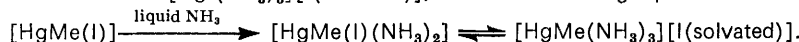# Solvation of Mercury(II) Halides and Alkylmercury(II) Halides by Liquid Ammonia: a Raman Spectroscopic Study

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Raman spectra are reported for HgX_2 (X = Cl, Br, or I), [HgEt(Cl)], [HgBr(Me)], and [HgMe(I)] dissolved in liquid ammonia and liquid ND_3. The spectra have been recorded at ambient temperatures and the results obtained for all six compounds are quite different to those reported previously for solutions in weakly co-ordinating non-aqueous solvents. The spectra for the chloro- and bromo-compounds have been satisfactorily interpreted in terms of $[Hg(NH_3)_4]^{2+}$ and $[HgR(NH_3)_3]^+$ cations, but the iodo-compounds generate different species. Mercury(II) iodide exists as $[HgI(NH_3)_3][I(solvated)]$, while the following equilibrium is shown to be present for [HgMe(I)]:

$$[HgMe(I)] \xrightarrow{\text{liquid } NH_3} [HgMe(I)(NH_3)_2] \rightleftharpoons [HgMe(NH_3)_3][I(solvated)].$$

THE Raman spectra of the mercury(II) halides dissolved in alcohol and the vibrational spectra of alkylmercury halides dissolved in nitromethane and benzene have been assigned previously. Delwaulle [1] showed that the dihalides behave as linear molecules in alcohol solution, and the presence of excess of halide results in the formation of the corresponding tetrahedral $[HgX_4]^{2-}$ species. Goggin and Woodward [2] interpreted the vibrational spectra of [HgMe(X)] (X = Cl, Br, or I) compounds in terms of the expected linear covalent structure having C_{3v} symmetry. No evidence for the presence of co-ordinated solvent molecules was obtained in either case. Only when Goggin and Woodward [3] examined [HgMe(ClO_4)] in aqueous solution did they find evidence for strong solvation effects. They interpreted their results in terms of a $[HgMe(OH_2)]^+$ species. Liquid ammonia is a strongly co-ordinating solvent and we have shown previously [4,5] that Raman spectroscopy is an important technique for studying the various types of interactions present in metal salt solutions over a range of concentration. This paper presents Raman spectroscopic evidence for the presence of two different kinds of solvated cation for both Hg^{2+} and $[HgMe]^+$ in liquid-ammonia solutions depending on the particular halide studied. An analysis of the data enables us to propose structures for the solvated cations which are very different to the very weakly solvated molecules found in alcohol, nitromethane, and benzene.

Tobias and his co-workers [6] previously reported the Raman spectrum of methylmercury iodide in liquid ammonia. They interpreted their data in terms of [HgMe(NH_3)]I but did not report the presence of a strong Hg–I stretching vibration which is observed in our spectra. This latter observation requires the presence of a solvated species containing a mercury–iodine bond.

EXPERIMENTAL

Raman spectra were recorded on a Cary 81 laser-modified spectrometer. The 530.8-nm line from a Coherent Radi-

ation model 52 krypton-ion laser (*ca.* 100 mW at the sample) was used for excitation. The polarisation data were obtained on the Cary 81 instrument after it had been converted into 90° operation by Anaspec Ltd. The conversion includes a large sample compartment, a Brookdeal 9511 quantum photometer, a triple-prism monochromator, and a cooled photomultiplier-tube mount. The spectra of the solutions contained in 3-mm diameter capillary tubes were recorded at ambient temperatures and were calibrated against carbon tetrachloride and indene.

All the compounds were thoroughly dried before use and samples were handled on a vacuum line or in a nitrogen-filled glove-bag to preserve their anhydrous condition. The mercury(II) halides (analytical grade) were recrystallised several times from pure anhydrous ammonia, and trace amounts of ammonium chloride were added to the solutions after the first filtration to repress the formation of amido-species. The final solution was filtered through a glass sinter (porosity 4). The alkylmercury halides were prepared by literature methods [7] and B.O.C. anhydrous NH_3 and ND_3 were used without further purification.

