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The State of Indium Ions in Nitrate Solutions: A Raman Spectroscopic Study

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Abstract

Raman measurements were carried out on aqueous indium nitrate solutions containing different additives ($NaNO_3$, HNO_3 and NaOH), on a crystalline hydrate $In(NO_3)_3 \cdot 3H_2O$, and on its melt. Band envelope fitting in the region of In–O stretching vibrations (350 to 550 cm^{-1}) yielded component bands which were assigned to different types of complexes present in the solutions: (i) 485 cm^{-1}: the totally symmetric 'breathing' vibration of $In-O(H_2)$ bonds in hexa-aquo indium cations, $[In(H_2O)_6]^{3+}$; (ii) 406 cm^{-1}: In–O vibrations of a partly hydroxylated aquo complex of indium; (iii) 465 and 425 cm^{-1}: $In-O(H_2)$ vibrations of aquo complexes containing one or more nitrate ions in the first coordination sphere of indium.

Depolarization ratios of the Raman bands in the 1200 to 1550 cm^{-1} region allowed us to decide whether mono- and bidentate nitrate complexes of indium are formed in some of these systems.

Introduction

Aqueous electrolyte solutions have been studied extensively by vibrational spectroscopy, and the main results of these works are reviewed in ref. [1]. Our more recent Raman spectroscopic studies dealt with aquo cations and hydroxy complexes of mercury, bismuth and zirconium [2–4], whereas the present work is devoted to the study of ion association and complex formation in aqueous indium nitrate solutions.

Among the few spectroscopic works on indium salt solutions [5–8] the Raman spectrum of a 4.2 M solution of indium nitrate containing a 2 M excess of nitric acid was reported by Hester *et al.* [5]. In the 350 to 550 cm^{-1} region a broad, polarized band was observed and assigned to the symmetric In–O stretching mode of an aquo–indium complex. The vibrational frequencies of nitrate ion indicated complex formation with indium, but the effect of hydrolysis on the spectra has not been discussed in detail, neither in ref. 5 nor in the other papers cited above. Moreover, in these papers no exact values but only approximate frequency intervals (without proper band resolution) were given for the proposed aquo complexes of indium.

TABLE I. Composition of $In(NO_3)_3$ Solutions.

Solution no.	I	II	III	IV	V
Added reagents and		NaOH	$NaNO_3$	HNO_3	HNO_3
their concn. (M)[a]		0.40	3.54	3.54	8.56
$R = NO_3^-/In^{3+}$	3.26	3.26	6.80	6.80	11.80

[a] The concentration of In^{3+} is 1 M in all solutions.

The aim of the present work is to determine the frequencies more precisely and offer more detailed assignments for the In–O stretching bands of hydrated indium complexes, and also to characterize the interaction of indium with the nitrate ion under different circumstances both in solution and in melt.

Experimental

A stock solution of indium nitrate was prepared by dissolving indium metal in nitric acid. Analysis for indium and nitrate content gave: $[In^{3+}] = 2.44$ M and $[NO_3^-] = 7.95$ M. The investigated solutions of different composition were obtained from the stock solution by adding aqueous sodium hydroxide, sodium nitrate or nitric acid solutions as given in Table I. By proper dilution, the indium concentration was adjusted to 1 M in all cases.

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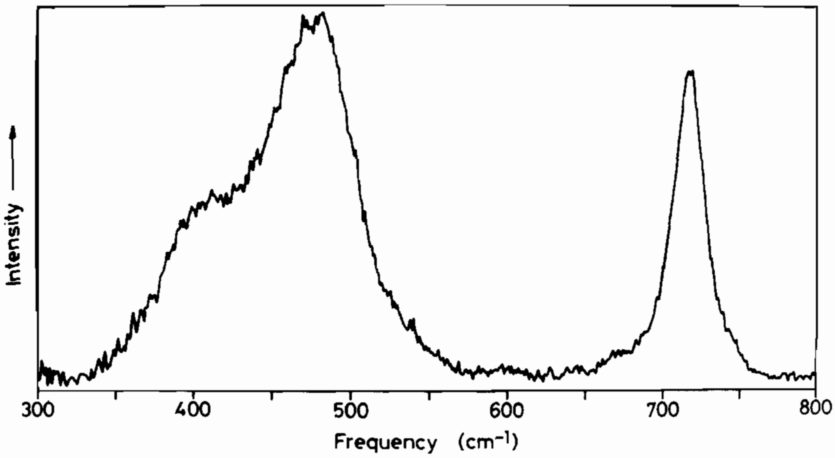

