ponent (urea, sucrose, etc.,) is larger than the water molecules and considered to be composed of "rigid, uncharged spheres of radius, a, it is clear that the center of any of these molecules will not be able to come closer than a distance, a, to the 'surface' of the sedimenting particle. This results in a region of thickness, $2a$, surrounding the macromolecules in which the density varies from that of water to that of the solution. According to Kauzmann, this region of varying density can be approximated by assigning a water layer of thick-

ness, a, to the macromolecules and assuming that the liquid more distant than a, from the surface of the macromolecule has the density of the bulk liquid.[13]" In such cases as these, it is still possible to use the equations developed in the theoretical section of this communication. The α_j will refer to the number of water molecules in the region from which salt is excluded, and the binding affinities, k^0, for such regions will be equal to zero.

(13) H. K. Schachman, "Ultracentrifugation in Biochemistry," Academic Press, Inc., New York, N. Y., 1959, p. 233.

A Raman Study of the Bromide Solutions of Zinc and Cadmium[1a]

BY WILBUR YELLIN[1b] AND ROBERT A. PLANE

Raman intensity measurements were made of zinc bromide solutions containing various ratios of total zinc to total bromide. These results led to the following as the most probable assignments for the three polarized lines: ν_{172} cm.$^{-1}$ ($\rho = 0.06$), ZnBr$_4$$^=$; ν_{186} cm.$^{-1}$ ($\rho = 0.09$), ZnBr$_2$; ν_{205} cm.$^{-1}$ ($\rho = 0.13$), ZnBr$^+$. Comparison with ZnBr$_2$ in non-aqueous solvents indicated that the aqueous ZnBr$_2$ molecule is different from that in other solvents and may be tetrahedral Zn(H$_2$O)$_2$Br$_2$. Stepwise formation constants for the three complexes were found in concentrated solution to be: (ZnBr$^+$)/(Zn^{++})(Br$^-$) = 0.3, (ZnBr$_2$)/(ZnBr$^+$)(Br$^-$) = 1, (ZnBr$_4$$^=$)/(ZnBr$_2$)(Br$^-$)^2 = 0.2. If ZnBr$_3$$^-$ were present, its principal Raman band was coincident with that of one of the other species. In cadmium bromide solution of various ratios of total Br$^-$ to total Cd^{++}, only one polarized line was found. Coincident with that line, at 166 cm.$^{-1}$ ($\rho = 0.08$) which was due to CdBr$_4$$^=$, was the principal line of one (or more) lower species. The lower species appeared to be of less importance than in the zinc system, while the tetrabromo species was of greater importance: (CdBr$_4$$^=$)/(Cd^{++})(Br$^-$)^4 > 1.

Of the methods used for studying complex ions in aqueous solution, none is more direct than the measurement of Raman spectra of solutions. This method is direct in that each different complex species present should exhibit its characteristic vibrational spectrum.[2] Thus, the Raman method differs from most other methods which determine some property characteristics of one species (often the activity of the completely dissociated species) and from variations of this property infer the presence of additional species. Furthermore, the very existence of a Raman spectrum shows that the complex species has kinetic identity (i.e., exists for times long enough to allow vibrations) and is bound together by something other than hard-sphere coulombic attractions (i.e., the mean molecular polarizability must change during vibration[3]). Thus, in principle, observation of Raman spectra is a general method for both defining and detecting complex ions in aqueous solutions.

The present work was undertaken in order to study as quantitatively as possibly Raman spectra of concentrated aqueous solutions containing relatively simple complex ions. For the investigation, the bromides of zinc and cadmium were chosen. Both had previously been studied qualitatively.[4,5]

Aqueous solutions of Zn^{++} and Br$^-$ had been found to show Raman lines at 172, 184 and 208 cm.$^{-1}$, while non-aqueous solutions of ZnBr$_2$ showed a line at (or near) 208 cm.$^{-1}$ and in some solvents a second line at 172 cm.$^{-1}$. On this basis, the line at 208 cm.$^{-1}$ was assigned to the linear ZnBr$_2$ molecule, that at 172 cm.$^{-1}$ to the tetrahedral ZnBr$_4$$^=$ (whose other frequencies were found to be 61, 82 and 210 cm.$^{-1}$) and the intermediate line (184 cm.$^{-1}$) found only in water was assigned to ZnBr$_3$$^-$. No Raman evidence was found for any other species such as ZnBr$^+$, for which non-Raman evidence exists.[6,7] Previous studies of aqueous cadmium bromide solutions detected the existence of only the tetrahedral CdBr$_4$$^=$.[5] Thus, a primary aim of the present investigation was to determine which lower complexes are formed in aqueous solutions of the bromides of zinc and cadmium. Quantitative intensity measurements were made both for this purpose and to determine the concentrations of the various species as a function of solution composition.