RESULTS

Mercury(II) Halides.—Raman spectra were obtained from mercury(II) halide solutions in liquid ammonia and ND_3 with the following mol ratios: 1 : 13 $HgCl_2$: NH_3, 1 : 12.5 $HgCl_2$: ND_3, 1 : 14.7 $HgBr_2$: NH_3, 1 : 14.8 $HgBr_2$: ND_3, 1 : 7 HgI_2 : NH_3, and 1 : 10.8 HgI_2 : ND_3. The results are given in Table 1 and typical spectra are shown in Figure 1(a) and (b). All the spectra show bands due to solvent NH_3 molecules and bands due to co-ordinated ammonia molecules [$\nu(Hg-N)$, $\nu(NH_3)$, $\delta(NH_3)$, and $\rho(NH_3)$]. Mercury(II) iodide alone has a band which can be assigned to a mercury–halogen vibration.

Alkylmercury(II) Halides.—Raman spectra were obtained from solutions of alkylmercury(II) halides in liquid NH_3 and ND_3 with the following mol ratios: 1 : 25.4 [HgEt(Cl)] : NH_3, 1 : 25.6 [HgEt(Cl)] : ND_3, 1 : 20.5 [HgBr(Me)] : NH_3, 1 : 19.1 [HgBr(Me)] : ND_3, 1 : 22.4 [HgMe(I)] : NH_3, and 1 : 29.3 [HgMe(I)] : ND_3. The results are given in Table 2 and the spectra are shown in Figure 2(a) and (b). The spectra provide evidence for the presence of both ' free ' and co-ordinated ammonia molecules. In addition, the

[1] M.-L. Delwaulle, *Bull. Soc. chim. France,* 1955, 1294.

[2] P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.,* 1966, **62,** 1423.

[3] P. L. Goggin and L. A. Woodward, *Trans. Faraday, Soc.,* 1962, **58,** 1495.

[4] D. J. Gardiner, A. H. Haji, and B. P. Straughan, *J.C.S. Faraday I,* 1976, 93.

[5] D. J. Gardiner, A. H. Haji, and B. P. Straughan, *J. Mol. Structure,* 1977, **37,** 79.

[6] H. Hagnauer, G. C. Stocco, and R. S. Tobias, *J. Organometallic Chem.,* 1972, **46,** 179.

[7] H. Gillman and R. E. Brown, *J. Amer. Chem. Soc.,* 1930, **52,** 3314.

TABLE 1

Raman bands (cm⁻¹) and assignments for solutions of mercury(II) halides in liquid NH_3 and ND_3

HgCl₂		HgBr₂		HgI₂		Assignment
NH₃	ND₃	NH₃	ND₃	NH₃	ND₃	
				123vs,p	123	Hg–I str.
401s,p	380	401s,p	379	352s,p	326	Hg–N str.
728vw	ca. 550	728vw	ca. 550	658vw	ca. 460	NH₃ rock
1 098mw	ca. 850	1 098mw,p	ca. 850	1 098mw,p	ca. 850	NH₃ sym def.
1 218mw,p	935	1 218mw,p	935	1 193mw,p	914	NH₃ sym def.
1 628w	1 193	1 628w	1 193	1 628w	1 191	NH₃ asym def.
ca. 3 170(sh)mw	ca. 2 315	ca. 3 170(sh)w	ca. 2 315	ca. 3 150(sh)w	ca. 2 304	NH₃ str.
3 217s	2 346	3 217s	2 346	3 217s	2 346	NH₃ overtone, 2ν₄
				3 255(sh)		NH₃ str.
3 297vs	2 399	3 297vs	2 399	3 297vs	2 399	ν₁ NH₃ sym str.
3 365s	2 506	3 365s	2 506	3 365s	2 506	ν₃ NH₃ asym str.

s = Strong, m = medium, w = weak, v = very, sh = shoulder, and p = polarised.

