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COMPOSITION AND STRUCTURE OF AMMONIUM URANATES

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ABSTRACT

The ammonium uranate system was studied by thermal analysis, ion-exchange measurements and infra-red spectroscopy. The results show that in all ammonium uranates, ammonia is combined as NH_4^+. Infra-red results indicate that the ammonium uranate system is single-phase in which the NH_3:U ratio can be varied continuously. In an aqueous environment the variation of composition occurs by a cation exchange mechanism.

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1. INTRODUCTION

There has been much discussion regarding the composition and structure of ammonium diuranate (ADU), and certain conflicting results and conclusions require explanation.

First, the term "ammonium diuranate" is a misnomer: a number of investigations (Deane 1960, Armson et al. 1959, Cordfunke 1962) provide adequate proof that an ammonium diuranate compound $(NH_4)_2U_2O_7$ can never be obtained in aqueous solution, even in the presence of a large excess of ammonia. ADU precipitates are now considered to be a complex mixture of ammonium uranate compounds, each with the composition $UO_3 . x\ NH_3 . (2-x)\ H_2O$. These compounds are prepared by precipitation from uranyl nitrate solution, or by reaction of $UO_3 . 2H_2O$ with NH_4OH solution or NH_3 gas. Cordfunke (1962) studied the system $NH_3-H_2O-UO_3$ and concluded that only four compounds existed in this system. These are:

$6UO_3 . 12H_2O$,	designated	Type I,	NH_3:U molar ratio	0.00
$6UO_3.2NH_3.10H_2O$	"	Type II,	" " "	0.33
$6UO_3.3NH_3.9H_2O$	"	Type III,	" " "	0.50
$6UO_3.4NH_3.8H_2O$	"	Type IV,	" " "	0.66

X-ray results (Debets and Loopstra 1963) were interpreted to mean that intermediate compositions represented two-phase mixtures of these compounds.

Second, there is some argument concerning the nature of ammonia in ammonium uranates. Deane (1960) concluded from an infra-red study that ammonia was present as coordinated NH_3 molecules. Hermans (1964) put forward a similar view; but Debets and Loopstra (1962) suggested that ammonia was combined as the NH_4^+ ion, although they did not present supporting experimental evidence. Brusset and Dao (1967) stated that the infra-red spectrum of an ammonium uranate ($2UO_3.NH_3.3H_2O$) showed absorbance bands characteristic of NH_4^+.

In this report we describe an investigation of ammonium uranates using, principally, infra-red spectrophotometry, thermogravimetric analysis (TGA) and differential thermal analysis (DTA). In our opinion the results show that ammonia is present as the NH_4^+ ion in all ammonium uranates. Also infra-red data indicate that there are not four distinct compounds as listed by Cordfunke; the ammonium uranate system is single-phase in which the NH_3:U ratio can be varied continuously. In an aqueous environment the variation of NH_3 content occurs by a cation exchange mechanism.

2. EXPERIMENTAL

2.1 Preparation of Samples

The dihydrate β-$UO_3.2H_2O$ was prepared by hydrating UO_3 in water vapour at room temperature. UO_3 was obtained by decomposition of $UO_4.2H_2O$ at 470 °C. The detailed method of preparation is given in Appendix 1.

Ammonium uranates were obtained by equilibration of β - $UO_3.2H_2O$ and NH_4OH solution.

2.2 Infra-red Spectrophotometry

Samples were ground with ethanol in an agate mortar; a few drops of slurry were placed on an Irtran II window and the ethanol allowed to evaporate. Further slurry was placed on the window to obtain a sample thickness sufficient to give suitable absorbance intensities. The amount of sample on the window was about 2 to 3 mg; this gave an absorbance value of 0.4 to 0.6 for the uranyl asymmetric stretching frequency. No sign of any C-H or C-O bands from the ethanol were ever observed.

Samples were also examined as Nujol mulls between NaCl plates, but this technique has the disadvantage that the region 1350-1450 cm^{-1} is obscured by the C-H bending modes of Nujol: thus an ammonium uranate band at 1410 cm^{-1} cannot be observed. The use of hexachlorobutadiene allows this region to be studied, but there is interference in the uranyl stretching region (1000 to 800 cm^{-1}).

However, by using a powder film on Irtran II the spectral range from 5000 to 700 cm^{-1} can be covered without interfering bands, and relative intensities of H_2O,NH_4^+ and uranyl bands can be determined. Light scattering was no problem in these powder films owing to the small particle size.

Spectra were recorded from 5000 cm^{-1} to 700 cm^{-1} using Perkin-Elmer Models 21 (with NaCl prism) and 237.

2.3 Thermogravimetric Analysis

All thermogravimetric data were obtained by means of a Cahn Electrobalance (Type RH) with associated data-logging 2-channel scanning equipment and typewriter printout.

2.4 Differential Thermal Analysis

DTA measurements were made using a Dupont High-Temperature (850 °C) cell employing a silver block and chromel-alumel thermocouples. Linear programming was achieved by means of a Hewlett-Packard F and M Type 240 temperature programmer.

3. RESULTS AND DISCUSSION

3.1 Nature of $UO_3.2H_2O$

Before considering the ammonium uranate system, it is necessary to discuss certain properties of the parent material, the dihydrate $UO_3.2H_2O$. These properties are important in deciding the nature and mechanism of formation of ammonium uranates.

Figure 1a shows the infra-red spectrum of β-$UO_3.2H_2O$. The absorption band at 953 cm^{-1} can be assigned to the asymmetric stretching frequency (ν_3) of the uranyl ion. A complex series of bands between 3100 cm^{-1} and 3650 cm^{-1} is due to O–H stretching vibrations, and the band at 1610 cm^{-1} arises from the vibrational bending mode of coordinated water molecules (δH_2O). After heating in air at 100 °C for 1 hour the 1610 cm^{-1} band disappears, indicating complete removal of water molecules (Figure 1b). A single O–H stretching band at 3350 cm^{-1} still remains and is removed only after heating at 300 °C (Figure 1c).

Thermoanalytical data support the infra-red evidence, showing that dehydration occurs in two quite separate steps. The DTA trace in Figure 2a shows an endothermal peak at 185 °C due to removal of H_2O molecules, and decomposition of the hydroxide gives an endothermal peak at 385 °C. Material preheated isothermally in air at 100 °C to remove H_2O molecules shows no endotherm at 185 °C (Figure 2b).

Clearly, these results show that $UO_3.2H_2O$ is more accurately a hydrated uranyl hydroxide, say $UO_2(OH)_2.H_2O$. There is some doubt concerning the most accurate formula to describe the molecular structure of the material. Data of Fodor et al. (1966) indicate a formula $(UO_2)_3.O.(OH)_4.4H_2O$, whereas according to our thermogravimetric data, complete removal of coordinated water molecules leads to a compound with the composition $UO_3.0.8H_2O$, suggesting $(UO_2)_5.O.(OH)_8.6H_2O$. However, for simplicity in this report we use the formula $UO_2(OH)_2.H_2O$.

