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Infrared Spectral Hole-Burning and Spectral Diffusion of Vibrational N–D Bands in a Disordered Tutton Salt *

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We have studied infrared spectral hole burning of the N–D stretching bands of NH_3D^+ in salt $[(\text{NH}_4)_2\text{Co}_{0.25}\text{Ni}_{0.75}(\text{H}_2\text{O})_6(\text{SO}_4)_2]$ at 10 K. We have observed that the spectral line broadening occurred on a logarithmic timescale, which is consistent with the theoretical prediction of a standard two-level system. The temperature of 10 K is also beyond the temperature limit in previous studies on spectral diffusion.

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The ammonium ion, with its simple geometry, can be considered as a model system to study molecule rotation or orientational changes in condensed phases.^[1] In many salts, the ammonium ion shows almost free rotation at high temperature and slow orientational tunnelling at low temperature. The ammonium ion of many ionic salts can be rotated using the resonant infrared (IR) irradiation, which is the so-called IR spectral hole-burning (SHB). Subsequently, the ion will rotate back to its original position. Both the IR irradiation-induced rotation and the dark decay are characteristics of the ammonium ion and its surrounding and provide unique information on energy transfer, tunnelling and kinetics in crystals and glasses. In the last decade, Strauss and co-workers^[2–7] have performed extensive studies on the IR spectrum and SHB of various ammonium ions containing a small part of deuterium at low temperatures.

In this letter, we demonstrate the observation of spectral diffusion (SD) of vibrational N–D bands in the $[(\text{NH}_4)_2\text{Co}_{0.25}\text{Ni}_{0.75}(\text{H}_2\text{O})_6(\text{SO}_4)_2]$ mixed crystal, by using the SHB method. SD is one of the immanent properties of the low-temperature spectra of amorphous solids. It can be characterized as time-dependent broadening of spectral lines of chromophores/impurities in an amorphous host. This anomaly is nowadays believed to result from the existence of a specific low-energy local state two-level system (TLS).^[8–10] The first observation of SD in optical spectra was made in an organic glass via SHB.^[8] In the past, SD was generally performed at temperatures below 4 K. Our present SHB was performed at 10 K, which is beyond the temperature limitation on the studies of SD in amorphous solids. SHB as well as photon echo, which may give the information on homogeneous line broadening, is an effective technique to study low-temperature dynamics of amorphous solids such as glasses and polymers.^[8,11] The mixed crystal $[(\text{NH}_4)_2\text{Co}_{0.25}\text{Ni}_{0.75}(\text{H}_2\text{O})_6(\text{SO}_4)_2]$, containing about

4% of deuterium, is prepared in the same way as the description in Ref. [7]. The basic apparatus consists of a Fourier transform infrared (FTIR) spectrometer equipped with a number of flip mirrors. The mirrors can be set to allow irradiation of the sample by a laser source or to allow the acquisition of a normal FTIR spectrum. The resolution of the FTIR spectrometer is 0.5 cm^{-1} . The pulsed source uses an LiIO_3 crystal as a difference-frequency generator (DFG). It produces the difference frequency between the 532 nm radiation and that generated by a dye laser (Spectra Physics PDL-3). The 532 nm radiation is the doubled output of an Nd:YAG laser (Spectra Physics GCR-150). The 532 nm power is split by a dichroic mirror so that 20% of the power goes directly to LiIO_3 and the remainder pumps the dye laser. The crystal generates about $160 \times 10^6\text{ J/pulse}$ at 2260 cm^{-1} in the infrared (5 ns pulse) spectrum. In the measurements, the sample was sandwiched between the two KBr windows and was put into a liquid-helium cycling system (10 – 300 K). The power density of burning light was $\sim 10\text{ mW/cm}^2$.

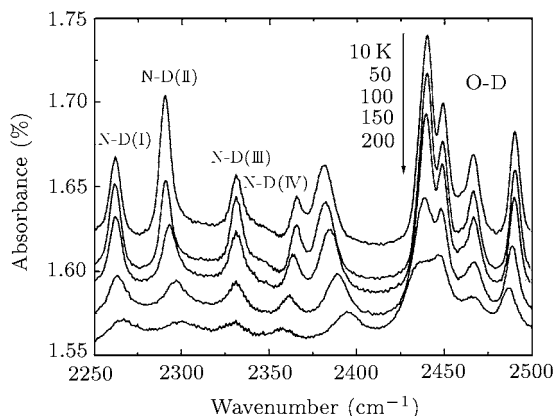


Fig. 1. FTIR spectra of stretched N–D bands at various temperatures (10 – 200 K).