Experimental

Measurements were made with a Cary Model 81 Raman spectrophotometer. This instrument was altered only in that the filter solution was replaced by pure isopropyl alcohol and sample tubes were used which were specially

(1) (a) This work was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-279. Reproduction in whole or in part is permitted for any purpose of the United States Government. Some of the results were reported at the 136th National Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1959. (b) Based on work performed for partial fulfillment of the degree of Doctor of Philosophy.

(2) G. W. Chantry and R. A. Plane, J. Chem. Phys., 33, 736 (1960).

(3) Cf. D. A. Long, Proc. Roy. Soc. (London), A217, 203 (1953); L. A. Woodward and D. A. Long, Trans. Faraday Soc., 45, 1131 (1949).

(4) M. L. Delwaulle, Compt. rend., 240, 2132 (1955); Bull. Soc. Chim., France, 1955, 1294 (1955).

(5) J. A. Rolfe, D. E. Sheppard and L. A. Woodward, Trans. Faraday Soc., 50, 1275 (1954).

(6) E. Ferrell, J. M. Ridgion and H. L. Riley, J. Chem. Soc., 1121 (1936).

(7) (a) L. G. Sillen and B. Liljequist, Svensk kem. Tidskr., 56, 85 (1944); (b) S. A. Shchukarev, L. S. Lilich and V. A. Latysheva, Zhur. neorg. Khim., 1, 225 (1956).
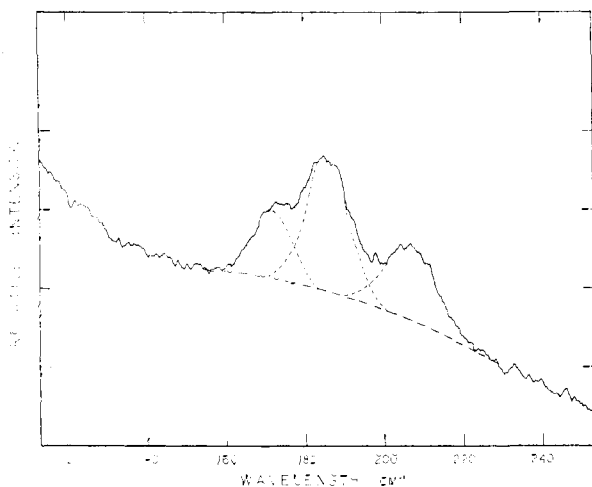
Fig. 1.—Raman spectrum of zinc bromide solution showing the three polarized bands.

constructed with Liebig-type water jackets so that 25° water could be circulated around the tube to provide thermostating. The sample volume was increased from 4.5 ml. to 12 ml.

In order to relate observed Raman intensities to concentrations of scattering species, internal standards were used which corrected for changes of refractive index and all geometric variations. The standard was in every case the A_1 line of ClO_4^- (dissolved in the solution being studied) whose absolute intensity is known.[8] Each measurement consisted of several alternately obtained traces of ClO_4^- and the species in question. The relative intensity was obtained by comparing the area of the line in question with that of the standard run just before and just after. All such comparisons (usually five or more) for a single solution were then averaged. The precision thus obtained and the accuracy found for solutions of known composition indicated that the final measurements contained a probable error less than ± 5% of the concentration of the species in question. Depolarization ratios were determined by the method previously described.[2]

The solutions studied were prepared from two or more of the following solutes: $ZnBr_2$, $Zn(ClO_4)_2$, $NaBr$, $LiBr$, $HClO_4$, $CdBr_2$, $Cd(ClO_4)_2$. All bromides and the $HClO_4$ were the purest grades commercially available, used without further purification. Zinc and cadmium perchlorates were prepared in solution by the exact neutralization of standardized $HClO_4$ with ZnO and $CdCO_3$, respectively. Stoichiometric concentrations were checked by analysis of zinc and cadmium by electrodeposition.