TABLE 2

Raman bands (cm⁻¹) [a] and assignment for solutions of alkylmercury(II) halides in liquid NH_3 and ND_3

[HgEt(Cl)]		[HgBr(Me)]		[HgMe(I)]		Assignment [b]
NH₃	ND₃	NH₃	ND₃	NH₃	ND₃	
				122vs,p	122	Hg–I stretch, (A)
260m	260					δ_asym (CCHg)
				ca. 430(sh)p	ca. 400	Hg–N str., (A)
446s,p	419	452s,p	422	453s,p	423	Hg–N str., (B)
				517m,p	517	Hg–C str., (A)
531vs,p	531	552vs,p	552	553vs,p	552	Hg–C str., (B)
1 068w,p	824	1 073w,p	820	1 072w,p	824	NH₃ sym def.
(ca. 1 190w)	984	(ca. 1 190w)	992	(ca. 1 190w)	889	NH₃ sym def.
1 193s	1 193	1 193s	1 193	1 193s	1 193	alkyl sym def.
1 630w	(ca. 1 190)	1 628w	(ca. 1 190)	1 630w	(ca. 1 190)	NH₃ asym def.
2 871m	2 871					CH₂ str.
2 931s	2 931	2 922s	2 922	2 922s	2 922	alkyl sym str.
3 000vw	2 998	2 998vw	2 998	2 998vw	2 998	alkyl asym str.
3 217s	2 346	3 216s	2 346	3 217s	2 347	2ν₄ NH₃
3 302vs	2 402	3 299vs	2 402	3 299vs	2 402	ν₁ NH₃ str.
3 378w	2 517	3 378w	2 517	3 378w	2 517	ν₃ NH₃ str.

[a] Expected weak bands which have been overlapped by stronger bands are given in parentheses. [b] For species (A) and (B) see Discussion section.

vibrations of the alkylmercury cation give rise to C–H and Hg–C bands. Again, however, the iodo-compound is different to the other two in that its spectrum contains two bands in the Hg–C stretching region and an intense band in the ν(Hg–I) region. No bands are observed in the ν(Hg–Br) or ν(Hg–Cl) region in solution spectra of [HgBr(Me)] or [HgEt(Cl)].

DISCUSSION

Mercury(II) Halides.—The bands observed in the Raman spectra of $HgCl_2$ and $HgBr_2$ dissolved in liquid ammonia can all be assigned to either vibrations of the free solvent or to vibrations of an ammonia-solvated Hg^{2+} cation. Confirmation of these assignments comes from the corresponding spectra of solutions in liquid ND_3 where the positions of all the bands in the spectra are substantially shifted to lower wavenumbers. There are no bands at all in the regions expected for ν(Hg–Cl) (*ca.* 300 cm⁻¹) and ν(Hg–Br) (*ca.* 200 cm⁻¹) stretching modes which would be much less sensitive to ND_3 isotopic substitution.

The N–H stretching region (3 100—3 500 cm⁻¹) consists principally of three bands at 3 365, 3 297, and 3 217 cm⁻¹. The band at 3 217 cm⁻¹ becomes markedly less intense, whilst that at 3 365 cm⁻¹ increases very slightly in intensity, as the solute concentration increases. Our interpretation of this region of the spectrum is based on the four-band hypothesis discussed previously.[4] In addition to these stretching modes of free ammonia, all the ammonia solutions show a weak shoulder at *ca.* 3 170 cm⁻¹ [see Figure 1(*b*)]. This feature remains as a shoulder on the side of the 2ν₄ mode in ND_3 and we assign it to a stretching vibration of co-ordinated NH_3.