3.2 Nature of Ammonia in Ammonium Uranates

A number of ammonium uranate samples with NH_3:U ratios up to about 0.7, were prepared either from $UO_2(OH)_2.H_2O$ or by precipitation from uranyl nitrate solution. Compounds obtained by precipitation were washed with ethanol until free of nitrate.

Infra-red spectra of all these samples exhibit a strong band at 1410 cm^{-1} and no other bands in this region (other than the δH_2O band at 1620 cm^{-1}). All ammonium-salts also show a band in this region, whereas, ammines such as $(CO(NH_3)_6)Cl_3$ have NH_3 deformation bands in the regions 1650 to 1560 cm^{-1} and 1350 to 1150 cm^{-1}. Spectral data for various ammonium salts, ammines and ammonium uranates are listed in Appendix 2.

There can be little doubt, then, that in ammonium uranate compounds NH_3 is combined as the ammonium ion NH_4^+. Previous infra-red studies by Deane (1960, 1962) may have been confused by the presence of nitrate impurities which exhibit some absorbance bands in the same regions as do coordinated NH_3 molecules.

It must be emphasised, however, that these conclusions apply to fully hydrated ammonium uranates equilibrated at room temperature (the system we are discussing in this report). During the thermal decomposition of ammonium uranate both in air and in vacuum we have observed the appearance of bands at 1590 cm^{-1} and 1250 cm^{-1} which we assign to ammoniate ($H_3N \rightarrow$) formation. But this phenomenon will be described more fully in a later report on the thermal decomposition of ammonium uranates.

3.3 Mechanism of Formation of Ammonium Uranates

The question then arises whether hydroxyl groups of $UO_2(OH)_2.H_2O$ can possess ion exchange properties and whether incorporation of NH_4^+ in the solid occurs by a cation exchange mechanism. With this in mind we studied the interaction of $UO_2(OH)_2.H_2O$ and solutions of ammonium nitrate and ammonium acetate. Various weights of the solid were equilibrated with 50-ml aliquots of solution, and the equilibrated solutions were then analysed for uranium, NH_4^+, and NO_3^- or acetate.

Figures 3 and 4 show the results of these experiments, with concentrations of the various species in solution plotted as a function of weight of solid. Clearly NH_4^+ is absorbed by the solid and some uranium is released into solution. Nitrate and acetate are not absorbed: the concentrations of these anions remain unchanged.

These results are consistent with a cation exchange mechanism of the type:

$$UO_2(OH)_2 + xNH_4^+ \longrightarrow UO_2(OH)_{2-x}\ (O^-\,NH_4^+)_x + xH^+ \quad . \tag{1}$$

Nitric acid or acetic acid, generated by release of protons into solution, dissolves a certain amount of solid to form soluble uranium salts. Absorption of NH_4^+ is favoured by higher pH, as one might expect from Equation 1. Thus somewhat higher NH_3:U ratios can be obtained by using ammonium acetate solutions which involve higher pH (Figure 5), whereas the pH of solutions obtained from equilibration of NH_4NO_3 remains constant at about 4.4.

The exchange process is not as simple as indicated by Equation 1. Figure 6 shows the variation of the δH_2O band (1615 cm^{-1}) with increasing NH_3 content, and indicates that coordinated water molecules are displaced by NH_4^+ formation. This is probably a steric effect.

3.4 Proposal that Ammonium Uranate System is Continuous and Homogeneous

3.4.1 Supporting evidence

The asymmetric stretching frequency (ν_3) of the uranyl ion varies with NH_3:U molar ratio as shown in Figure 7. The important point is that frequency decreases continuously with NH_3:U ratio: in all cases the bands are of similar half-widths, and there is no sign of splitting of the band into two components. Frequency shifts involved are substantial (up to about 60 cm^{-1}); the resolution of the instrument in this region is about 1 cm^{-1}, and the frequencies are accurate to 2 cm^{-1}. Thus any band splitting would be readily observed.

A synthetic mixture of Type I (the dihydrate) and Type II (NH_3:U = 0.3) was made to give an overall NH_3:U molar ratio of 0.13; the two components were ground for a few seconds in an agate mortar and the mixture was deposited as a powder film on Irtran II. The spectrum of the mixture (Figure 8) shows clearly two bands at 954 cm^{-1} and 930 cm^{-1} as one might expect from a two-phase mixture. The 954 cm^{-1} band of this doublet is at the dihydrate (Type I) frequency (953 cm^{-1}). There is an apparent shift in the second component of the doublet (921 cm^{-1} to 930 cm^{-1}) but this is due to band overlap.

Thus in the synthetic mixture two uranyl bands are clearly present. On the other hand, an ammonium uranate sample, prepared by equilibration of $UO_2(OH)_2.H_2O$ with NH_4OH solution to give an NH_3:U ratio of 0.135, was examined in an identical manner and showed only a single band at 947 cm^{-1}.

In no ammonium uranate samples did we observe any splitting of the uranyl band into components such as occurs in synthetic mixtures. (Samples were prepared by precipitation from uranyl nitrate solutions; by equilibration of $UO_2(OH)_2\ H_2O$ with solutions of NH_4OH, NH_4NO_3 or ammonium acetate and by reaction of gaseous NH_3 with $UO_2(OH)_2H_2O$).

In our opinion, these results provide sufficient proof that the ammonium uranate system at equilibrium is a homogeneous system in which the NH_3:U ratio (and H_2O:U) can be varied continuously. Each ratio represents a homogeneous single-phase compound.

This concept of a continuously variable system is consistent with the cation exchange process, proposed for the mechanism of formation.

3.4.2 Variation of uranyl bond length with NH_3:U ratio

A secondary matter worth noting concerns the variation with composition of the uranyl bond length, as indicated by the shift in ν_3. The relation between uranyl bond lengths and infra-red vibrational spectra has been investigated by several authors (Jones 1958, McGlynn et al. 1961, Hoekstra 1963). Uranyl bond lengths may be evaluated using Jones' (1958) application of Badger's relationship to force constants calculated from infra-red data:

$$R_{UO} = \beta F_{UO}^{-1/3} + d_{UO} \quad , \qquad (2)$$

where R_{UO} is the uranyl bond length, F_{UO} is the force constant, β = 1.08 and d_{UO} = 1.17 are empirical constants.

Thus at 900 cm^{-1} a shift of about 23 cm^{-1} in ν_3 to a lower frequency involves an increase in uranyl U—O bond distance of 0.01 Å. The maximum changes in ν_3 that we observed in ammonium uranate samples corresponds to a variation of 0.03Å in uranyl U—O bond length.

3.5 X-ray Diffraction Patterns of Ammonium Uranates

One issue remains. This is the apparent conflict between the infra-red evidence and X-ray data. Cordfunke (1962) suggested that there are four distinct compounds, each with its own X-ray diffraction pattern (Debets and Loopstra 1962), and there is no doubt that changes in composition induce quite detectable changes in diffraction pattern.