Results

Solutions containing separately varied concentrations of Zn^{++} and Br^- showed a total of three relatively intense Raman lines at $\Delta \nu = 172$, 186 and 205 cm.$^{-1}$. In most solutions two of the strong lines were found, but at certain compositions, all three were present to limited extents. Such a spectrum, by its nature one of the poorest obtained, is given as Fig. 1. The strong lines were in addition to the weak, depolarized lines observed at 63, 81 and 213 cm.$^{-1}$ which, with the 172 cm.$^{-1}$ line, comprise the Raman spectrum of $ZnBr_4^=$.[4] The intensities of the strong lines changed markedly one to another as the ratio of total dissolved Br^- to total dissolved Zn^{++} was changed. It, therefore, was apparent that the three lines arose from separate chemical species. Each of the lines showed a small depolarization ratio ($\rho_{172} = 0.06$, $\rho_{186} = 0.09$, $\rho_{205} = 0.13$) as would be expected for symmetrical stretching

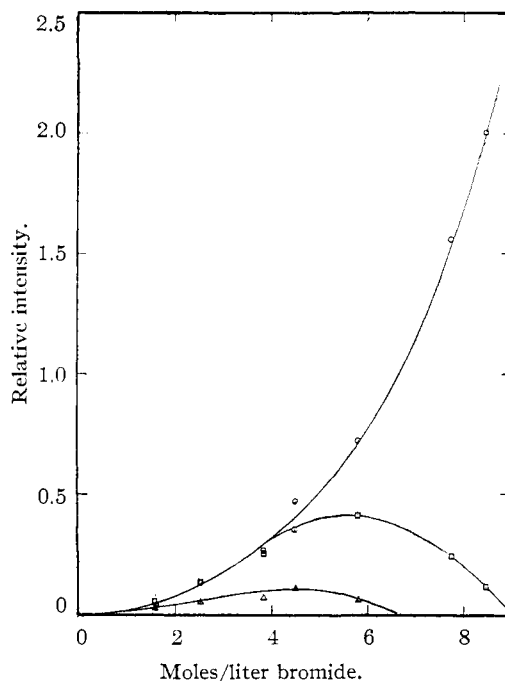(8) G. W. Chantry and R. A. Plane, J. Chem. Phys., 32, 319 (1960).

Fig. 2.—Raman intensities (relative to molar ClO_4^-) of the three polarized bands for 1.50 M zinc solutions with various concentrations of bromide. Circles refer to 172 cm.$^{-1}$ band; squares, to 186 cm.$^{-1}$; triangles, to 205 cm.$^{-1}$.

modes of nearly symmetrical species. The three lines were relatively sharp but varied in width somewhat (average deviation of the three ±10%) with solution composition. The average values for the width at half height were 13.6 cm.$^{-1}$ for 172 cm.$^{-1}$, 12.3 for 186 cm.$^{-1}$, 15.1 for 205 cm.$^{-1}$. All observations made confirmed the previous assignment of the 172 cm.$^{-1}$ band as the A_1 frequency of tetrahedral $ZnBr_4^=$ ion. The bands at 186 and 205 cm.$^{-1}$ apparently arose from species containing other than four Br atoms per Zn. Any depolarized bands (asymmetric stretches or bending modes) from these species were either coincident with those of $ZnBr_4^=$ or were too weak to be observed under the conditions and composition range studied.

The spectra of solutions containing Cd^{++} and Br^- were markedly different from the zinc solutions in that at all ratios of Br^-/Cd^{++} only a single polarized line ($\rho = 0.08$) at 166 cm.$^{-1}$ was found. In addition, weak depolarized bands were observed at ca. 56 cm.$^{-1}$ (broad and probably ν_2 and ν_4 unresolved) and at 187 cm.$^{-1}$ (ν_3). This single spectrum had previously been assigned to tetrahedral $CdBr_4^=$.[4,5] Unlike Zn^{++}, Cd^{++} either formed only $CdBr_4^=$ or if other complexes were formed, the frequencies were nearly identical with those of the tetrabromo complex.