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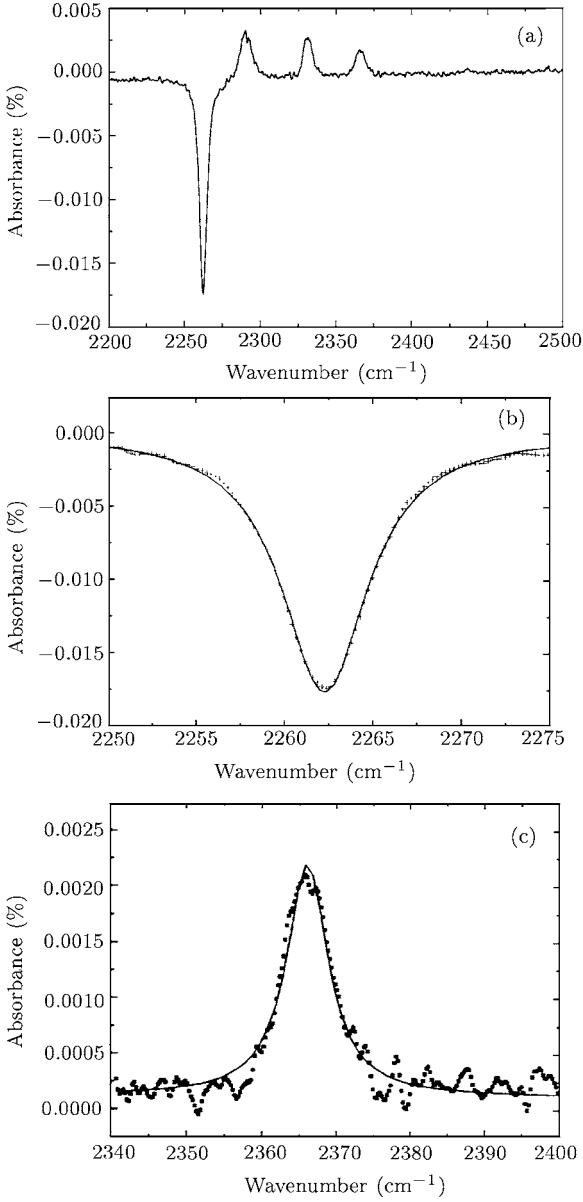


Fig. 2. (a) IR hole-burning spectrum at 10 K. (b) Hole profile and its Lorentzian fitting function. (c) Anti-hole profile and its Lorentzian fitting function. The hole was burnt at 2262 cm^{-1} for 15 min.

The deuterium forms some NH_3D^+ ions and some HDO molecules. The N–D and O–D stretching region shows four N–D bands, one for each orientation of the NH_3D^+ , and six O–D bands, one for each distinguishable O–D band. Figure 1 shows the stretched N–D bands at various temperatures. If the temperature is varied from 10 to 50 K, the widths of each band remain approximately constant. When the temperature is above 50 K, the widths will broaden continuously with temperature and in a $\sim T^2$ power law above 100 K. As is well known, the width of an absorption line can generally be described in terms of inhomogeneous and homogeneous contributions. The former are due to a static distribution of transition frequencies, whereas the latter are determined by life-

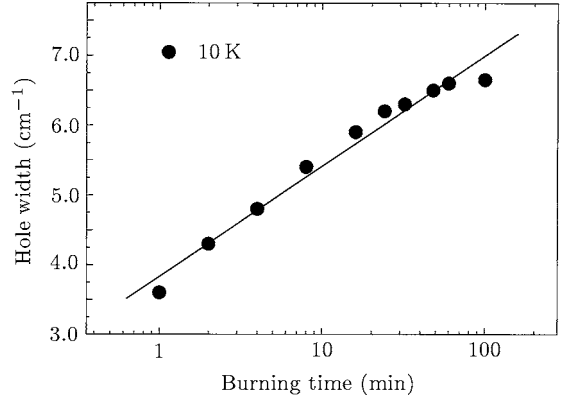


Fig. 3. Dependence of hole width on burning time (the hole was measured immediately after burning).

