"True" infrared absorption spectra of polycrystalline rubidium and cesium nitrate: a new method of sample preparation

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Abstract—A new method for preparing powders of very small particle size from vitrified dilute aqueous solutions is reported. In these powders particle size effects seem to be eliminated even for samples absorbing very strongly in the i.r. As an example the i.r. spectra of polycrystalline $RbNO_3$ and $CsNO_3$ and their temperature dependences are reported where "true" absorption spectra of the antisymmetric stretching transition seem to have been obtained.

INTRODUCTION

In the i.r. absorption spectrum of solid nitrates and other oxyanions, the most intense band is the antisymmetric stretching transition. The great intensity of this transition poses problems because small particle size becomes important and, in addition to absorption, light losses by reflection and scattering occur, both diminishing the "true" intensity of the transition [1–10]. To obtain an i.r. spectrum insensitive to sample size, the particle dimension must be smaller than the wavelength of the exciting radiation. It has been shown that for intense bands particle diameters of $< 0.1\ \mu m$ are necessary to attain the limiting value of the absorbance [1]. Such a fine dispersion has often been impossible to achieve, and the i.r. antisymmetric stretching transitions from powders of oxyanion salts generally are very broad and poorly resolved [11]. During an investigation of vitrified aqueous electrolyte solutions [12], prepared in the same way as vitrified liquid water [13, 14], I observed that removal of the solvent *in vacuo* at $\sim 200\ K$ gives a dry solute of very small particle size, such that the "true" absorption spectrum seems to have been obtained. So far the antisymmetric stretching transitions of solid nitrates, sulfates and perchlorates prepared this way have been investigated, all the spectra showing improved resolution and additional bands in comparison with the spectra of powders reported in the literature. In this paper the i.r. transmission spectra of solid $RbNO_3$ and $CsNO_3$, the two substances with the most pronounced effects, are reported as examples of a generally applicable method.

EXPERIMENTAL

To obtain the finely divided solids, dilute aqueous electrolyte solutions were vitrified as described previously in detail [12–14] by depositing the aerosols at high vacuum on a KBr cryoplate, and by pumping off the solvent at $\sim 200\ K$. This procedure leaves behind an opaque, uniform looking, thin film of dried solute. For $RbNO_3$ a 1.0 molar solution was used for aerosol formation, for $CsNO_3$ a 0.50 and 0.25 molar solution.

For the polycrystalline $RbNO_3$ sample, shown in Figs 1 and 2, absorbances at 300 K were 0.50 and 0.14 for the peak

maximum of the v_3 region and for v_2, and at 20 K 0.82 and 0.21, respectively. Peak positions of the non-degenerate nitrate transitions, v_1 and v_2, were 1054 and 836 cm^{-1} at 300 K, and 1057 and 838 cm^{-1} at 20 K. For the poly-
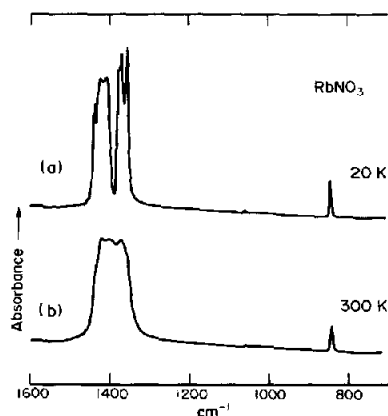

Fig. 1. Infrared transmission spectrum of polycrystalline $RbNO_3$ on a KBr cryoplate at 20 and 300 K.
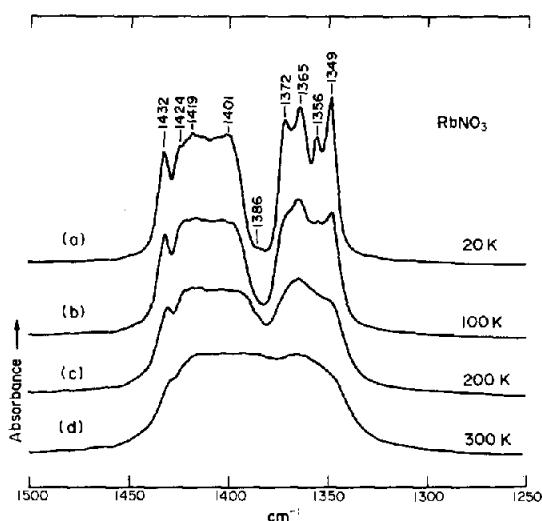