In order to identify chemical species with the lines at 186 and 205 observed in Zn^{++}–Br^- solutions, a number of experiments at a variety of solution compositions were performed. In each experiment, the intensity, relative to dissolved ClO_4^-, of each of the three main lines was determined. In doing so, two difficulties were encountered. As Fig. 1 shows, the lines were close enough to the
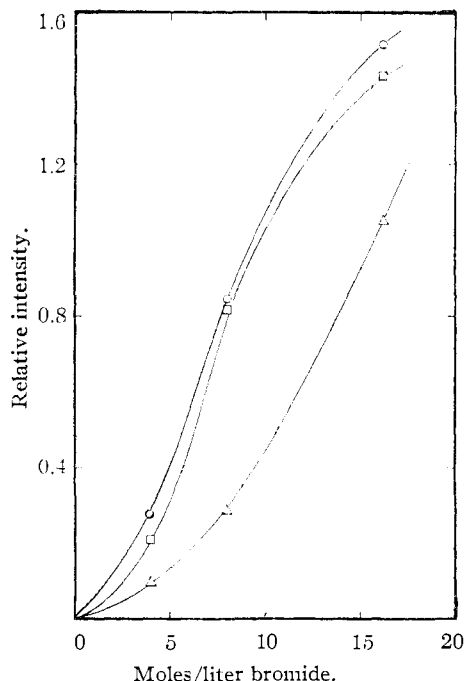
Fig. 3.—Raman intensities (relative to molar ClO_4^-) of the three polarized bands for $ZnBr_2$ solutions at various concentrations with added 0.300 M $HClO_4$. Circles refer to 172 cm.$^{-1}$ band; squares, to 186 cm.$^{-1}$; triangles, to 205 cm.$^{-1}$.

Rayleigh line so that the base line was not horizontal. Furthermore, the three peaks were sufficiently broad and close together so as to not be completely resolved. To assign intensities to each peak, a base line was sketched in to resemble that found in the absence of complexes. Individual peaks were assumed to be symmetrical and were graphically resolved for each spectral trace. Although the precision was found to remain $\pm 5\%$ of the peak intensity, the uncertainty most probably increased.

Three series of experiments were performed. In one, seven solutions were prepared, each containing a total zinc concentration of 1.50 M (obtained from approximately equimolar $Zn(ClO_4)_2$ and $ZnBr_2$) with varying amounts of added $NaBr$ so that the total concentration of Br^- covered the range 1.6 to 8.5 M. The intensities (relative to 1.00 M ClO_4^-) observed for each of the three Raman lines is plotted as function of total Br^- concentration in Fig. 2.

A second series of experiments was performed with solutions each containing 0.300 M $HClO_4$ (to serve as the intensity standard) and varying concentrations of $ZnBr_2$ without additional Zn^{++} nor Br^-. The intensities (relative to molar ClO_4^-) obtained for these solutions are given in Fig. 3.

Finally, a series of experiments was performed which was designed according to the Job method of continuous variation.[9] In these, the total stoichiometric concentration of Zn^{++} + Br^- equalled in every case 6.0 M. The twelve individual solutions were prepared from the appropriate mixture of two of the solutes: $ZnBr_2$,
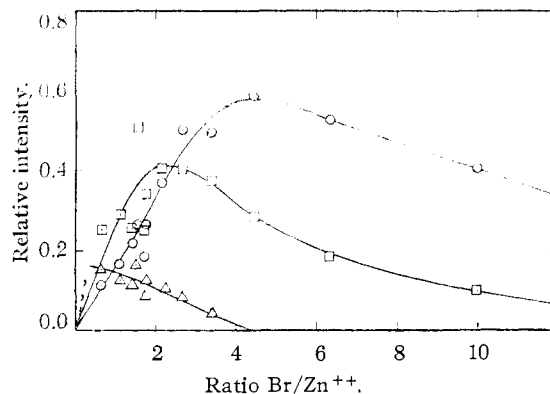
(9) P. Job, Ann. Chim., (10) 9, 113 (1928).

Fig. 4.—Raman intensities (relative to molar ClO_4^-) of the three polarized bands for solutions in which the total concentration of zinc plus the total concentration of bromide equals 6.0 M. Circles refer to 172 cm.$^{-1}$ band; squares, to 186 cm.$^{-1}$; triangles, to 205 cm.$^{-1}$.

$Zn(ClO_4)_2$, $NaBr$. The intensities found are plotted $vs.$ the ratio Br^-/Zn^{++} in Fig. 4.

