

The influence of moisture on potassium bromide disks used in infrared spectrometry*

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Abstract—When using the alkali-halide disk technique in infrared spectrometry we noticed that moisture from the atmosphere can penetrate into a KBr disk, causing recrystallization of the KBr. A critical relative humidity was observed above which moisture is taken up. This value depends on the fineness and structure of the KBr; for optical grade, handground KBr (Merck) it is about 70 per cent. "Wet" disks lose water if stored in an atmosphere of a lower humidity; replaced in the original atmosphere, they take up water again but to a lower extent.

In order to study the water sensitivity of KBr disks containing a sample, KSCN was used. KSCN has two $C\equiv N$ stretching bands dependent on the form in which it occurs: as a solution at 4.84μ and in the solid phase at 4.87μ . The latter can be converted into the former by water uptake of the disk; on drying of the disk the band is shifted back to its original wavelength.

In the disk are small cracks through which condensed moisture and dissolved sample can be transported. This is demonstrated by the behaviour of KSCN. If a KBr disk, containing a single KSCN crystal completely surrounded by carrier material, is exposed to a moist atmosphere the KSCN is transported through the whole disk.

The same transport, due to the presence of water in a disk, was observed with a number of similar inorganic salts. Sometimes the accompanying bandshifts could be eliminated by drying, sometimes they persisted, probably indicating that a solid solution has been formed. In the absence of water none of these phenomena were observed.

Interaction between sample and water can be demonstrated also with D_2O . In a moist D_2O atmosphere active H atoms of sample molecules in a disk are substituted by D atoms. This phenomenon can be applied successfully in structure determination.

Introduction

THE KBr disk technique is a valuable sampling method in infrared spectrometry. A number of substances however, show or can show anomalous spectra if prepared according to this method (e.g. benzoic acid). If a disk containing benzoic acid in the anomalous form is exposed during some time to an atmosphere with a rather high relative humidity a complete conversion into the normal form of the acid takes place, as was found some time ago in our laboratory [1].

The work presented here deals with:

- A. The water content of KBr disks.
- B. Redistribution of sample material by penetrating water.
- C. Conversions caused by water.
- D. The use of a D_2O atmosphere.

Methods and materials

In the experiments two kinds of KBr were used: Merck reagent grade and Merck optical

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[1] A. TOLK, *Spectrochim. Acta* **17**, 511 (1961).

grade resp. After grinding in an agate mortar, these materials were stored at about 130°C ready for use. The sample materials were reagent grade.

The atmospheres with distinct relative humidities were obtained with the help of saturated solutions of LiCl, K₂CO₃, NaBr, NaCl and Na₂S₂O₃ giving relative humidities of respectively 12, 44, 57, 75 and 78 per cent at room temperature according to ROCKLAND [2].

Different amounts of sample and always about 300 mg KBr were mixed in an agate mortar and put into an evacuable die with splittable cone (internal diameter 13 mm) according to SCHIEDT [3]. The mixture was evacuated for 3 min and then a pressure of 12 tons was applied for 3 min under maintenance of the vacuum.

The spectra were recorded with a Perkin-Elmer 21 spectrophotometer linear in wavelength and equipped with a NaCl prism.

Experiments, results and discussion

A. The water content of KBr disks

We investigated the amount of water which is taken up by disks if they are stored in atmospheres with various relative humidities. The amount was calculated from the IR band at 2.9 μ , using an extinction value of 1.25 per mg H₂O [4]. The results are given in Table 1 for two kinds of KBr and for KBr containing some KSCN.

Table 1. The water-content in μ g per disk of about 300 mg KBr. First number: instantly after pressing; Second number: after 96 hr storage at the indicated relative humidity. For the experiments with KSCN 0.2 mg of this salt was mixed with about 300 mg KBr.

