned. Irradiation results in a hole in the band being burned and antiholes in the other three bands. This shows that the infrared-driven process is a rotation of the ammonium ion that carries the D to a different position. Examples of this process have been demonstrated for simple salts such as ammonium sulfate,¹ double salts such as the Tutton salts^{2,3} and disordered salt systems such as $\text{K}_x(\text{NH}_4)_y\text{SO}_4$,^{4,5} as well as for the ammonium salts of organic systems such as anionic polymers.⁶

In all the salts we have examined, the ammonium ion is hydrogen bonded to its surroundings, typically to the oxygen of a sulfate or nitrate ion and absorption bands are about 5 cm^{-1} [full width at half maximum (FWHM)] wide, implying fast relaxation times. The N–D stretching bands burn homogeneously on the time scale of our experiment (minutes), and we have shown that the widths of the absorption bands and those of the holes vary systematically as a function of the frequency of the N–D band. The frequency of the band is in turn a function of the strength of the hydrogen bond.⁵ This observation led us to conclude that the width of the N–D bands is due to a relaxation process of the atoms that form the hydrogen bond itself. It is surprising then that even though the relaxation of the N–D stretches is rapid, burning these bands transfers sufficient energy into the librational modes of the ammonium ion to rotate them. Here we show a

more surprising result: Irradiation in spectral regions far from the N–D stretches also rotates the ammonium ions. In this “indirect” hole burning, the indicator remains the formation of one or two holes and three or two antiholes among the N–D stretching bands. In the indirect process, the energy must transfer through more “steps” to drive the libration. The production of holes far from the irradiation also serves to identify the presence of vibrational combination bands. We note that the irradiations that are effective can occur in regions of the spectrum in which no discrete absorption can be seen.

In this Communication, we describe the experiments and then review the literature on other systems before concluding.

EXPERIMENT

Our current investigations are all on the ammonium nickel Tutton salt $[(\text{NH}_4)_2\text{Ni}(\text{H}_2\text{O})_6(\text{SO}_4)_2]$. The salt is crystallized from a solution containing a few percent D_2O , and this provides NH_3D^+ and HDO in the resulting crystals. The samples were prepared as mulls in Fluorolube (fluorocarbon grease) or mineral oil. Previously, we have used the fluorocarbon,^{4,5,7,8} but switched to the mineral oil when we realized that the possible existence of long tails on the bands was an issue (see below). The spectral background in the O–D, N–D stretching region (2600–2100) is flatter in the hydrocarbon.

The infrared spectrum in this region consists of the four clearly resolved N–D stretching bands and six overlapped O–D bands (Fig. 1). The infrared irradiation was accomplished with laser diodes (Muttek H2 lead salt diodes) and with a difference frequency laser (DFL). The DFL provides tunable infrared radiation in approximately 5 ns pulses by

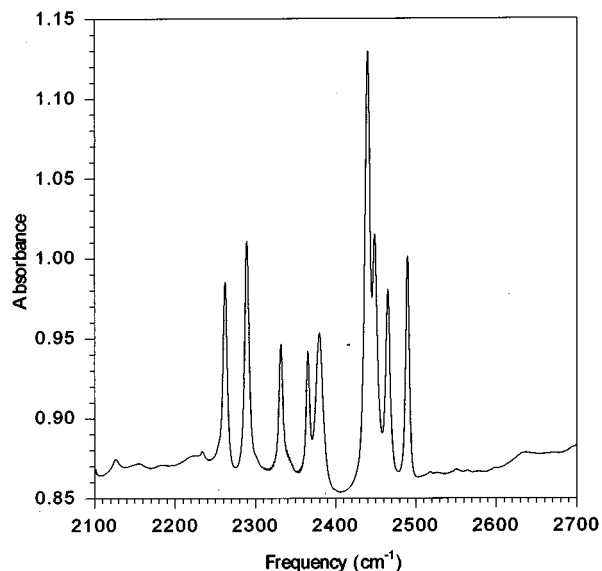


FIG. 1. Infrared spectrum of ammonium nickel Tutton salt doped with 4% of deuterium. The O–D (six bands from 2380 to 2500 cm^{-1}) and the N–D (four bands from 2260 to 2364 cm^{-1}) stretching bands are shown (the two O–D bands at 2436 appear as one in this spectrum). The temperature is 20 K.

mixing the output of a doubled Nd–YAG laser (green) with the output of a dye laser (yellow) in a LiIO_3 crystal.⁹ After seeing the effects far from the exciting line, which we describe below, we took care to eliminate the possibility of stray radiation from the DFL. Possibilities are optical parametric oscillation (OPO) in the crystal,¹⁰ amplified spontaneous emission (ASE) in the dye laser¹⁰ and other unknown causes. Each laser beam was blocked in turn. Without the yellow beam no infrared was seen, and so no OPO radiation was present. The main dye laser beam was suppressed by blocking the grating in the dye laser and a few percent of ASE radiation was detected, but found not to result in enough infrared radiation to have any effect. For some of the experiments a variable notch filter¹¹ was placed in the irradiating infrared beam. This notch filter has a transmission with a half-width at half-height of about 25 cm^{-1} and completely eliminated any possibility that we were introducing stray radiation at the position of the observed hole, which was typically 200 cm^{-1} away. From this and other experiments, we conclude our radiation is “clean.”