Fig. 1. The Raman spectrum (300–800 cm^{-1}) of indium nitrate solution **II**: $[NO_3^-]/[In^{3+}]$ = 3.26, $[NaOH]/[In^{3+}]$ = 0.4.

The crystalline trihydrate $In(NO_3)_3 \cdot 3H_2O$, (m.p. 62–74 ℃) was obtained by precipitation from a saturated indium nitrate solution containing excess of nitric acid.

The Raman spectra of solutions **I** to **V** were measured on a Cary 82 spectrometer on-line with a Nicolet 1180 computer [9]. The latter was equipped with a magnetic disk unit, digital plotter and display. The 514.5 nm line (at 1600 mW output power) of a Spectra-Physics Model 164 argon ion laser was used for excitation. The observed composite band systems were resolved into symmetric omponent bands by means of an interactive curve analysis program (CAP) based on visual comparison of experimental and calculated band contours. Pure Lorentzian band shapes were used since they gave smaller root-mean-square errors than did Gaussian or mixed functions.

The Raman spectra of the trihydrate were recorded on a Ramanor HG.2S spectrometer equipped with a Zeiss ILA 122 argon ion laser (514.5 nm line, 240 mW) at 25 ℃ for the crystalline sample and at 80, 90, 100 and 110 ± 3 ℃ for the melt.

Results and Discussion

The Raman spectra of all the five different indium nitrate solutions studied (solutions **I** to **V**; see Table I for their composition) exhibit bands corresponding to the vibrations of free nitrate ions of D_{3h} symmetry at 716 (ν_4, E$'$), 1050 (ν_1, A$_1'$) and 1420 cm^{-1} (ν_3, E$'$). Besides, there are bands near 1300–1350 and 1510 cm^{-1} that are characteristic of associated nitrate ions [1].

The broad, polarized scattering in the 350 to 550 cm^{-1} region was observed to vary in shape and in the position of its maximum (from 460 to 485 cm^{-1}) depending on the composition of the solution, which indicates overlap of several components in this band. Also, a well pronounced shoulder appears near 400 cm^{-1} in the spectrum of solution **II** (Fig. 1). In order to characterize the state and environment of indium ions in the solutions under investigation, we need to account first for these spectral features. It is also of interest to study the region of $\nu_4(NO_3^-)$ around 720 cm^{-1} which may also contain additional components.

In–O Vibrations: the 350 to 550 cm^{-1} Region

The result of spectral curve resolution for solution **I** is shown in Fig. 2 as an example. Similar results, *i.e.* three component bands with varying intensities but nearly the same frequencies, were also obtained for solutions **II**, **III** and **IV** (see Tables II and III).

For an aqueous solution of indium nitrate, the totally symmetric In–O stretching vibration ('breathing') of the hexa-aquo indium cation, $[In(H_2O)_6]^{3+}$, is expected to have the highest frequency and highest intensity in this region. Thus, it is straightforward to assign the 485 cm^{-1} band (component A) of solution **I** to this species.

Earlier studies on the solutions of a number of salts [10, 11] have shown that the new bands appearing in the region of metal–oxygen vibrations upon the addition of base (NaOH) belong to hydroxy complexes.