Relative humidity %	KBr optical		KBr reagent		KBr + KSCN	
12	7	7	10	14	20	30
44	7	7	10	17	20	124
57	3	7	10	20	23	309
75	7	69	7	99	17	611
78	7	295	10	325	opaque	

As can be seen there is no great difference between optical and reagent grade KBr. At a relative humidity of 57 per cent or lower no water is taken up. At 75 per cent or higher the water uptake is significant (0.007 mol H₂O/mol KBr). Since stable crystals of KBr absorb water only at a relative humidity of 84 per cent [5], we must conclude that the KBr in the disk, or part of it, is present in a less stable state.

Furthermore we observed that "wet" disks lose water if stored at lower relative humidities; replaced in the original atmosphere they take up water again but to a lower extent.

The KBr disks, containing some KSCN show a significant increase in water uptake. At 44 per cent it is quite considerable already. Since the critical relative

[2] L. B. ROCKLAND *Anal. Chem.* **32**, 1375 (1960).

[3] U. SCHIEDT, *Z. Naturforsch.* **8b**, 66 (1953).

[4] A. TOLK, Thesis, University Utrecht (1959).

[5] J. OBERMILLER and M. GOERTZ, *Z. physik. Chem. Leipzig* **109**, 145 (1924).

humidity for KSCN (pure) is about 47 per cent [5], the water uptake of KBr disks containing a solid sample, seems to be influenced by the properties of this sample.

B. Redistribution of sample material by penetrating water

For these experiments disks containing some KSCN were used. Dry KBr (300 mg) and KSCN (0.2 mg) were mixed carefully and directly after pressing a spectrum was run. A very small water band at 2.9μ was observed and a rather

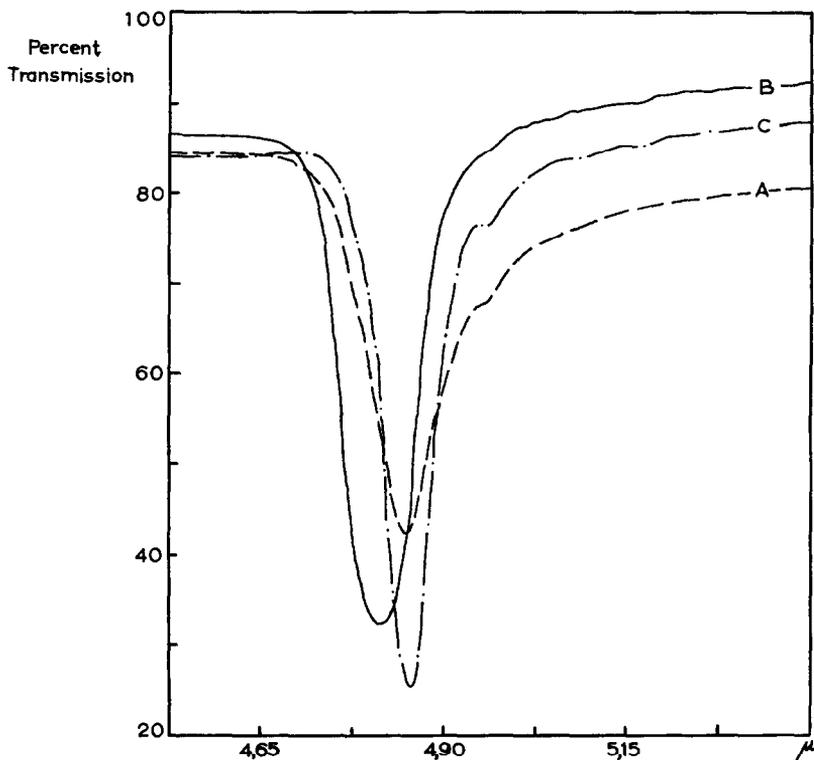


Fig. 1. The $C\equiv N$ stretching vibration of KSCN. Curve (a) After pressing. (b) After storage at 57 per cent relative humidity. (c) After drying.

strong band at 4.87μ due to the $C\equiv N$ stretching vibration of KSCN in the solid state (Fig. 1, curve a).

After 3 hr storage at a relative humidity of 57 per cent the spectrum showed a very strong waterband at 2.9μ , while the maximum of the $C\equiv N$ stretching band was shifted to 4.84μ (Fig. 1, curve b).