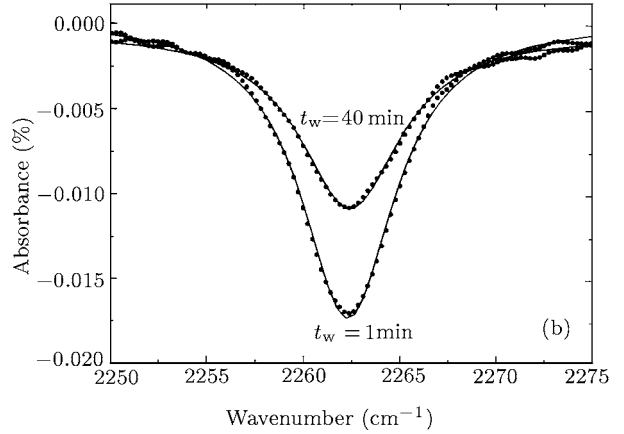
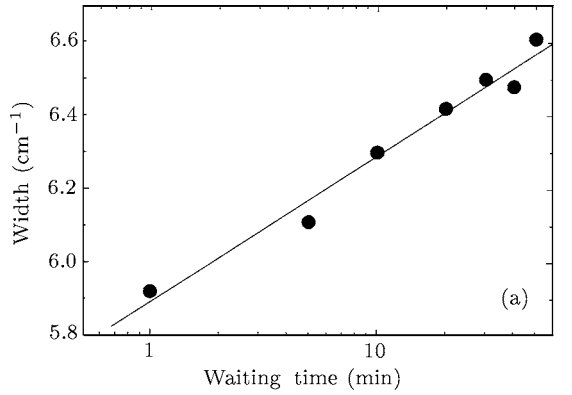


Fig. 4. (a) Dependence of hole width on waiting time (the hole was measured after burning for 15 min). (b) Hole spectra at different waiting times.

time T_1 of the relevant energy level and a temperature-dependent pure dephasing time T_2^* of the excitation, $\Gamma_{\text{hom}} = (2\pi T_1)^{-1} + (\pi T_2^*)^{-1}$. T_1 is largely independent of temperature, whereas T_2^* is dependent on temperature, which is dominated by the electron–phonon interactions.^[12] The homogeneous width (HW) is a constant below 50 K, indicating that the HW is probably dominated by the lifetime of the relevant energy level. The contribution of electron–phonon interactions to the line broadening is negligible in comparison

with that of the lifetime. As the temperature is above 80 K, the vibrational bands are strongly broadened by interaction with photons. T_1 is estimated to be ~ 2 ps provided that T_2 is much longer than T_1 .

Figure 2 shows the IR hole spectrum of the mixed crystal after burning for 10 min (the hole spectrum was immediately measured after IR irradiation). A deep hole is formed at the N–D (I) band, while three shallow anti-holes are formed at the positions of the other N–D bands. The width of the hole is $\sim 5.8 \text{ cm}^{-1}$, which is slightly narrower than the width of the global line. On the other hand, the width of the anti-holes is almost the same as that of the global lines. The insets (a) and (b) show that the hole and anti-hole profiles can be well fitted by Lorentz functions. This indicates that the hole and anti-holes are homogeneously broadened.

Figure 3 shows the hole width as a function of burning time. The hole width after burning for 1 min is 3.6 cm^{-1} . It broadens logarithmically with the increase of burning time. Figure 4 shows the hole width as a function of waiting time. It is evident that the hole width increases with time, although the variation ($\Delta\Gamma/\Gamma$) is relatively small. It is also proportional to logarithmic time in the measured timescale. The line width of the probe molecules doped in disordered solids is caused, to a large extent, by various dephasing mechanisms, coupling to tunnelling centres (TLS) being the most prominent at low temperatures. The main features of TLS dynamics follow from the assumption of a broad distribution of energies and an extremely broad distribution of relaxation rate, ranging roughly from 10^{11} to beyond 10^{-6} s^{-1} . TLS dynamics may lead to a line broadening. In the standard TLS, the line broadening can be written as

$$\Delta\Gamma = \bar{P} c \ln\left(\frac{t}{t_0}\right). \quad (1)$$

The broadening is proportional to the TLS number density \bar{P} , the TLS–dye coupling constant c , and follows a logarithmic time dependence. The line broadening of the stretching N–D bands is very consistent

with the prediction of standard TLS. This means that SD of the N–D band may originate from the interaction of standard TLS with the N–D vibrational transition. Differing from the crystal, the local environment of the mixed crystal is not neat. This is the reason for the existence of tunnelling states. It should be noted that very recently the deviations from the logarithmic time behaviour were reported in the long-time regime.^[13] At present, we cannot produce detailed knowledge of the origin of TLS in the mixed crystal. Further work should be performed on definitely revealing the origin of TLS in the mixed crystal.

In conclusion, FTIR spectra and IR SHB have been studied at 10 K in a mixed Tutton salt $(\text{NH}_4)_2\text{Co}_{0.25}\text{Ni}_{0.75}(\text{H}_2\text{O})_6(\text{SO}_4)_2$. It was observed that the hole width as well as the homogeneous line width was broadened logarithmically with the increase of waiting time. This can be attributed to the interaction of flipping TLS with the vibrational transition of N–D bands.

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