Their shift on deuteration (ν_H/ν_D = 1.01–1.03) is smaller than that of the In–O(H$_2$) band of the hexa-aquo cations (1.05–1.07). Hence, we assign the 406 cm^{-1} band (component C) showing such a behaviour to the In–O vibration of a hydroxy complex of indium. This assignment is supported by ref. [12], where it is shown that in aqueous solutions of indium salts at high concentrations an equilibrium is established between hexa-aquo cations and various polynuclear hydroxy complexes, $[In_q(OH)_p(H_2O)_m]^{(3q-p)+}$. In solutions of indium perchlorate, for instance, potentiometric titration revealed [In$_2$-

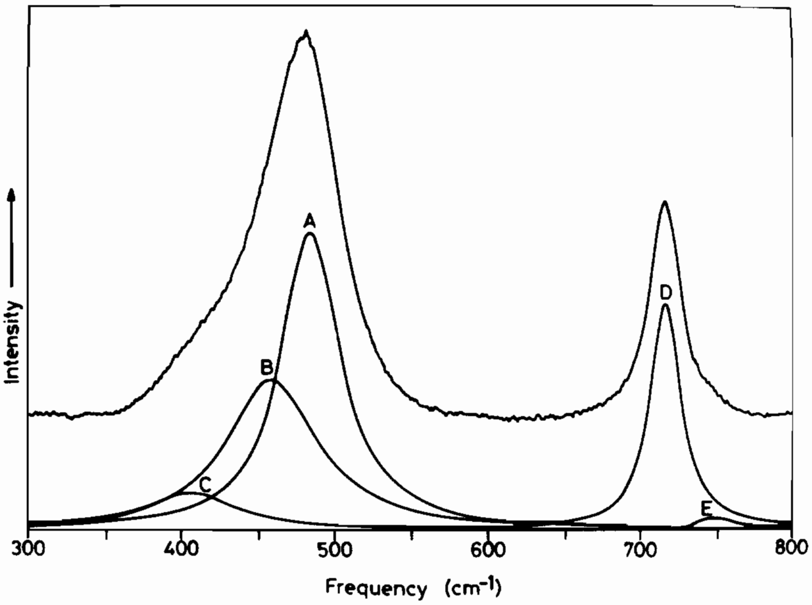

Fig.2. Spectral band resolution for solution I in the region of 300 to 800 cm^{-1}.

TABLE II. Vibrational Frequencies (cm^{-1}) of Different Components in the 300 to 800 cm^{-1} Region of the Raman Spectra of Solutions I–V.

Component[a]	Solutions of $In(NO_3)_3$				
	I	II (NaOH)	III ($NaNO_3$)	IV (HNO_3)	V (HNO_3 concd.)
A (p)	485	486	484	482	
B (p)	459	459	459	463	467 425[b]
C (P)	406	406	406	402	
D (dp)	716	716	718	717	719
E (p)	748		748	754	755
F (p)				689	689
G (dp)				642	641

[a] Polarization characteristics are shown in parentheses. [b] Component B′ (see text).

TABLE III. Percentage Contributions of Different Components to the General Integrated Scattering Intensity of In–O Vibrations.

Component	Solutions of $In(NO_3)_3$				
	I	II (NaOH)	III ($NaNO_3$)	IV (HNO_3)	V (HNO_3 concd.)
A	51	43	32	25	
B	39	20	61	73	88 12[a]
C	10	37	7	2	

[a] Component B′ (see text).

