

HYDROXYLAMMONIUM SULFATE - INFRARED SPECTRA AND SPECTRA-STRUCTURE CORRELATIONS

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An attempt is made to correlate the number, position and/or intensity of some of the bands in the infrared spectra with the structural features of hydroxylammonium sulfate.

The crystal structure of hydroxylammonium sulfate (space group $P2_1/c$, $Z = 4$) has been recently determined by one of us /1/. It consists of discrete hydroxylammonium and sulfate ions (two types of the former and one type of the latter) connected by hydrogen bonds. The two strongest such bonds have lengths O...O of 259.2 and N...O of 274.6 pm, the second O...O bond is 272.0 pm long, whereas the rest of the N...O bonds are characterized by distances equal to 292.0, 290.4, 284.3, 280.6 and, once again, 280.6 pm. The N-O distances within the hydroxylammonium ions are found to be equally long (141.0 pm). The infrared spectra of the title compound have been studied several times /2,3/ and the INS spectra have also been measured /3/ but the availability of structural parameters not known before justifies the reinvestigation of the infrared spectra, especially when spectra-structure correlations are the main goal. Some of these will be discussed in the present paper, whereas a more complete account will be published at a later date.

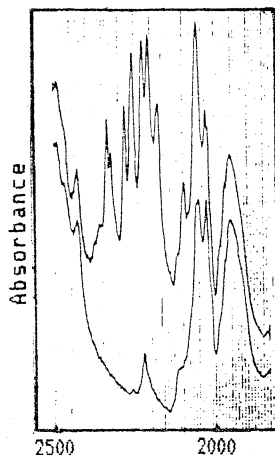


Fig. 1. The OD stretching region in the spectra of slightly deuterated (a) and protiated (b) hydroxylammonium sulfate

RESULTS AND DISCUSSION

As mentioned above, there are seven crystallographically non-equal hydrogen bonds so that a corresponding number of bands is expected in the ND/OD stretching region of samples with low deuterium content. Contrary to the expectations, however, at least eight bands not present in the spectra of the protiated compound are found (Fig. 1) in this region for samples containing a small amount of deuterium (under such circumstances the hydroxylammonium ions contain isotopically isolated NH_2D^+ or OD groups). The bands having the highest frequencies (2335, 2322 and 2280 cm^{-1}) undoubtedly correspond to the three weakest hydrogen bonds, the band at the lowest frequency is probably due to the vibration of the OD groups which form the strong O...O bond whereas that at 2258 cm^{-1} apparently corresponds to the second such bond. If this assignment is correct, then

the bands at 2208 and 2180 cm^{-1} should be related to the two nominally equal N...O bonds. It would thus appear that the infrared spectra are more sensitive to some structural differences than the X-ray diffraction.

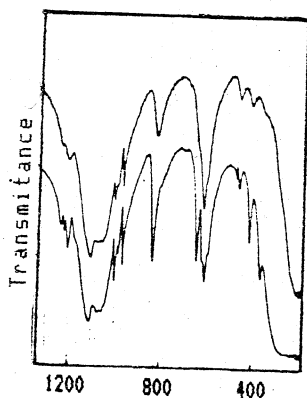


Fig. 2. The low-frequency region in the RT (a) and LNT (b) spectra of hydroxylammonium sulfate

Nominally equal according to the crystallographic data, as pointed out earlier, are also the N-O distances in the two hydroxylammonium ions. However, three bands are actually present in the region around 1000 cm^{-1} where the corresponding N-O stretches (together with the symmetric SO_4 stretch) are expected to appear (Fig. 2). Of these, the two highest shift somewhat on deuteration and are, correspondingly, assigned as due to the N-O stretches, whereas the band at around 980 cm^{-1} is attributed to the symmetric SO_4 stretch. Somewhat surprising is the intensity of this latter band, especially in view of the rather small distortion of the sulfate ions /1/. It should, however, be noted that around 470 cm^{-1} a band, attributable to the doubly degenerate SO_4 bend, is observed, the corresponding mode being infrared inactive for the ideal tetrahedral sulfate ions.

The lowering of the temperature produces similar changes (shift to higher frequencies and increase in intensity) in the case of the rather broad and weak RT band at 830 cm^{-1} (never before mentioned) and of the shoulder at around 640 cm^{-1} (Fig. 2). The similarity in the behaviour of these two bands suggests a similar origin and it is easy to assign them to the two out-of-plane OH bendings. The appreciable frequency difference between them could be understood if the differences in the strengths of the OH...O bonds are taken into account and the frequency difference in the case of the two bands (at 425 and 370 cm^{-1}) already assigned /3/ to NH_3 torsions can be explained in a similar way (for one of the NH_3^+ groups, namely, the average N...O distance is 279.8 and for the other such group it is 287.7 pm).

REFERENCES

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