RESULTS

The qualitative results are briefly stated. Irradiation at spectral positions many hundreds of wave numbers higher than the N–D stretching bands produces holes in these bands. Since the holes are the result of rotation of the ammonium ion, the holes and antiholes grow together. Irradiation at different wave numbers has different effects—just as does irradiation at the different fundamental N–D bands. Irradiation at lower energies than the fundamentals also results in rotation—an effect that extends at least 80 cm^{-1} below the position of the lowest N–D stretching band. Figure 2 shows the difference bands resulting from irradiation frequencies

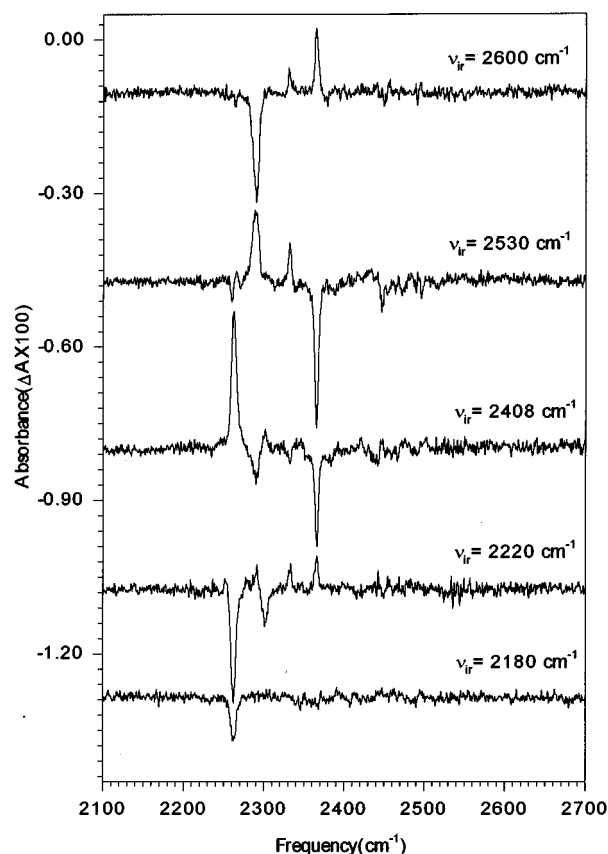


FIG. 2. Difference spectra showing the result of irradiation at different frequencies. Note the frequency scale is the same as that for Fig. 1. The spectra are displaced along the vertical for clarity. The “holes” are the peaks that go down on the diagram. All the irradiating frequencies are outside the region of the large bands of Fig. 1, except for 2408 cm^{-1} , which is right in the middle at a position of an absorption minimum. Note that the four N–D indicator bands (2262, 2290, 2330, 2365 cm^{-1}) show a variety of different reorientations of the NH_3D^+ ions. The spectra are taken at $T=20$ K after 5 minutes of irradiation with about 8 mW of ir power.

well above (>2530 – 2600 cm^{-1}), just above (2408 cm^{-1}) or well below (2180–2220 cm^{-1}) the N–D indicator bands.

The changes observed are a few percent of the indicator band height. The hole appears in various of the N–D bands, as indicated in Fig. 3. The OD bands do not change.

Three changes are apparent from the holes burned by direct irradiation of the ND bands; the indirect holes are about one order of magnitude smaller, the maximum depth to which the hole can be burned by long irradiation is considerably less (12% vs 50%) and the relaxation of the holes produced by the indirect irradiation is about a factor of 2 slower. Irradiation into the OD stretching bands produces no systematic observable changes. The magnitude of the hole produced by direct irradiation of an N–D band can be done with either the cw or pulsed laser and is approximately linear in the total power.