In none of the experiments described above was $ZnBr_4^=$ the only zinc-containing species present. Thus, Fig. 2, for example, shows the concentration of $ZnBr_4^=$ rising even at the highest Br^- concentration used. It was necessary to prepare a solution with all the Zn as $ZnBr_4^=$ in order to determine the inherent molar Raman intensity of $ZbBr_4^=$. For this purpose $NaBr$ could not be used since precipitation of $NaClO_4$ occurred before more than about 80% of the total zinc was converted to $ZnBr_4^=$. The desired solution was prepared by using $LiBr$ to make a solution of the stoichiometric concentrations: 0.218 M $Zn(ClO_4)_2$ and 12.38 M $LiBr$. The spectrum of this solution contained only the ClO_4^- peaks and the 172 cm.$^{-1}$ peak ($i.e.$, 185 and 205 cm.$^{-1}$ were absent and no new peaks appeared). Thus, from the total zinc concentration, the observed molar intensity of $ZnBr_4^=$ was found to be 1.35 times that for the A_1 line of ClO_4^-.[10] The reliability of the assumptions made in obtaining this value was indicated by the fact that the intensity per unit concentration of total zinc for less concentrated solution asymptotically approached this value.

For comparison with the previous study,[4] solutions of approximately molar $ZnBr_2$ in methanol and in acetone were measured. The first showed a peak at 211 cm.$^{-1}$, with width at half-height 14.8 cm.$^{-1}$ and a depolarization ratio of 0.03. The acetone solution showed a peak at 209 cm.$^{-1}$, with width at half-height of 15.6 cm.$^{-1}$ and a depolarization ratio of 0.01.

In an attempt to learn more about the cadmium bromide system, a series of solutions were prepared from $Cd(ClO_4)_2$ and $NaBr$ in which the total stoichiometric concentration of Cd^{++} + Br^- was 2.0 M. The results, plotted in Fig. 5, exhibit a maximum near Br^-/Cd^{++} = 4 and a marked shoulder below 2. Additional experiments were performed

(10) This value does not contain correction for instrument response as a function of frequency. A calibration curve utilizing the absolute intensities of CH_2Cl_2 [D. A. Long, D. C. Milner and A. G. Thomas, Proc. Roy. Soc. (London), A237, 197 (1956)] showed that the absolute intensity can be obtained by multiplying this value, and those of the other complexes discussed here, by 1.16.

on a variety of solutions prepared from $CdBr_2$, NaBr and $HClO_4$. The results of these are given in Table I.

TABLE I

RAMAN INTENSITIES OF $Cd^{++}-Br^-$ SOLUTIONS

Stoichiometric concentrations			Intensity of 166 cm.$^{-1}$ relative to molar ClO_4^-	Relative intensity per molar Cd total
CdBr$_2$	NaBr	HClO$_4$		
0.297	0	0.499	0.15	0.50
.285	0.330	.499	.25	0.88
.302	0.585	.499	.37	1.22
.290	1.195	.499	.58	2.00
.304	2.424	.499	.79	2.60
.306	5.032	.499	.80	2.61
.499	0	.249	.26	0.52
.499	0.998	.249	.68	1.36
.500	2.000	.249	1.14	2.28
.500	6.000	.249	1.33	2.66
.099	5.995	.249	0.26	2.63

From either of the two series of experiments recorded in the table, it can be noted that the intensity divided by total Cd concentration (last column) increases with excess Br^- and eventually becomes constant. The final value, 2.63[10] thus represents the molar intensity of the complex $CdBr_4^=$.

Conclusions

It is apparent from Figs. 2 and 4, that of the several complexes formed by Zn^{++} and Br^-, $ZnBr_4^=$ (172 cm.$^{-1}$ peak) represents the one of highest Br^-/Zn^{++} ratio. The other two strong peaks must originate from species of lower Br^- content. Thus, from Fig. 2, for example, these two species are seen to reach their maximum concentrations at lower $[Br^-]$ than does $ZnBr_4^-$. To formulate these species, the Job experiments recorded in Fig. 4 are helpful. For simple systems containing but one complex species, the maximum concentration and hence the maximum Raman intensity occurs (for solutions of constant concentration metal ion plus ligand) at the ratio of ligand to metal ion corresponding to the species formula.[9] However, in the present system, which contains three complex species, the situation is more complicated.[11] It can be shown that for ideal solutions containing i complexes of the type AB_n, a maximum is reached in- the plot of intensity vs. $[B_{total}]/[A_{total}]$ when