This question was at least partly resolved by the following experiment:

A synthetic mixture of $UO_2(OH)_2H_2O$ (Type I) and ammonium uranate (Type II NH_3:U = 0.31) was made up to give an overall NH_3:U ratio of 0.15. The X-ray diffraction pattern of this mixture is seen (Figure 9) to be an exact composite of the separate components. However ammonium uranate compounds with similar NH_3:U ratios show quite different patterns which do not relate to a two-phase mixture (Figure 10).

The effect of composition on structure of course needs to be studied more closely by X-ray diffraction techniques, and an investigation is being undertaken with this end in view. But in our opinion, the evidence already presented here shows the ammonium uranate system to be similar in many ways to a zeolite, in which a continuous range of composition can be induced by exchange of cations interposed within a rigid aluminosilicate lattice. By analogy we propose that ammonium uranates involve a fairly constant uranium-oxygen lattice with exchangeable H^+ or NH_4^+. Changes in diffraction pattern could then arise from slight variations in the positionsof oxygen or uranium atoms, or by changes in symmetry arising from replacement of H^+ by NH_4^+.

This does not mean, of course, that completely homogeneous compositions are obtained in ADU production. Indeed, non-equilibrium conditions prevailing during rapid precipitation on a large scale could possibly lead to a heterogeneous mixture. However, our results indicate that a chemically homogeneous product exists at equilibrium.

4. ACKNOWLEDGEMENTS

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APPENDIX 1

PREPARATION OF β-$UO_3.2H_2O$

1. Dissolve 100g uranyl nitrate (AR grade) in 2 litres H_2O at 50 °C.

2. Add uranyl nitrate solution with stirring to the following mixture at 50 °C:

   500 ml H_2O_2 (AR grade) 100-vol.

   1 litre H_2O.

   9 ml concentrated HNO_3 (AR grade).

3. Keep well stirred for 5 minutes and allow to stand for 1 hour.

4. Decant clear supernatant liquid and centrifuge $UO_4.2H_2O$ precipitate.

5. Slurry precipitate in 1 litre H_2O. Make up to 10 litres with H_2O and stir well. Allow precipitate to settle, and decant H_2O. Repeat this washing procedure three times.

6. Filter precipitate and wash with about 1 litre H_2O.

7. Dry precipitate in vacuum oven at 70°C. Break up cake as precipitate dries.

8. Dry further in air oven at 120 °C for 16 hours.

9. Heat slowly in flowing air to 470 °C and calcine at 470 °C for 1 hour.

10. Stand UO_3 in vacuum desiccator in H_2O vapour for about one week or until complete hydration is achieved.

APPENDIX 2

INFRA-RED SPECTRA OF AMMONIUM SALTS, AMMINES AND ADU

Compound	Infra-red Frequencies in cm^{-1}			
NH_4ClO_4		3330(s)		1420(s)
NH_4Cl	3150(s)	3070(s)	2860(m)	1410(s)
$(NH_4)_2Cr_2O_7$	3170(s)	3060(s)	2850(m)	1410(s)
NH_4VO_3		3200(s)		1415(s)
$(NH_4)_2SO_4$	3165(s)	3055(s)		1410(s)
NH_4SCN	3149(S)	3060(s)	2860(m)	1420(s)
ADU	3460(m)	3200(s) 3050(w)	2820(w)	1410(s)
$NH_3:U$ = 0.48	–OH		NH_4^+	
Ammines e.g. $[Co(NH_3)_6]Cl_3$	3350–3200(m)	1650–1560(s)	1350–1150(s)	