Drying of the wet disk above P_2O_5 *in vacuo* resulted in a spectrum with little or no water absorption at 2.9μ and a $C\equiv N$ stretching band at 4.87μ which is even stronger than before the water treatment (Fig. 1, curve c).*

Since a KSCN solution in water absorbs at 4.84μ [7] the KSCN in the wet

* Due to this sensitivity for moisture KSCN cannot be used as internal standard as proposed by WIBERLEY *et al.* [6].

[6] S. E. WIBERLEY, J. W. SPRAGUE and J. E. CAMPBELL, *Anal. Chem.* **29**, 210 (1957).

[7] L. H. JONES, *J. Chem. Phys.* **25**, 1069 (1956).

disk is hydrated to a structure, resembling or even identical with, its structure in water solution. We therefore are inclined to assume the following mechanism: water from the surrounding atmosphere condenses and penetrates into the disk through small cracks. The KSCN particles are hydrated or even dissolved, and the SCN ions are transported through the whole disk, resulting in a more homogeneous distribution of the KSCN. On drying the water evaporates, while the KSCN crystallizes into smaller particles than before, resulting in a stronger absorption at 4.87μ . Perhaps it even forms a solid solution in KBr.

Besides, the transport of the SCN ions by the penetrating water was demonstrated as follows: a small KSCN crystal was mounted excentrically in a disk in such a way that it was completely surrounded by KBr. This disk did not show a KSCN spectrum because only the centre part of the disk is used for absorption measurements. Storage of the disk for some weeks in a dry atmosphere had no effect. After storage during 20 min in an atmosphere with a relative humidity of 57 per cent however, the 4.84μ band appeared. After storage for $1\frac{1}{2}$ hr this band was strong. A superficial study of the disk using the Perkin-Elmer micro-illuminator showed that the water and thiocyanate concentrations were high in the close vicinity of the KSCN particle. The concentrations decreased with increasing distance.

From another disk treated in the same way we determined after drying the thiocyanate concentration, again with the help of the micro-illuminator, along the x - and y -axis. The results are given in arbitrary units in Fig. 2, using the 4.87μ band for calculations. They are in agreement with the expectations.

So we may conclude, that water from the surrounding atmosphere enters the disk where the crystal(s) is (are) embedded; it dissolves the sample and transports it through the whole disk.

We have found that potassium acetate, KNO_2 , KNO_3 , NH_4SCN , KHF_2 and NH_4HF_2 are transported also (at relative humidity of 78 per cent), though there is a significant difference in transport speed, presumably due to the difference in solubility, e.g. NaHF_2 is transported very slowly and is indeed less soluble.

C. Conversions caused by water

Water proved to initiate conversion of a salt in a disk as was found by VRÁTNY [8] in the case of some nitrates.

We observed this phenomenon also with NH_4SCN : a KBr disk containing some ammoniumthiocyanate remains unchanged if the disk is perfectly dry. After storage during 60 min at a relative humidity of 78 per cent and drying afterwards, the spectrum in the $10\text{--}11 \mu$ region indicates that the NH_4SCN has been transformed: the bands at 10.5 and 10.7μ are shifted to 10.3 and 10.5μ respectively (Fig. 3, curve a and c). Recording the spectrum after 30 min without drying, shows that the conversion has taken place only partially. (Fig. 3, curve b).

This phenomenon can be due to either a conversion of ammonium into potassium thiocyanate, or to the formation of a solid solution in KBr. In the last case

[8] F. VRÁTNY, *J. Inorg. & Nuclear Chem.* **10**, 328 (1959).

we must assume that the spectrum of the SCN ions surrounded by K^+ and Br^- ions is the same as that of pure KSCN, because the spectrum of this salt is not shifted after ageing and drying, as we saw before.