$$([B_T]/[A_T])_{\text{at max.}} = 1 + \frac{\sum_{n=0}^{i}(n-1)I_n C_n}{\sum_{n=0}^{i} I_n C_n}\left[1 + \frac{\sum_{n=0}^{i} n C_n}{\sum_{n=0}^{i} C_n}\right] - \frac{\sum_{n=0}^{i} n(n-1)C_n}{\sum_{n=0}^{i} C_n}$$

where C_n is the concentration of AB_n and I_n its molar intensity. For a resolvable peak due only to the species AB_j, all I_n except I_j vanish and the expression reduces to

$$([B_T]/[A_T]) \text{ at max.} _{\text{of } I_j} = j + \frac{\sum_{n=0}^{i} n(j-n)C_n}{\sum_{n=0}^{i} C_n}$$
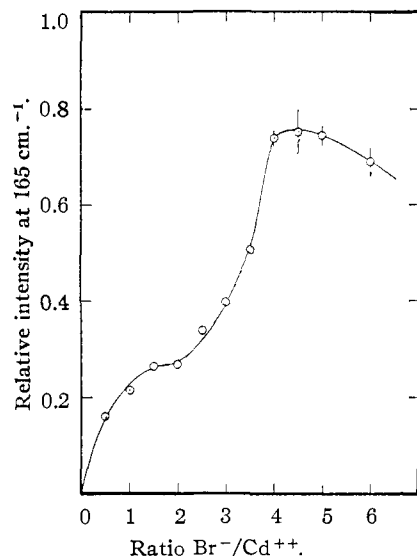
(11) L. I. Katzin and E. Gebert. J. Am. Chem. Soc., 72, 5455 (1950).

Fig. 5.—Raman intensities (relative to molar ClO_4^-) of the 166 cm.$^{-1}$ band of solutions in which the total concentration of cadmium plus the total concentration of bromide equals 2.0 M.

The final expression consists of a leading term which is that for the case where but a single complex species is present and a correction term which is a weighted average of the other complexes present. The correction term is such as to cause positive deviations for high j and negative deviations for small j. For intermediate j's, there should be some cancellation. Furthermore, the maximum deviation should occur for high j since higher n values are involved and near the corresponding maximum, C_0 will be nearly 0 which is not true for a low j. Finite values of C_0 increase the denominator of the correction, without adding to the numerator (since $n = 0$). Although it is difficult to access the role of solution non-ideality, this treatment can be used to interpret Fig. 4. The known species $ZnBr_4^=$ shows its maximum just above the ratio of 4. Since this deviation should be greater than that for either lower species, the positions of the other two maxima indicate that the 205 cm.$^{-1}$ band characterizes $ZnBr^+$ and the 186 cm.$^{-1}$ band characterizes $ZnBr_2$.

The assignment suggested by the experiments summarized in Fig. 4 is in disagreement with the earlier assignment.[4] The present assignment is, however, supported by the concentration calculations to be described below which show that using the molar intensities indicated by the experiments and justified on theoretical grounds, there is insufficient bromide in the solutions to form species containing more than 1 and 2 Br atoms, respectively. Furthermore, if the reasonable molar intensities were abandoned, it would not be possible for the solutions to contain any $ZnBr^+$ (independent of whether or not it had a Raman spectrum). Because this species is a priori more likely than $ZnBr_3^-$, for example, the present assignment seems further justified. It thus seems more likely that the following is the explanation for the correlation between experiments done in various solvents. The peak at ca. 210 cm.$^{-1}$ in non-aqueous solvents is

due to the linear molecule but is absent from aqueous solutions (as supported by the fact that only in non-aqueous media is the line completely polarized). The line in aqueous solution at 186 cm.$^{-1}$ assigned to a species of formula $ZnBr_2$ is, in fact, due to a hydrated, perhaps tetrahedral, molecule such as $Zn(H_2O)_2Br_2$, with ν_1 frequency thus quite similar to tetrahedral $ZnBr_4^=$. On this basis, the similarity of the frequencies of $ZnBr^+$ and the other two species can be understood in terms of a hydrated ion such as tetrahedral $Zn(H_2O)_3Br^+$.