The NH_3 deformation region shows a band due to free NH_3 solvent at 1 628 cm⁻¹ (ν₄), but the bands at 1 218, 1 098, and 728 cm⁻¹ provide evidence for the presence of co-ordinated ammonia molecules. In pure liquid NH_3 ν₂ symmetric deformation occurs at 1 046 cm⁻¹. When ammonia is co-ordinated to a cation this mode is known to shift to *ca.* 1 100 cm⁻¹ and it may increase significantly in intensity.[5] In the spectra of the mercury(II) halides in liquid NH_3, a doublet appears in the 1 100 cm⁻¹ region and we suggest that this additional effect arises from asymmetry in the outer solvation sphere of these solvated cations, caused by the presence of the halide anions. The $Hg-NH_3$ rocking mode, which is expected to be present when ammonia becomes co-ordinated to a cation, is observed as a very weak feature at 728 cm⁻¹. The bands of co-ordinated ammonia are shifted to lower
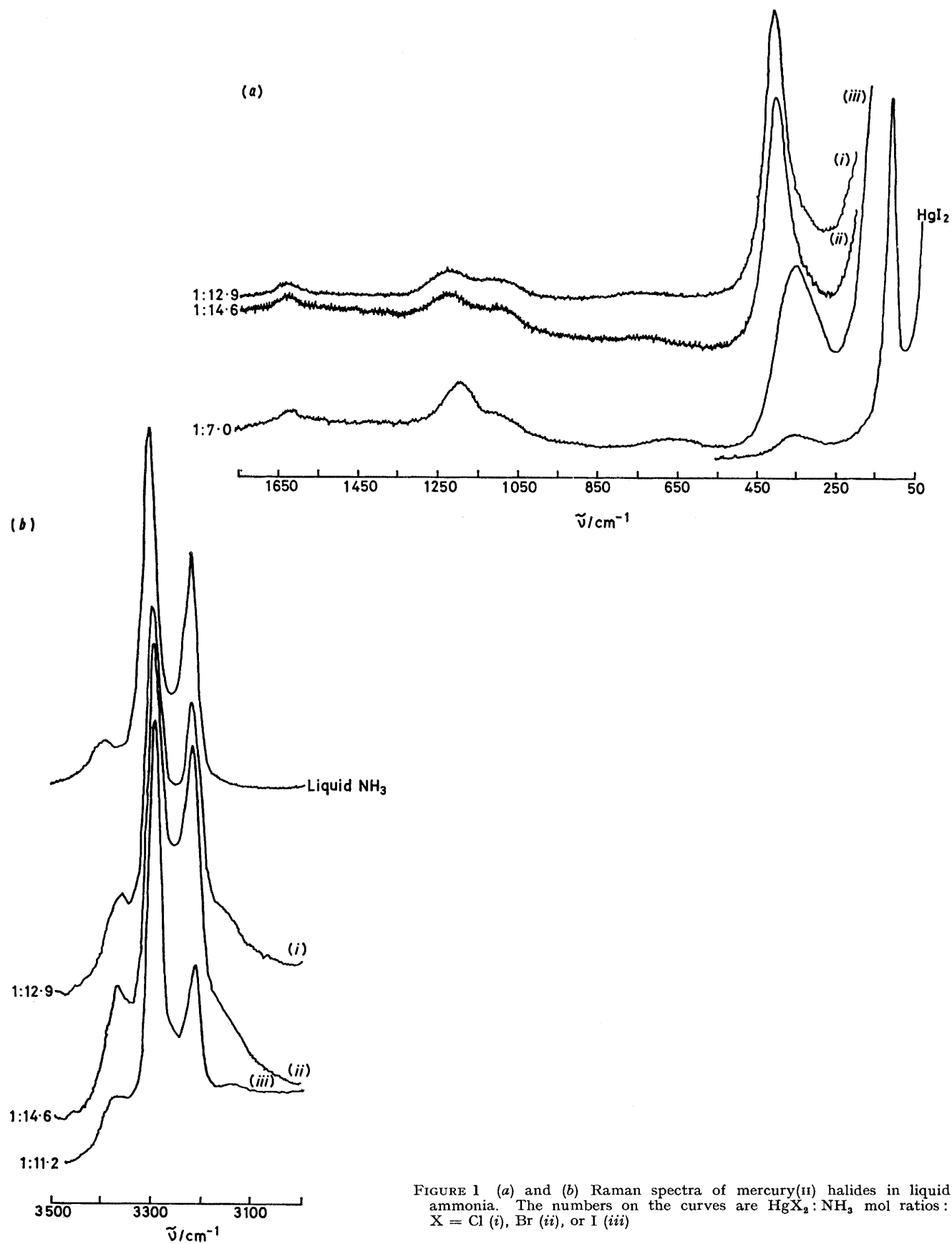
(a)