Fig. 2. The antisymmetric stretching transition region of Fig. 1 expanded, using identical gain.
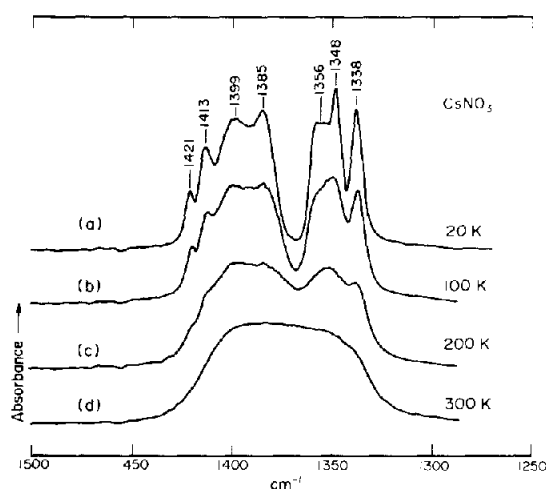
Fig. 3. Expanded i.r. transmission spectrum of the antisymmetric stretching transition region of polycrystalline $CsNO_3$.

crystalline $CsNO_3$ sample, Fig. 3, absorbance of the most intense peak at 300 K was 0.27, and at 20 K 0.40. The peak positions of the nondegenerate nitrate transitions, v_1 and v_2, were 1048 and 833 cm^{-1} at 20 and 300 K.

The spectra were recorded in absorbance on a Pye Unicam SP 3-300 instrument with SP 3-050 data processing system, and calibrated with CO_2 and polystyrene film. Resolution was 3 cm^{-1}. The reported peak positions are believed to be accurate to $\pm 2 cm^{-1}$.

RESULTS AND DISCUSSION

The spectrum in Fig. 1 was obtained from a thin film of polycrystalline $RbNO_3$ on a KBr cryoplate in vacuo. The antisymmetric stretching transition is expanded in Fig. 2, and that of a $CsNO_3$ sample in Fig. 3. The overall pattern of Figs 2 and 3 is very similar, the $CsNO_3$ bands being shifted to lower frequency as expected. From the approximate thickness of the vitrified dilute aqueous $RbNO_3$ and $CsNO_3$ solutions ($\sim$ 12 and 6 μm, obtained by using the peak absorptivity of the librational band of vapor deposited amorphous solid water [15] for evaluation) it follows that the average thickness of the dry salt films must have been < 0.1 μm. The temperature effects observable in the figures were completely reversible. Most important, identical spectra were obtained from even thinner samples, with constant intensity ratios of the v_3 region to the v_2 mode. Therefore I believe that for these solids particle size has already been reduced sufficiently to obtain the "true" absorbance of the antisymmetric stretching transition. A comparison with published powder spectra [16-19] shows much smaller band widths, increased resolution and multiplets at low temperatures, and strongly increased peak intensity of the antisymmetric stretching transition relative to the v_2 mode. The band positions of the v_2 mode and of the weak v_1 transition were identical with those reported previously within their accuracies [16-19].

Possible artefacts are reaction of the dry solid with the KBr cryoplate, and orientation of the particles [1].

The first can be excluded because the spectrum of KNO_3 is different and has not been observed. Even $AgNO_3$ prepared this way does not exchange with KBr over hours at room temperature if water vapor is rigorously excluded. This is understandable because the dry salts adhere very loosely to the KBr plate. Orientation of the polycrystalline samples is more difficult to exclude. I consider it unlikely: first, because of the excellent reproducibility of the spectra from different samples; second, because orientation would be most likely started by expitaxial growth on the KBr plate, and the weak adhesion of the powders indicates that this does not occur.

To obtain spectra of the quality shown in the figures, vitrification of the dilute solutions is essential. Only then will removal of the solvent in vacuo give a powder with sufficiently small particle size. Powders from frozen solutions, which were prepared simply by spraying a solution with a retouching air brush onto a precooled KBr plate at normal pressure, gave spectra of much lower quality. The latter cooling method gives crystalline ice and phase segregated solute of apparently larger particle size.

I see applications for investigating very intense i.r. absorption bands of powders without particle size effects for the following systems. (i) The water soluble oxyanion salts, $RbNO_3$ and $CsNO_3$ are just one example. (ii) For salts poorly soluble in water such as $CaCO_3$ it is obviously impossible to make a vitrified solution. However, it might be possible to prepare $CaCO_3$ of small particle size during warming up from successive layers of vitrified solutions of the single components, i.e. of vitrified $CaCl_2$ and Na_2CO_3 solutions. (iii) The technique can possibly be extended to organic systems by choosing a suitable solvent. An advantage in comparison with the alkali halide disc technique is that exchange reactions of the powders with the KBr cryoplate are very slow, even for $AgNO_3$ powder on a KBr plate at room temperature. The major disadvantage is that the experimental setup requires matrix isolation equipment together with some device to generate and introduce an aerosol into the high vacuum system, and that the technique is much more time consuming than the established methods for investigating powders.

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