DISCUSSION

We have shown that direct irradiation of weak infrared bands can couple energy into the librational degrees of freedom of the NH_3D^+ ions and cause them to rotate.^{2,3} The coupling is mode specific, since irradiating at different fre-

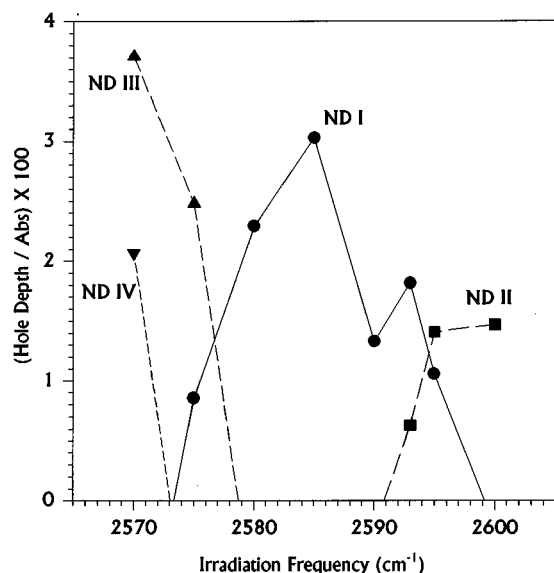


FIG. 3. Excitation spectra for the holes produced in the ND bands by irradiation approximately $200\text{--}350\text{ cm}^{-1}$ higher in frequency. Typically, holes in one or more of the N–D bands are accompanied by antiholes of various sizes in the other N–D bands. The lines are drawn to aid the eye and those that cross the x axis go to regions in which the holes change to antiholes.

frequencies causes holes in different N–D bands. This means that the different ions, i.e., those with the D in specific different positions, rotate. The clearest indirect excitation is indicated by ND–I at 2262 cm^{-1} with an irradiating frequency of about 2585 cm^{-1} . The difference of the two frequencies, 323 cm^{-1} , can be assigned to the librational frequency of the NH_3D^+ ions by comparison with infrared and Raman spectra of NH_4^+ containing Tutton salts. These NH_4^+ assignments, which are based on single crystal polarized spectra, are 330 and 366 cm^{-1} for $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and 364 cm^{-1} for both the Zn and Mn salt.^{12–14} Our ammonium ion contains a deuterium atom, which should lower one of the librational frequencies, and so the identification is reasonable.

In the gas phase, the occurrence of mode-specific effects is well known; for example, in the nonstatistical behavior in the dissociation of HFCO, in which combinations of the out-of-plane band are only weakly mixed with the background states and different states show very different dissociation behavior.¹⁵ In rare gas matrices, hole burning in various combination bands has been shown to isomerize small molecules such as 2-fluoroethanol.¹⁶ Here, all of the bands of the burned isomer serve as indicator bands. The burning efficiency varies smoothly with energy in Rice–Ramsperger–Kassel–Marcus (RRKM) fashion, except that combinations that contain the OH stretch are much more efficient at isomerization. A more complex example is provided by hole burning of NO_2^- bands in KI.^{17–19} This system has been studied by many methods and bands of various isotopes ranging from the far infrared (70 cm^{-1})¹⁷ to the mid-infrared¹⁸ have been identified. Irradiating bands that are combinations of the NO_2^- fundamentals with a variety of phonon-gap modes is effective in burning corresponding fundamental bands.¹⁹ Most of the bands are narrow—as narrow as 0.01 cm^{-1} . However, one mode, the ν_1 fundamental, is 3 cm^{-1} wide and

shows a long tail to low frequency. This band burns homogeneously when irradiated in the central band or a few wave numbers away in the tail.¹⁸ The tail is attributed to rapid vibrational relaxation due to interaction with sidebands of the asymmetric ν_3 vibration.

In the Tutton salts, all the N–H and O–H hydrogens participate in hydrogen bonding and give rise to absorption bands and holes that are homogeneous and broad, implying fast relaxation times. The T_1 times of free and hydrogen-bonded OH and OD groups have been measured in zeolites.²⁰ The relaxation measurements have been interpreted to mean that the O–H and O–D stretch relaxes into other modes intrinsic to the hydrogen bond and that this relaxation is faster for a hydrogen bonded O–H than for a free O–H. The relaxation times are about 10^{-10} s . We take the zeolite measurements as the closest available analog to the Tutton salt measurements. In both, the hydrogen bonding is to adjacent O–X groups. The T_1 time is much shorter than the pulse width on our DFL and explains why the DFL gives results similar to those of our CW laser. It leaves unexplained how a significant amount of energy arrives in the librational degrees of freedom.

The hole burning at wave numbers below the N–D region requires a different explanation. The band shape of the ν_1 stretch in NO_2^-/KI suggests a possibility; rapid relaxation to nearby modes causes a N–D band with a very long tail to lower frequencies. Note that at the temperature of these experiments, 20 K , there cannot be difference combination bands as far as the $\sim 80\text{ cm}^{-1}$ below 2262 cm^{-1} at which we observe burning.

ACKNOWLEDGMENTS

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