(iii)

(i)

(ii)

HgI₂

1:12·9
1:14·6

1:7·0

1650 1450 1250 1050 850 650 450 250 50

$\tilde{v}/cm^{-1}$

(b)

Liquid NH₃

(i)
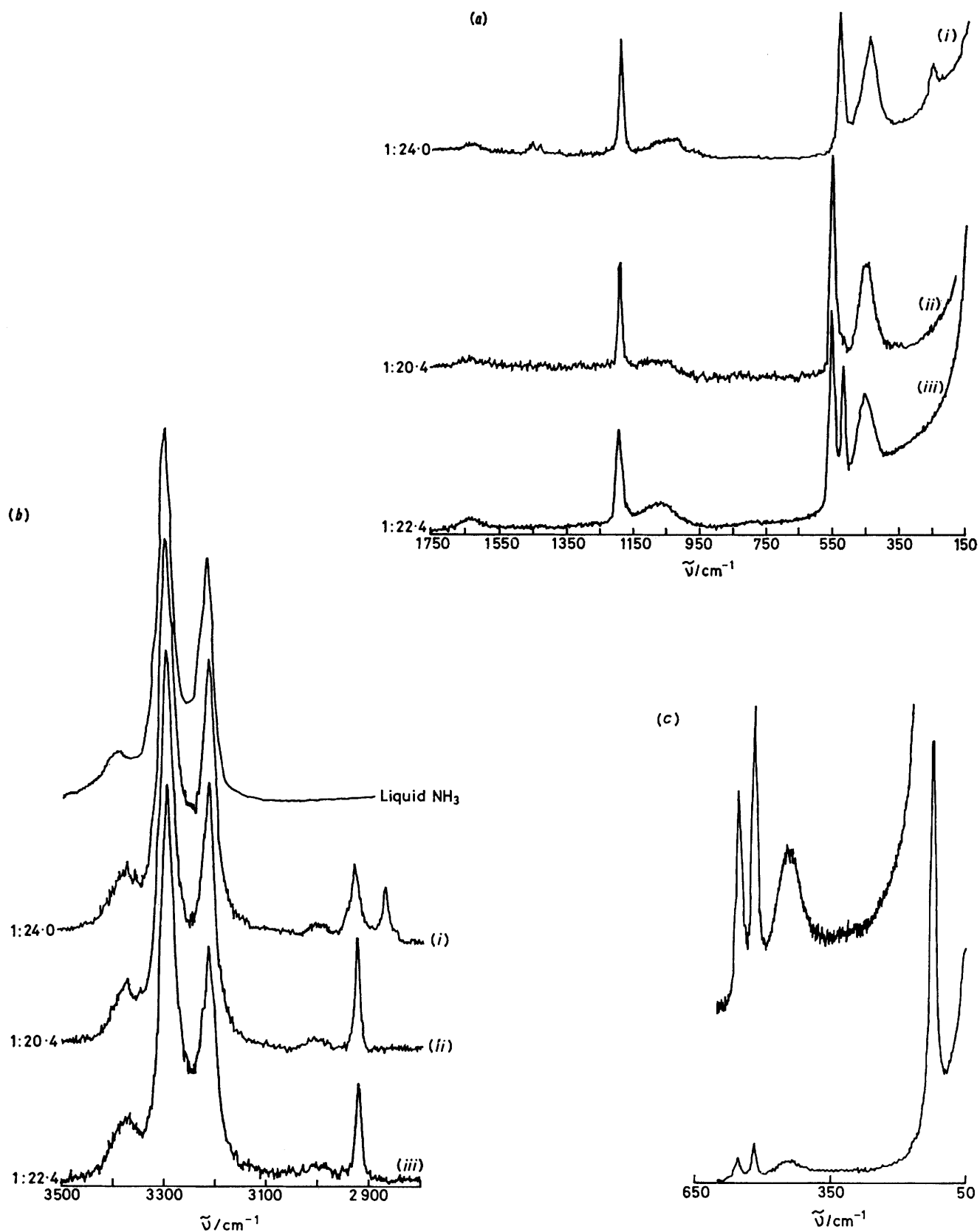
1:12·9

(ii)
(iii)