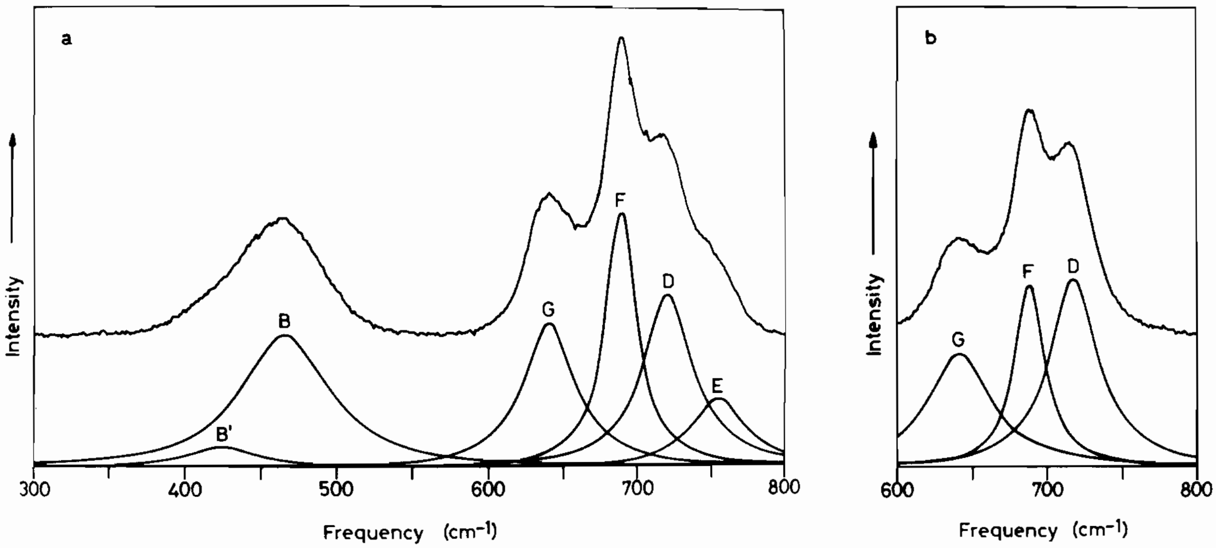

Fig. 3. Band resolution for indium nitrate solution V (a) and for an 8.56 M solution of nitric acid (b).

$(OH)_2]^{4+}$ and $[In_4(OH)_6]^{6+}$ as the prevailing forms [13]. In solutions of indium nitrate, however, there might exist other types of hydroxy complexes due to the presence of a complexing ligand (NO_3^-).

The remaining third component (B) in this region can be assigned to vibrations of the indium–water bonds affected by the presence of nitrate ions in the complex (presumably $[In(H_2O)_5NO_3]^{2-}$), since this is the dominating component band in the solutions with high nitrate concentration. Note that in large excess of nitric acid (solution V) components A and C disappear from the spectrum, and beside the remaining component B a further component, B′, occurs at 425 cm^{-1}. It seems likely that B′ is due to indium–water bonds in a different type of association. A further decrease in the In–O(H_2) stretching frequency is consistent with the weakening of this bond brought about by the formation of a second In^{3+}–NO_3^- bond with the same indium ion (this interpretation is analogous to that proposed by Jarv *et al.* [8] for indium chloride solutions).

Perturbation of the Nitrate Vibrations

a) The 600 to 800 cm^{-1} Region

The resolved curves in the region of $\nu_4(NO_3^-)$ show that in addition to the free nitrate band at 716 cm^{-1} there is a Raman feature near 750 cm^{-1} (component E) in the spectra of all solutions except solution II (see Table II), which indicates complex formation of indium with the nitrate ion [1]. This band has low intensity (perhaps this is why it could not be observed in the spectrum of solution II), but it should be noted that its contribution to the common band contour increases with increasing nitrate concentration. This behaviour parallels that of component B, thus confirming the assumption that component B can be assigned to the vibration of In–O(H_2) bonds influenced by interaction with nitrate ions in the first coordination sphere of indium.

The components at 689 (F) and 642 cm^{-1} (G) are due to the excess nitric acid, as follows from the comparison of the spectrum of solution V with that of an aqueous nitric acid solution of the same concentration (Fig. 3).

b) The 1200 to 1550 cm^{-1} Region*

Raman depolarization measurements in this region allow us to judge whether mono- and bidentate nitrate complexes [14, 15], or mixed dinitrate complexes (with two non-equivalent nitrates) [16, 17], are present. For this purpose the depolarization ratios of the component bands were determined. We found (see data in Table IV) that the high frequency band of bonded nitrate ions near 1510 cm^{-1} in the spectra of solutions I, II and V is polarized; consequently, in these systems bidentate $In{=}O_2NO$ complexes are present. The lower frequency band of bonded NO_3^- ions near 1310 cm^{-1} appears to be completely polarized in solutions I and II. From this we can conclude that in addition to bidentate complexes, monodentate In–ONO_2 complexes are also present in these solutions. The spectrum of solution V is a mixture of the spectral features of an 8.56 M solution of nitric acid and those of solution I. Although the band at 1304 cm^{-1} (ρ = 0.15) could not be resolved

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*The 800 to 1200 cm^{-1} region has not been analysed in this work since it appeared to be less informative for our purposes.