Although it was possible to obtain the relative molar intensity of $ZnBr_4^=$, it was not possible to prepare solutions in which all the zinc, or all the bromide, was converted only to $ZnBr_2$ or only to $ZnBr^+$ (cf. Fig. 2). However, in certain solutions (of relatively high Br^-_T/Zn^{++}_T) $ZnBr^+$ was absent. If it is assumed that Zn^{++} was also absent, the relative molar intensity of $ZnBr_2$ can be determined. On this basis, it was found to be 0.6. At slightly lower ratios of Br^-_T/Zn^{++}_T it seems reasonable to assume that a negligible fraction of the Zn^{++}_T is uncomplexed. Thus, from these solutions, in which the concentrations of $ZnBr_4^=$ and $ZnBr_2$ are determined, the concentration of $ZnBr^+$ is found by difference and its molar intensity turns out to be ca. 0.25.

The values of molar intensities for $ZnBr_2$ and $ZnBr^+$ based on solution stoichiometry are not especially precise. There is, however, an alternate method for obtaining these values which indicates that the above values cannot be far from correct. The Wolkenstein theory,[12] for which strong support has recently been found,[13] states that the quantity $\partial\alpha/\partial Q$ (the change of mean molecular polarizability during vibration, which is responsible for Raman intensity) is a bond property. Thus, it is reasonable that the quantity is directly transferrable from $ZnBr_4^=$ to the lower complexes. This would mean that the molar intensity would (with correction made for differences of frequency and degree of depolarization by using the equation

(12) M. Wolkenstein, Compt. rend. acad. Sci. U.R.S.S., **32**, 185 (1941).
(13) G. W. Chantry and L. A. Woodward, Trans. Faraday Soc., **56**, 1110 (1960).

$$I_p = KM(\nu_0 - \nu_p)^4 \, 45(\partial\bar{a}/\partial Q_p)^2 \, [6/(6-7\rho)]/$$
$$\nu_p[1 - \exp(-h\nu_p/kT)]$$

described in ref. 8) be proportional to the number of Zn–Br bonds in the complex. With the corrections, the calculated molar intensities[10] are 0.62 for $ZnBr_2$ and 0.27 for $ZnBr^+$.

From the values of the relative molar intensities, the data of Figs. 2, 3 and 4 can be directly converted to solution concentrations. Furthermore, approximate values of molarity equilibrium constants can be determined. These are

$Zn^{++} + Br^- = ZnBr^+$	$K = 0.3$
$ZnBr^+ + Br^- = ZnBr_2$	$K = 1$
$ZnBr_2 + 2Br^- = ZnBr_4^=$	$K = 0.2$
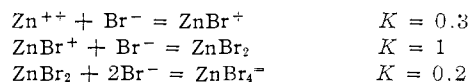
Considering the wide range of solution composition (ionic strength varied from 3.5 to 8.5) these constants are remarkably constant. Within a random scatter (average deviation of all reliable values 28%), the constants showed no detectable trend with ionic strength. The values themselves are in fair agreement with those found previously,[7] except that the second (formation of $ZnBr_2$) is larger and $ZnBr_3^-$ is not detected in the present work. These facts could be taken as evidence that the peak at 186 cm.$^{-1}$ is due to both $ZnBr_2$ and $ZnBr_3^-$. If true, however, the coincidence must be nearly perfect since this peak is even sharper than the other two.

From Fig. 5 it is apparent that although species with less than 4 Br^-/Cd^{++} are formed, they are of less importance than in the zinc system. If they are assumed to be of negligible importance, an estimate can be made, using the relative molar intensity of $CdBr_4^=$ found to be 2.63, for the molar equilibrium constant $(CdBr_4^=)/(Cd^{++})(Br^-)$.[4] The values found are far from constant particularly at low $(Br^-_T)/(Cd^{++}_T)$ where the neglected lower species are most important. If, however, these solutions are ignored, the constant is found to be greater than unity, as compared with 6×10^{-2} for the corresponding zinc constant. Thus for Cd^{++} as compared to Zn^{++}, the lower Br^- complexes are of less importance while the tetrabromo complex shows greater tendency to form.