1:14·6

1:11·2

3500 3300 3100

$\tilde{v}/cm^{-1}$

FIGURE 1   (a) and (b) Raman spectra of mercury(II) halides in liquid
ammonia.   The numbers on the curves are HgX₂ : NH₃ mol ratios :
X = Cl (i), Br (ii), or I (iii)

FIGURE 2   (a) and (b) Raman spectra of alkylmercury(II) halides in liquid ammonia.
mol ratios: (i) X = Cl, R = Et; (ii) X = Br, R = Me; (iii) X = I, R = Me.
NH₃ at a [HgMe(I)] : I⁻ : NH₃ mol ratio of 1 : 3.2 : 29

The numbers on the curves are [HgRX] : NH₃
(c) Raman spectra of [HgMe(I)]–NaI in liquid

wavenumbers by the expected amounts in liquid-ND_3 solutions.

A new, broad, polarised band assigned to the $\nu(Hg-N)$ stretching mode occurs at 401 cm^{-1} (380 cm^{-1} in ND_3). The position compares well with those found for both $Tl[NO_3]$ (ca. 400 cm^{-1})[4] and $Hg[NO_3]_2$ (415 cm^{-1})[8] in liquid NH_3. Finally, the spectrum of a 1 : 1 mixture of $HgCl_2$ and $HgBr_2$ in liquid ammonia is identical with those of the single systems.

Thus we may conclude that both $HgCl_2$ and $HgBr_2$ exist in liquid-ammonia solutions as solvated cationic species $[Hg(NH_3)_n]^{2+}$. The halide counter ions are presumably solvated through a hydrogen-bonded inter-action with the solvent. We have no spectroscopic evidence to support this. It is not evident from these data what value n may take, but a value of $n = 4$ has been inferred from the Raman data for HgI_2 (see later).

Mercury(II) iodide behaves in a different way when dissolved in liquid ammonia as can be seen from Table 1 and Figure 1(a) and (b). Apart from the same bands assigned to free solvent, there are bands due to co-ordinated solvent, at slightly lower wavenumbers than observed for the other two halides. In addition, there is a very intense polarised line (123 cm^{-1}) in the Hg–I stretching region and its position does not alter when the compound is examined in the deuteriated solvent. The position is very close to the reported frequency for $[HgI_4]^{2-}$ in alcohol[1] (119 cm^{-1}), where the Hg^{2+} is considered to have a co-ordination number of four. This is in contrast to the much higher wavenumbers observed for $[HgI]^+$ in aqueous solution[9] (191 cm^{-1}) and HgI_2 in alcohol solution[1] (150 cm^{-1}). The maximum co-ordination number of Hg^{2+} in both these latter species is considered to be two, the second co-ordination position for $[HgI]^+$ being occupied by a water molecule. Thus it seems reasonable to interpret our data in terms of the four-co-ordinate mercury cation $[HgI(NH_3)_3]^+$. An interpretation based on the species $[Hg(NH_3)_4][HgI_4]$ in liquid-ammonia solution can be discounted for three reasons. (i) The cationic species $[Hg(NH_3)_4]^{2+}$ is present in the chloro- and bromo-systems and $\nu(Hg-N)$ occurs at 401 cm^{-1}. For the HgI_2 system, the $\nu(Hg-N)$ mode is observed at 352 cm^{-1} (see Table 1). (ii) For a 1 : 16 mol ratio in solutions of both $HgCl_2$ and HgI_2 in liquid NH_3, the intensity of the $\nu(Hg-N)$ stretching mode relative to that of the totally symmetric NH_3 stretching mode is 1.6 and 7.3 respectively. This is indicative of two very different Hg–N species. (iii) The depolaris-ation ratio for $\nu(Hg-I)$ in $[HgI_4]^{2-}$–MeOH is zero as measured on our instrument, whereas the ratio for HgI_2–NH_3 under the same conditions is 0.1. Again this is indicative of different species.