s – strong m – medium w – weak

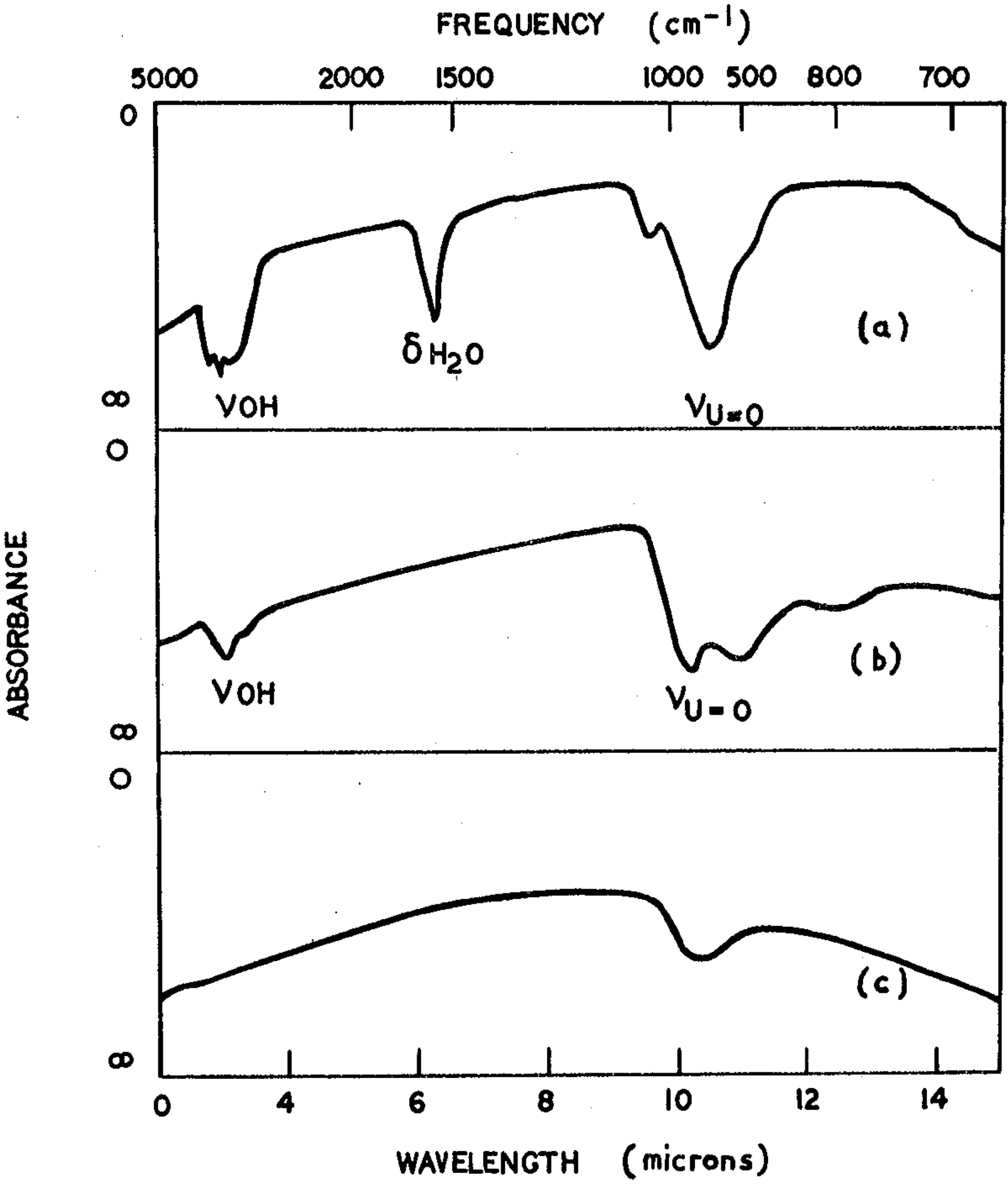

FIGURE 1. (a) $UO_3.2H_2O$
(b) $UO_3.2H_2O$ AFTER 1 HOUR IN AIR AT 100°C
(c) $UO_3.2H_2O$ AFTER 1 HOUR IN AIR AT 300°C

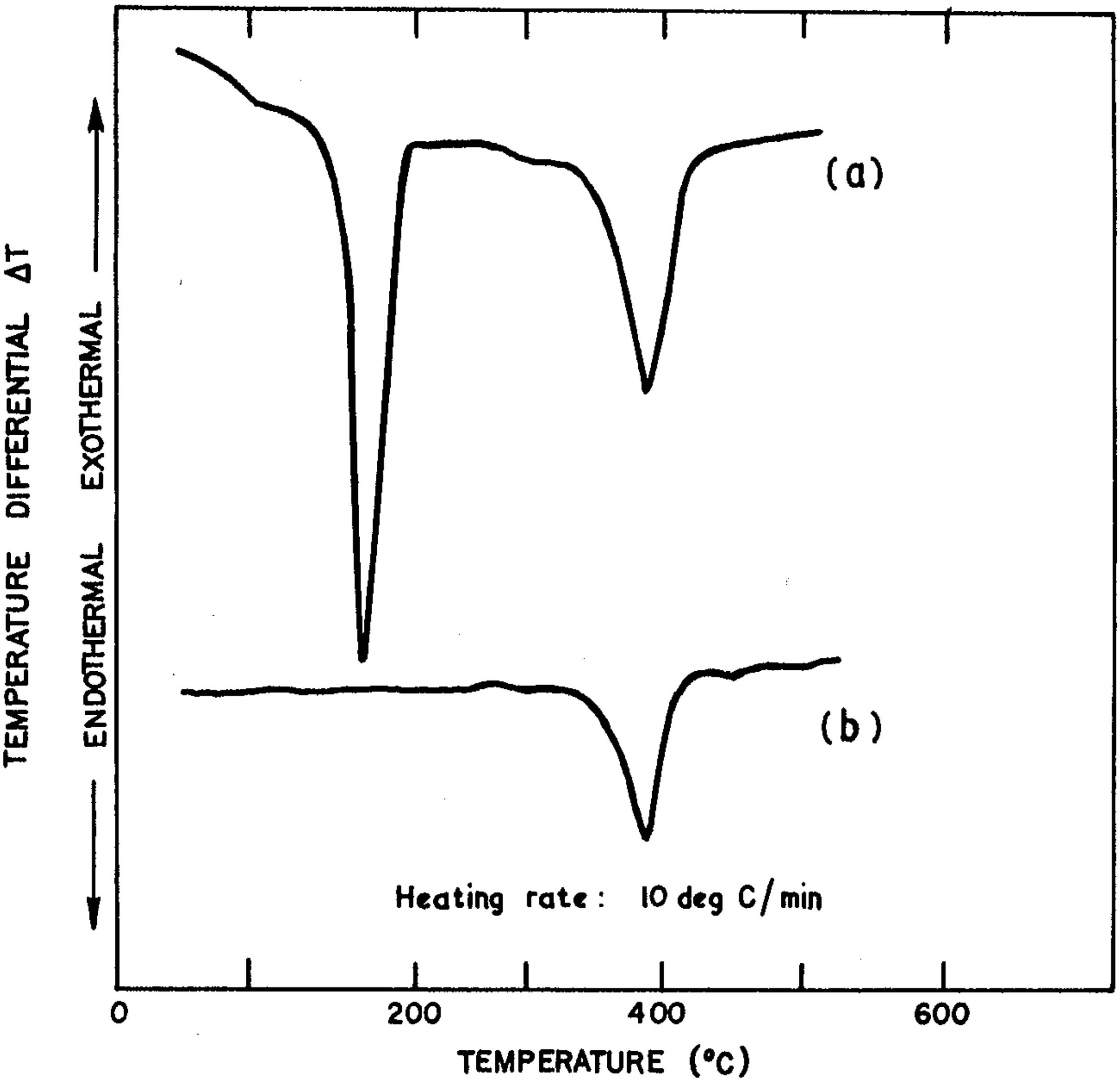

FIGURE 2. DTA TRACES OF $UO_3.2H_2O$ $[UO_2(OH)_2.H_2O]$
(a) $UO_3.2H_2O$ AS RECEIVED
(b) $UO_3.2H_2O$ PREHEATED IN AIR AT 100°C FOR 1 HOUR