If disks with respectively K, NH_4 and $NaHF_2$ are exposed to a moist atmosphere (78 per cent) new bands are observed at 6.55 and 7.98μ in all cases, belonging to HF_2^- vibrations. KETELAAR *et al.* [9] ascribe these new bands to the formation of

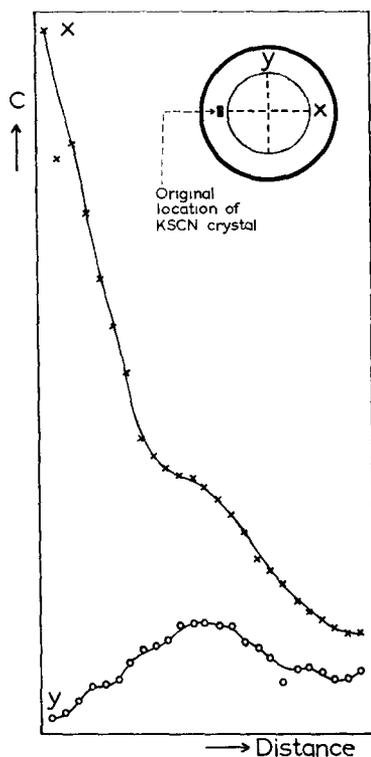


Fig. 2. The KSCN concentration C (in arbitrary units) in small volumes of a disk along the x - and y -axis, as indicated in this figure.

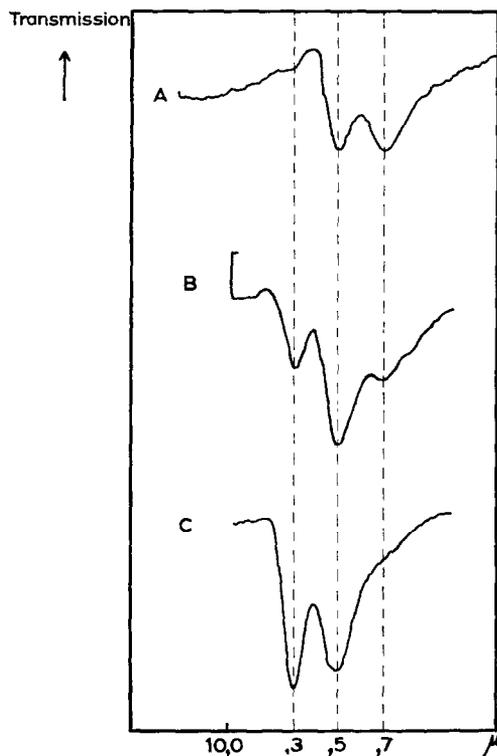


Fig. 3. The conversion of NH_4SCN followed in the $10-11 \mu$ region. (a) Directly after pressing (no conversion). (b) After 30 min storage at a relative humidity of 78 per cent (partially converted). (c) After 60 min storage and drying (completely converted).

mixed crystals; the original vibrations of the HF_2^- ions correspond with bands on other places.

We have found that the shifts do *not* occur if water is absent, e.g. a disk containing NH_4HF_2 after storage for three months above P_2O_5 showed still the same spectrum as instantly after pressing. In a moist atmosphere however the original HF_2^- bands of the K and NH_4 salt disappear completely during ageing; those of the Na salt nearly and after a longer ageing period. This is presumably due to the small transport speed as mentioned earlier. In our opinion it is probable that in all three cases solid solutions occur.

Comparing these results with those obtained with NH_4SCN we are inclined to suppose that there too the formation of a solid solution is possible or even likely, though a definite judgement cannot be given yet.

Our over-all conclusion is that the presence of water is essential for the conversion of a sample in a KBr disk and that this water can be taken up easily from the surrounding atmosphere.

D. *The use of a D_2O atmosphere*

For an application of the results discussed above deuteriumoxyde was used.

If a disk containing a sample is stored for a couple of hours in a moist D_2O atmosphere (relative humidity 75 per cent), active H atoms of the sample molecules can be substituted more or less by D atoms from the penetrated D_2O . This will cause significant bandshifts, which can be applied in structure determination.

Such experiments were done with: benzoic, cinnamic, salicylic and phthalic acid and with resorcin, α -naphthol, androsteron, urea and acetamide. In all these cases bandshifts have been observed indeed.

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