Thus we feel convinced that the species present in NH_3 solution are best represented as $[HgI(NH_3)_3]^+$ and $[I(solvated)]^-$. By analogy, the most likely species present in ammonia solutions of the chloro- and bromo-compounds would be $[Hg(NH_3)_4]^{2+}$. The wavenumbers

shown by the co-ordinated ammonia molecules in this cation are slightly higher than for the $[HgI(NH_3)_3]^+$ cation, but this probably results from the increased charge on the mercury atom.

Alkylmercury(II) *Halides.*—The spectra may be dis-cussed again in terms of free-solvent bands, bands due to co-ordinated solvent, and bands due to the cation. The results are given in Table 2 and Figure 2(a) and (b).

The Raman bands due to the solvent are very close in frequency to those for pure liquid ammonia, except for the ν_2 deformation mode which shifts to a higher wave-number (ca. 1 070 cm^{-1}) for the alkylmercury halide solutions studied. This shift in the position of ν_2 is usually encountered when a solute is dissolved in liquid ammonia. However, the intensity of the band is found to be markedly sensitive to the nature of the dissolved solute and, in particular, dependent on the polaris-ability of both the cation and anion of a dissolved electrolyte.[5] The $2\nu_4$ mode at 3 217 cm^{-1} in solution shows the usual reduction in intensity compared with that in pure liquid ammonia: this is again accounted for by a four-band hypothesis for the NH_3 stretching region.[4]

The bands expected for co-ordinated ammonia are not as prominent for these solutions as they were for the mercury halide solutions. This is mainly because the alkylmercury halides are much less soluble in liquid ammonia and hence the solutions are less concentrated. However, the spectra of all the three compounds exhibit a strong, broad, polarised band at ca. 450 cm^{-1} which shifts to ca. 420 cm^{-1} in ND_3. The appearance of this band together with the weaker co-ordinated-ammonia features at ca. 1 100 cm^{-1} leaves no doubt that the Hg^{2+} ion is strongly solvated.
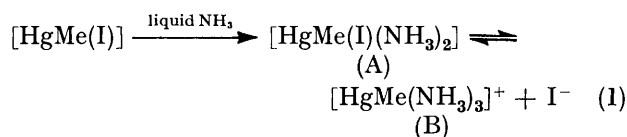
The remaining bands have been assigned to internal modes of the solute and they are interesting because again the chloro- and bromo-compounds behave differ-ently to the iodide. All the solutions show bands due to alkyl stretching and bending modes, but solutions of the chloro- and bromo-compounds exhibit no $\nu(Hg-Cl)$ or $\nu(Hg-Br)$ modes respectively while solutions of the iodide show a strong polarised line at 122 cm^{-1} The low wavenumber of this Hg–I stretching mode in liquid-ammonia solution (compared with 181 cm^{-1} in nitro-methane solution) suggests that the mercury atom is four-co-ordinate. This conclusion is consistent with our spectra of the $[HgI(NH_3)_3]^+$ species, discussed earlier, where the Hg–I stretch appeared at 123 cm^{-1}. It is apparent also that solutions of the iodo-compound show two polarised bands in the Hg–C stretching region (553 and 517 cm^{-1}). In addition, the broad asymmetrical band observed in the 400—500 cm^{-1} region, which shifts to lower frequency in the ND_3 solutions, is thought to comprise two bands each due to a $\nu(Hg-N)$ mode [see Figure 2(a)]. The appearance of two $\nu(Hg-C)$ and two $\nu(Hg-N)$ modes suggests the existence of two solvated methylmercury species (A) and (B), where (A) is $[HgMe(I)(NH_3)_2]$ and (B) is $[HgMe(NH_3)]^+$.

[8] P. Gans and J. B. Gill, *J.C.S. Dalton*, 1976, 779.