TABLE IV. Frequencies and Depolarization Ratios (in parentheses) of Raman Bands of $In(NO_3)_3$ Solutions **I**, **II** and **V** in the 1200 to 1550 cm^{-1} Region.

I	II	V	Approximate Assignment
		1270 (0.10)	HNO_3
1307(0)	1310(0)	1304[a](0.15)	Complexed nitrate
1337(0.65)	1342(0.68)	1333 (0.38)	ν_3(E'), free nitrate
1412(0.70)	1412(0.65)	1436 (0.78)	
1510(0.47)	1518(0.55)	1517 (0.44)	Complexed nitrate

[a] This band of the complex overlaps with the NOH bending band of undissociated nitric acid molecules.

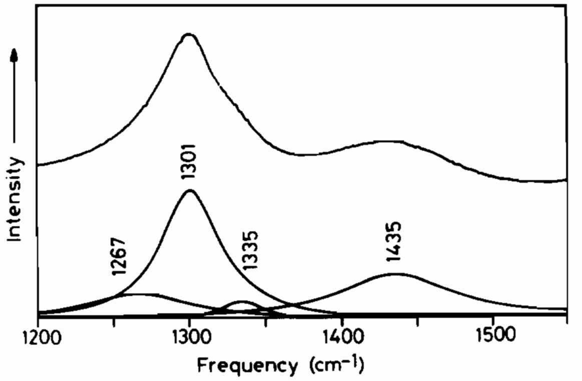

Fig. 4. Band resolution for an 8.56 M nitric acid solution in the 1200 to 1550 cm^{-1} region.

further by curve analysis, we know that it may consist of two close-lying components of similar band width: the band of undissociated nitric acid [18] with ρ = 0.11 and the band of the bonded nitrate ion. Due to this overlap the polarization behaviour of the latter cannot be ascertained.

Raman Spectra of the Crystalline Hydrate, $In(NO_3)_3 \cdot 3H_2O$, and its Melt

The Raman spectra of indium nitrate trihydrate recorded at different temperatures bear close resemblance with the spectra of the solutions: they exhibit the spectral features of free and bonded nitrate ions and those of $In-O(H_2)$ vibrations (Fig. 5, Table V). A peculiar feature is that the Raman band of the $In-ONO_2$ stretching mode (assigned by Hester and Grossman [7]) observed in the melt at 290 cm^{-1} is much stronger than that of either the solid trihydrate or the solutions (where it is hardly seen). This can be regarded as an evidence for the increase in covalent character of the bond between In^{3+} and NO_3^- ions in the melt.

The strengthening of the process of complexation in the melt is also shown by the substantial decrease of scattering intensity in the region of ν_3(E') vibration of free nitrate ions (virtually no bands are

TABLE V. The Raman Bands (cm^{-1}) of Polycrystalline $In(NO_3)_3 \cdot 3H_2O$ and its Melt.

Solid (t = 25 °C)	Melt (t = 80–110 °C)[a]	Assignment
725	720(dp)	ν_4(E'), free nitrate
1060	1050 (p)	ν_1(A_1'), free nitrate
1335	?	ν_3(E'), free nitrate
1425	?	
1615	1610(p)	$2\nu_2$(A_2'') free nitrate
760	750(p)	complexed nitrate
	770(p)	complexed nitrate
1030	1030(p)	complexed nitrate
1305	1310(p)	complexed nitrate
1515	1520 (?, ρ = 0.61)	complexed nitrate
455	465 (p, ρ = 0)	$In-OH_2$
270–290	290 (p, ρ = 0)	$In-ONO_2$

[a] The spectrum of the molten hydrate remains unchanged in this temperature interval.