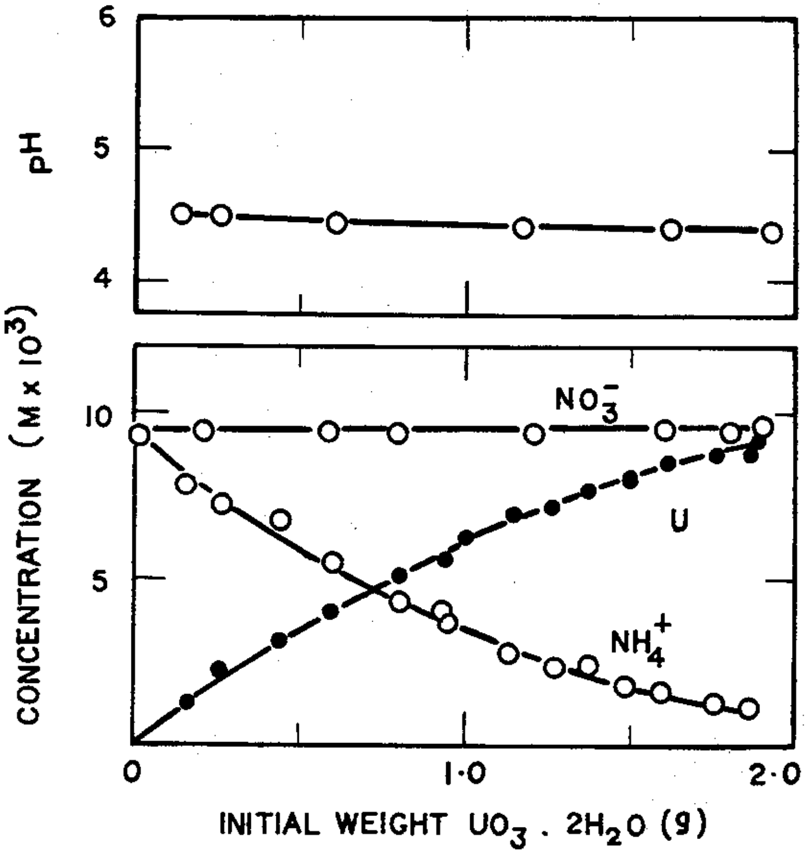

FIGURE 3. INTERACTION OF AMMONIUM NITRATE SOLUTION AND $UO_3.2H_2O$.
50ml ALIQUOTS

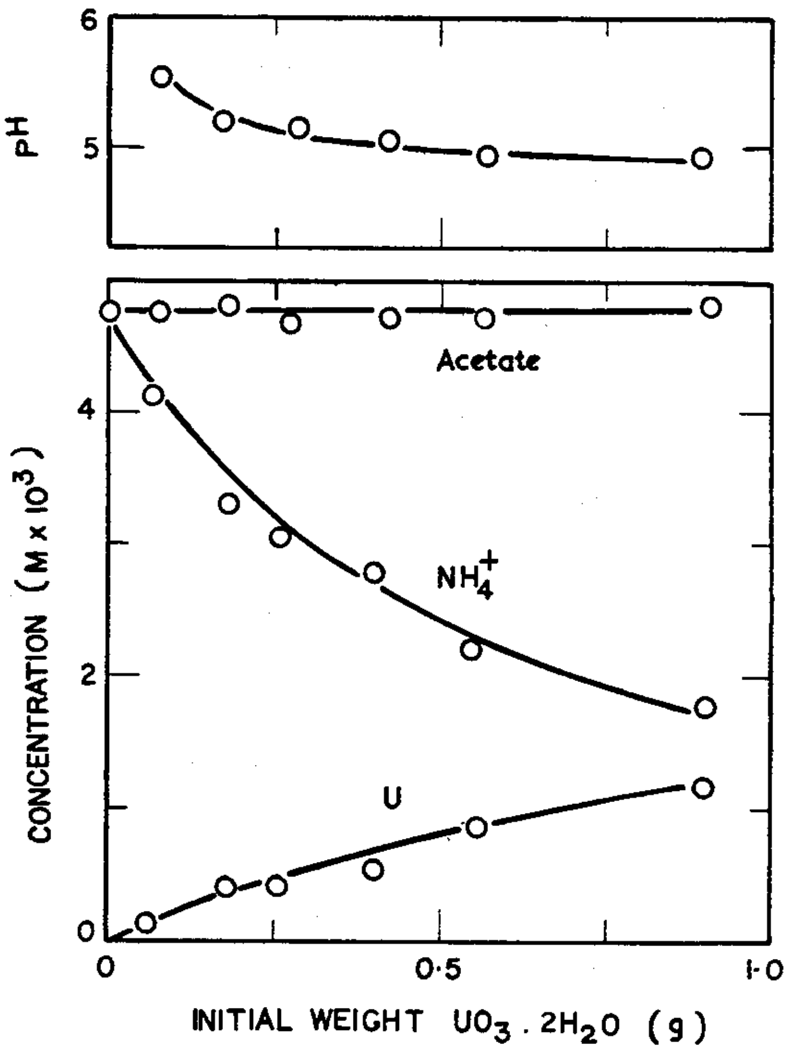

FIGURE 4. INTERACTION OF AMMONIUM ACETATE SOLUTION AND $UO_3.2H_2O$.
50ml ALIQUOTS

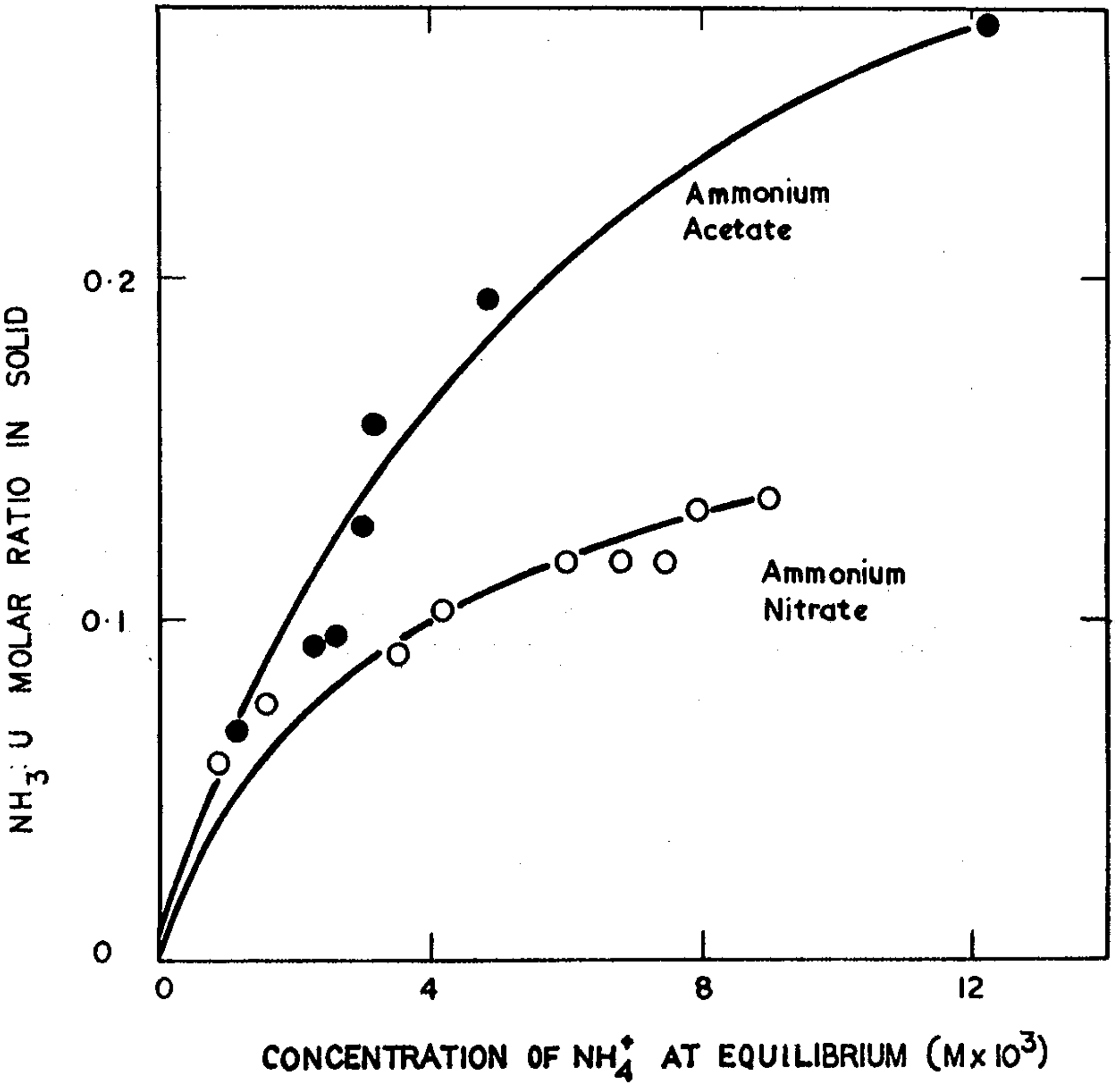