[9] J. H. R. Clarke and L. A. Woodward, *Trans. Faraday Soc.*, 1965, **61**, 207.

The presence of two such species in solution is supported by ^{1}H n.m.r. spectroscopy using methylene chloride as an external standard. The proton signal for the solvent protons was observed at 4.37 p.p.m., the signal for one HgMe species occurred at 4.67 p.p.m. $[J(\text{H}-^{199}\text{Hg})$ 213 Hz], and the protons of the other HgMe species gave a signal at 5.20 p.p.m. $[J(\text{H}-^{199}\text{Hg})$ was too weak to be observed].

The Raman spectrum of a solution of [HgMe(I)] saturated with anhydrous sodium iodide [see Figure 2(c)] shows an increase in intensity of the bands at 517 and 122 cm^{-1}. Due to overlap of the band at 453 cm^{-1}, it was not possible to observe any changes in intensity in the weak band at 430 cm^{-1}. These observations lead us to conclude that species (A) and (B) are involved in an equilibrium with iodide ions as in (1). The Raman bands

$$[\text{HgMe(I)}] \xrightarrow{\text{liquid NH}_3} [\text{HgMe(I)(NH}_3)_2] \rightleftharpoons$$
$$(A)$$
$$[\text{HgMe(NH}_3)_3]^+ + \text{I}^- \quad (1)$$
$$(B)$$

centred at 553 and 453 cm^{-1} have been assigned to species (B) by comparison with the bands observed for solutions of [HgBr(Me)] in liquid NH$_3$. The bands observed at ca. 430, 517, and 122 cm^{-1} can be assigned to species (A). The equilibrium is attained too quickly to observe any intensity variations of the key bands with time. These results for the iodo-compound do not agree completely with the work of Tobias and his co-workers [6] who reported no Raman bands at <450 cm^{-1} for their liquid-NH$_3$ solutions. They concluded that the mercury ion is present in solution as [HgMe(NH$_3$)]$^+$ since the latter species has been isolated in the solid state as the chloride

¹⁰ K. Brodersen, Chem. Ber., 1957, 90, 2703.

salt.[10] However, a close examination of their published spectrum shows a weak unlisted frequency in the Hg–C stretching region at ca. 517 cm^{-1} which we observe also. We prefer to think of the mercury atoms as four-co-ordinate in all these species, by analogy with the mercury(II) halides themselves. The fact that the two-co-ordinate cation [HgMe(NH$_3$)]$^+$ has been isolated in the solid state does not rule out the likelihood of four-co-ordination in ammonia solutions.

$$2[\text{HgMe(I)}] \xrightarrow{\text{NH}_3(l)} \text{HgMe}_2 + \text{HgI}_2 \quad (2)$$

$$\text{HgI}_2 \xrightarrow{\text{NH}_3(l)} [\text{HgI(NH}_3)_3]^+ + \text{I}^- \quad (3)$$

An alternative explanation based on the disproportionation (2) followed by (3) does not seem likely since there is no ν(Hg–N) mode at 352 cm^{-1} arising from [HgI(NH$_3$)$_3$]$^+$ as observed for solutions of HgI$_2$ in liquid ammonia.

There is no evidence in any of the spectra to suggest that deprotonation of the co-ordinated ammonia has taken place to form species such as [HgMe(I)(NH$_2$)$_2$]$^{2-}$ or [HgMe(NH$_2$)$_3$]$^{2-}$.

We conclude from these data that liquid NH$_3$ is a sufficiently strong co-ordinating solvent to displace both chloride and bromide completely by the formation of Hg–N bonds in HgCl$_2$, HgBr$_2$, and alkylmercury(II) halides (X = Cl or Br). In contrast, only one of the Hg–I bonds in HgI$_2$ is broken, forming [HgI(NH$_3$)$_3$]$^+$ in ammonia solution. The inability of ammonia to completely displace iodide is again shown for solutions of [HgMe(I)], and this results in the formation of both [HgMe(I)(NH$_3$)$_2$] and [HgMe(NH$_3$)$_3$]$^+$ + I$^-$.