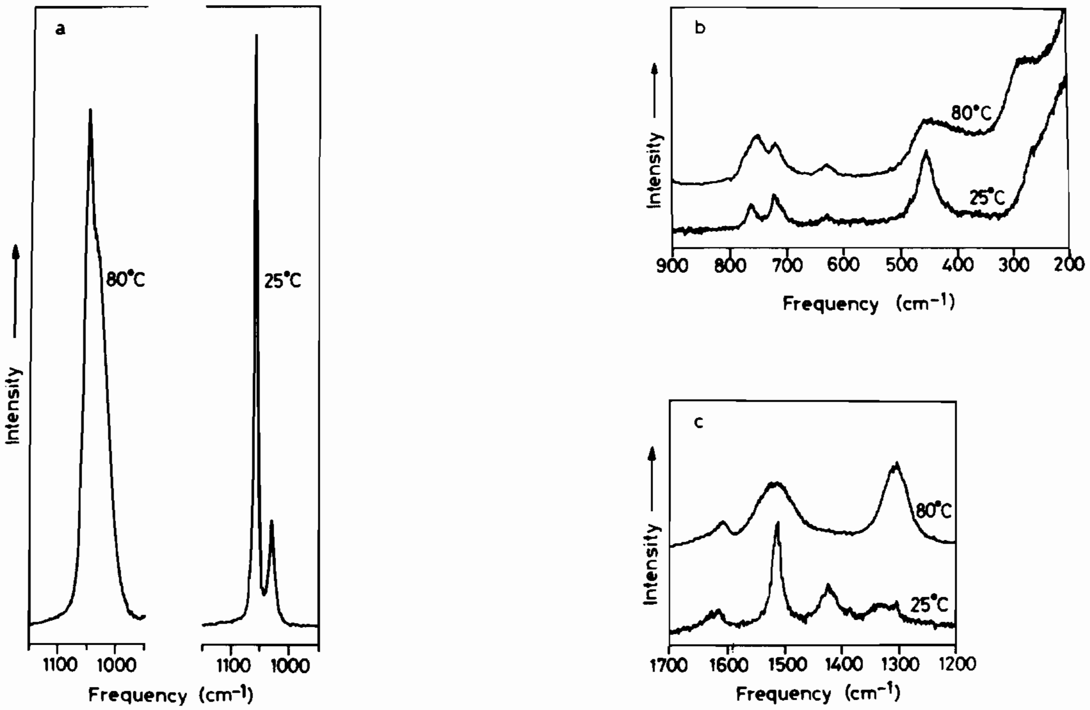

Fig. 5. The Raman spectra of polycrystalline indium nitrate trihydrate, $In(NO_3)_3 \cdot 3H_2O$ (t = 25 °C), and of its melt (t = 80 °C). The spectrum of the molten sample, in parts (b) and (c), is shown at three-fold ordinate expansion with respect to (a).

present near 1335 and 1425 cm^{-1}). In the spectra of the melt the band due to the coordinated nitrate ions (750 cm^{-1}) is stronger than that of the free nitrate ions (720 cm^{-1}). This pattern is exactly the reverse of that observed for solutions or for the crystalline sample. In addition, a shoulder appears near 770 cm^{-1} in the spectrum of the melt which, by the analogy with complexation in zinc nitrate [19], could be assigned to dinitrate complexes.

The polarized character of the 1310 cm^{-1} Raman line gives evidence of the formation of monodentate nitrate complexes in the melt. The 1520 cm^{-1} band has an intermediate depolarization ratio (0.61), and is thus inconclusive regarding the presence or absence of bidentate complexes.

Conclusion

The above analysis has helped us to distinguish between several indium-containing species formed under different circumstances, and allowed us to assign their characteristic Raman bands.

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