FIGURE 5. INTERACTION OF $UO_3.2H_2O$ AND AMMONIUM NITRATE OR AMMONIUM ACETATE SOLUTIONS: ISOTHERM DATA

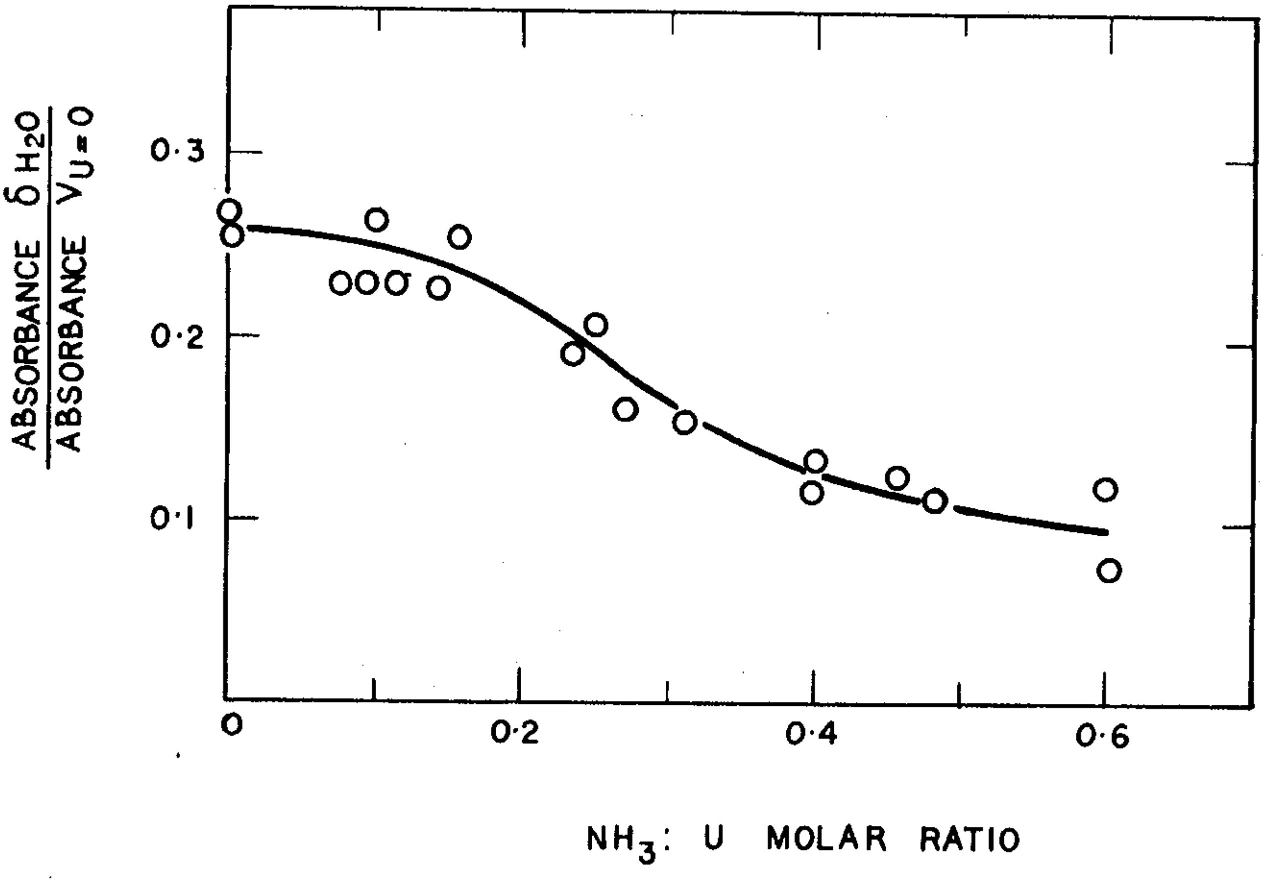

FIGURE 6. VARIATION OF INTENSITY OF H_2O BENDING BAND AT 1620 cm^{-1} WITH NH_3 : U MOLAR RATIO

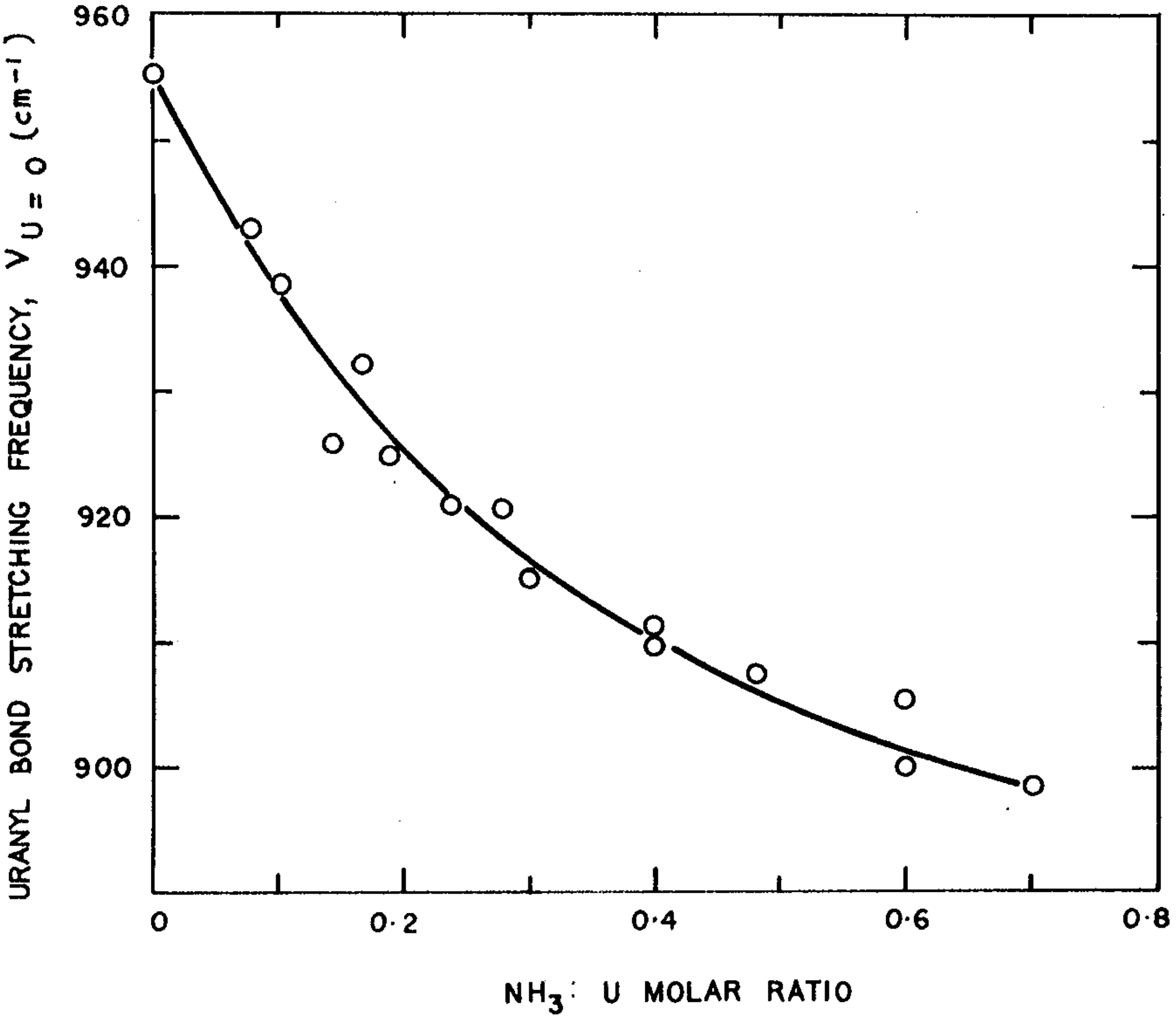

FIGURE 7. VARIATION OF URANYL BOND STRETCHING FREQUENCY ($\nu_{U=O}$) WITH NH_3 : U MOLAR RATIO

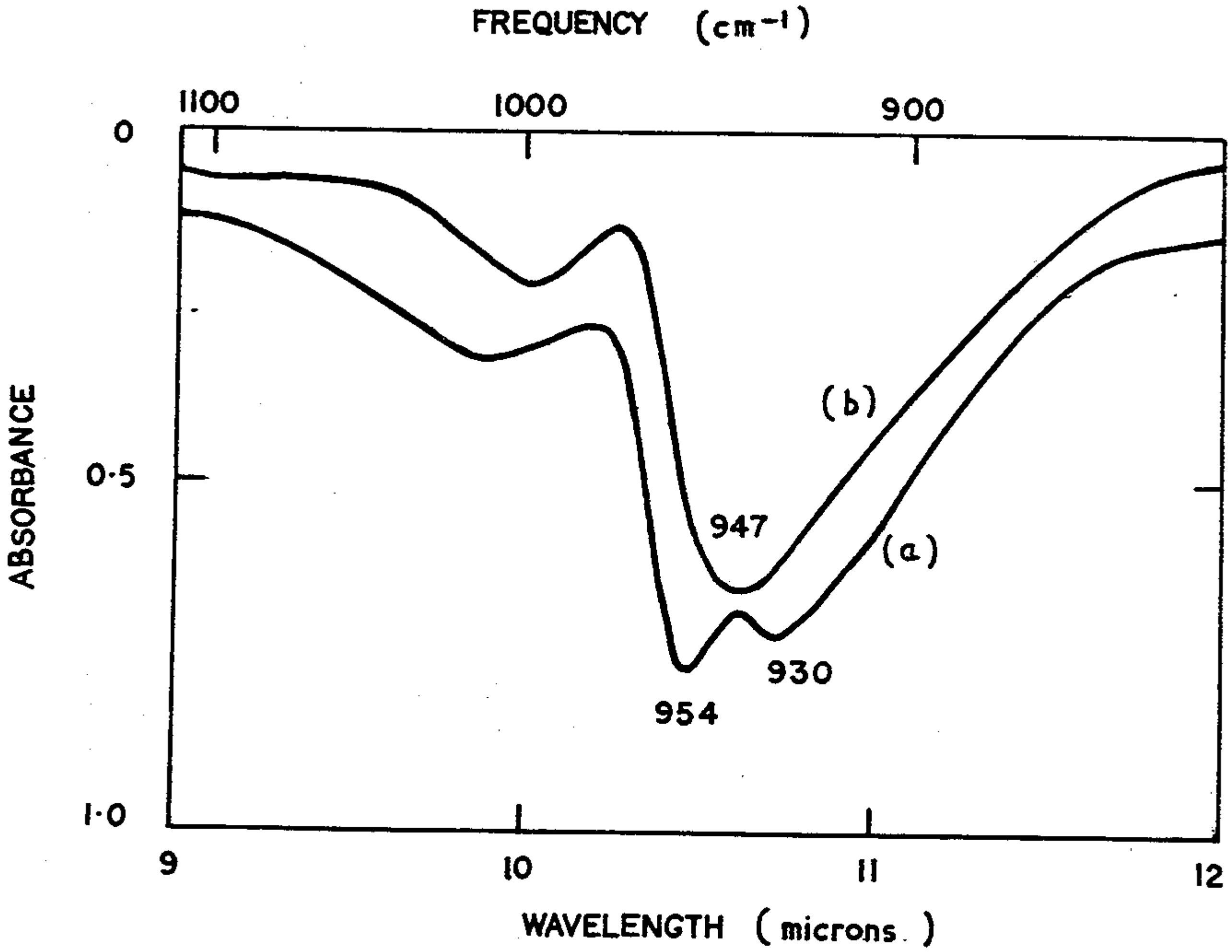

FIGURE 8. a) INFRA-RED SPECTRUM OF SYNTHETIC MIXTURE OF $UO_3.2H_2O$ AND AMMONIUM URANATE (NH_3 : U = 0.31) OVERALL NH_3 : U RATIO = 0.13

b) INFRA-RED SPECTRUM OF AMMONIUM URANATE SAMPLE NH_3 : U = 0.13

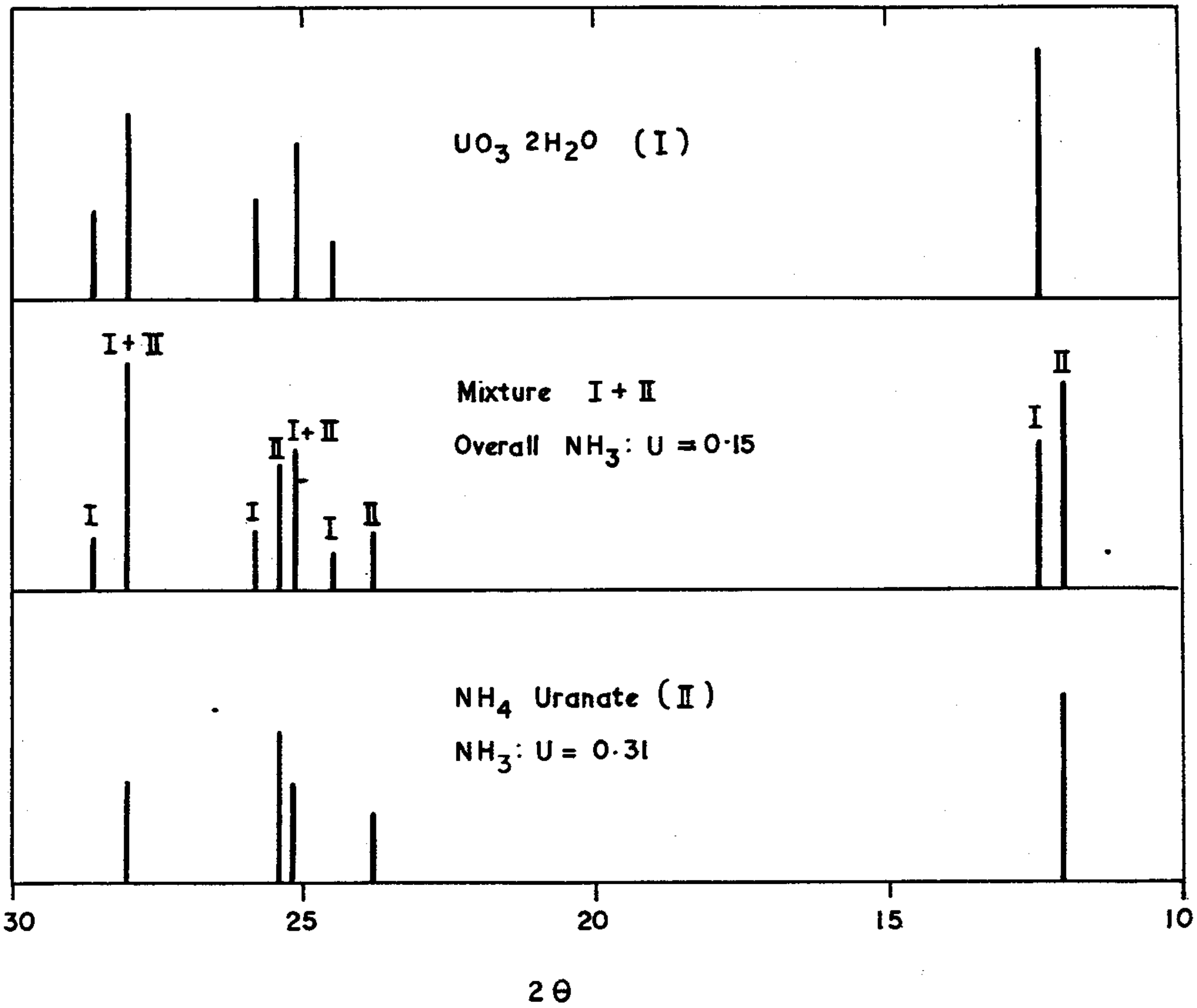

FIGURE 9. X-RAY DIAGRAMS SHOWING MAJOR LINES OF $UO_3{\cdot}2H_2O$, AMMONIUM URANATE AND SYNTHETIC MIXTURE OF THESE TWO COMPONENTS (Cu Kα RADIATION)

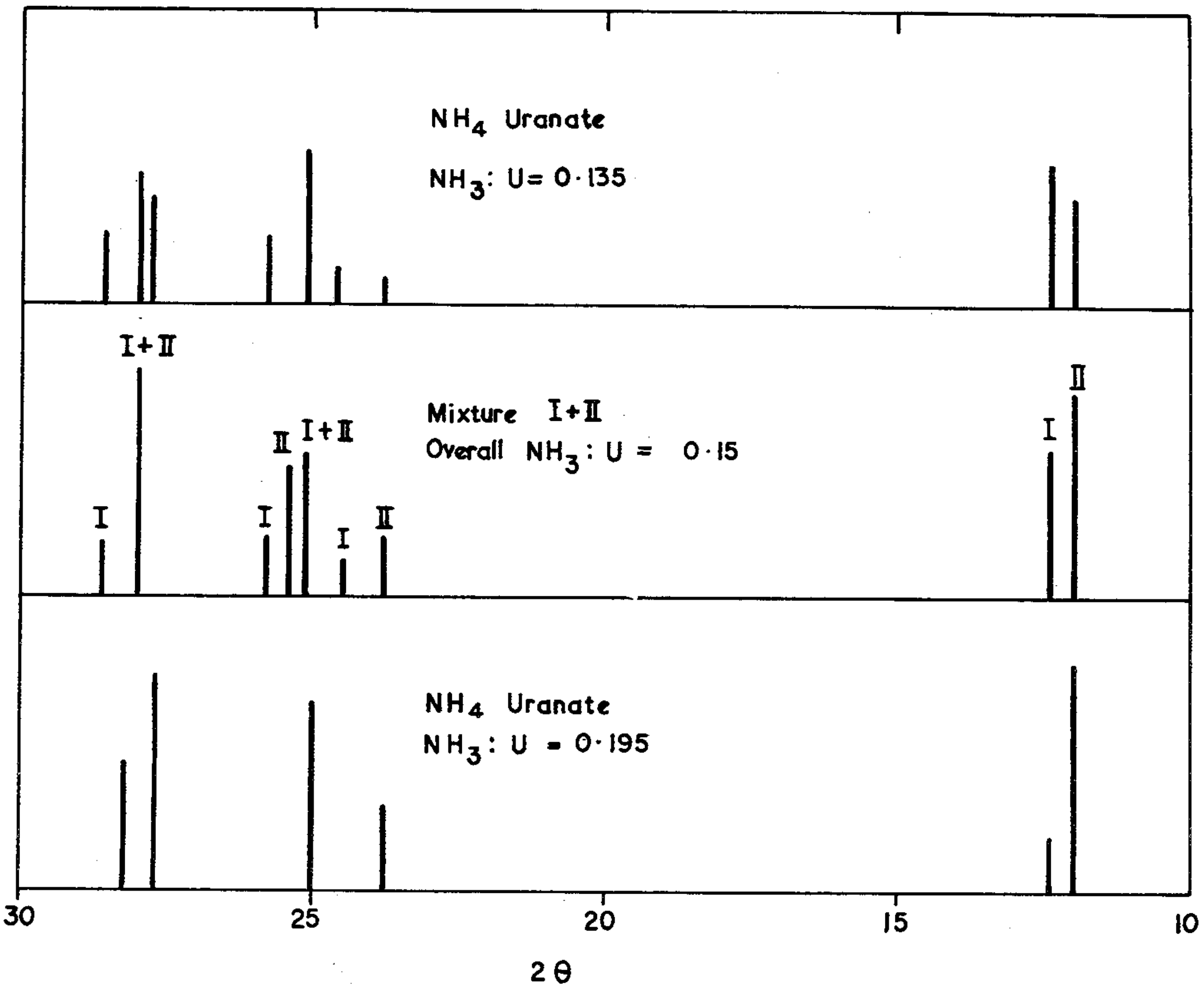

FIGURE 10. X-RAY DIAGRAMS SHOWING MAJOR LINES OF AMMONIUM URANATES AND SYNTHETIC MIXTURE