Electronic Spectra and Geometries of HgX_{3}^{-} in Water and an Assessment of various Computing Procedures for revealing Hidden Spectra

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The electronic absorption spectra, in the visible and ultraviolet regions, of HgX_3^- (X = CI, Br or I) have for the first time been obtained, by computer techniques, free from any contributions of HgX_2 or HgX_2^{-} . Four different independent methods are described and evaluated for this system and for general use. For systems where the desired spectrum is completely hidden below other bands, here for $HgBr_3^-$ and $HgCl_3^-$, a combination of two methods is needed. Additional tests to validate the computed spectra are described and advised. The spectra of HgX_3^- were resolved into their component Gaussian bands and the transitions identified and assigned. This permitted the identification of $HgCl_3^-$ as planar with D_{3h} symmetry, and Hgl_3^- as pyramidal, with C_{3v} symmetry, suggesting that the solvated species are trigonal-bipyramidal and tetrahedral, respectively. The spectrum of $HgBr_3^-$ appears to show features of both symmetries, but it is closer to pyramidal geometry.

The halide complexes of mercury(II) have been extensively studied by many workers using a variety of techniques. Several reviews have been written, that of Deacon¹ being the most comprehensive, but now rather out-of-date. Other reviewers have discussed the halogenomercurates as part of the general chemistry of mercury^{2,3} or of the halogens.⁴ The trihalides are difficult to characterize, and have thus received less attention. Solids of the formula MHgX₃ are known (M = univalent cation, X = Cl, Br or I), but in the case of chlorides $HgCl_3^-$ is not present.⁵ For bromides the structure is intermediate between $HgBr_3^-$ chains and individual ions with trigonal structure.⁶ For iodides an approximately trigonal-planar structure is also found.⁷ Attempts to elucidate the structure of the trihalides in aqueous solution are hampered⁸ because these anions disproportionate, and addition of X^- to HgX₂ never yields exclusively HgX₃. However, Raman studies on HgCl₃⁻ and HgBr₃⁻ in dipolar aprotic solvents have been performed by Waters et al.,9,10 where these species are formed under stoichiometric conditions.

Other techniques have, for example, led to the proposal that a tetrahedral species $[HgBr_3(OH_2)]^-$ occurs in aqueous solution, in order to explain why the observed entropy of $HgBr_4^{2-}$ exceeds that of the tribomo species, when the calculated entropies show the reverse.¹² Gallagher and King¹³ found the entropy of the trichlorospecies best explained by the configuration $[HgCl_3(H_2O)_3]^-$. X-Ray diffraction studies of the trichloro species suggest⁸ a pentagonal bipyramid with the chlorine atoms co-planar $[HgCl_3(H_2O)_2]^-$, although this is uncertain since the solutions could not be obtained free from $HgCl_2$ or $HgCl_4^{2-}$.

We have a preliminary report¹¹ of the electronic spectra of the system HgX₂ with added halide. At X/Hg mole ratios of just over 2–20, HgX₂ and HgX₃⁻ were present; at greater ratios, HgX₄²⁻ was also present. Further halide addition soon resulted in a two-species equilibrium, between HgX₃⁻ and HgX₄²⁻, up to a mole ratio of *ca.* 200, after which essentially only HgX₄²⁻ was present in solution. We computed, and then resolved, for the first time, the discrete spectrum in water for each of the three HgX₃⁻ species, and now discuss these results in more detail.

We have earlier also reported upon the effect of ionic strength on the stability constants, determined from spectra, of the halogeno complexes of mercury(II) in water,¹⁴ but our spectroscopically derived stability constants for the mixed^{15,16} mercury(II) dihalides, HgXY, have been ques-

tioned by Belevantsev and Shoovayer,¹⁷ who obtained their constants from stability constant data determined around 1949. We have responded and briefly pointed out our considered reasons for the disagreement.¹⁸ Because our procedures again yield accurate formation constants from definitive spectra, we therefore have also given details of the various methods which may, in principle, be used for deriving HgX_3^- spectra. These methods are suited to many other similar systems, and we comment upon the relative merits of the various methods. We then discuss the assignments of the bands resolved from HgX_3^- spectra, and their implications for the structure of these species in water.

Experimental

Spectroscopic Measurements

Spectra were recorded on an Applied Physics Cary 14H spectrophotometer, modified to yield spectra in digitised form on paper tape. Details of the system have been published.¹⁹⁻²¹ Thermostatted cell holders were used, and the water circulated from a thermostat bath maintained the solutions in the cells at 20 ± 0.1 °C.

Chemicals and Solution Preparation

All chemicals were of the highest purity, thoroughly dried, and stored in a vacuum desiccator. Water was distilled and deionised before use. Standard solutions of HgCl₂, HgBr₂, NaClO₄ and the halides of sodium and potassium were prepared by weighing into graduated flasks. Because of the low and slow solubility of HgI₂ in water, solutions were prepared by mechanical stirring in water at ca. 40 °C for several hours. After they were cooled and filtered, the solutions were transferred to a graduated flask and made up to volume. An aliquot was mixed with KI solution such that the iodide/ mercury ratio was at least 30 000, and the solution ca. 1.5 mol dm^{-3} in KI. HgI₂ was thus quantitatively converted to HgI₄²⁻, which has an absorbance peak at 323 nm. The HgI₂ concentration was determined from a calibration plot established by dissolving weighed quantities of HgI₂ in 1.5 mol dm⁻³ KI solution. Concentrations were accurate and repeatable to within < 0.5%.

Solutions for spectral measurements were prepared by transferring known volumes of stock solutions to a graduated

flask with a burette or pipette, as appropriate, and making up to volume. Solutions requiring constant ionic strength were prepared by adding the calculated volume of NaClO₄ solution required. All glassware was grade A and the airconditioned laboratory was maintained at 20 ± 1 °C.

Solution Stability

For the different concentrations studied the mercury(II) halide solutions obeyed the Beer-Lambert law. Solutions containing added iodide, for example, were stable for several hours in the dark, but for only 2 h in the spectrophotometer light beam, because the reversed-beam optics of the spectrophotometer exposed the sample to the full radiation of the quartz-halogen lamp. Test solutions were measured, stored in the dark, and their spectra recorded some weeks later. After 9 weeks the peak maximum of HgI₂, for example, had decreased by 3%. Fresh solutions were therefore used in all experiments so that photolysis and any possible sidereactions were insignificant during the period of use. Belevantsev and Shoovayev²² insist that aqueous solutions of mercury halides, and subsequent calculations, must always include consideration of hydrolysis and the reaction $HgX_2 \rightleftharpoons$ $HgX^+ + X^-$. Our above findings indicate otherwise, and we note that the electrochemical studies in the 1940s, from which they take their data, generally assumed that these reactions would occur.23

Computing Procedures

The pen noise inherent in spectroscopic measurements may be reduced by multiple scanning, but this is time-consuming and unrealistic. Noise reduction was therefore achieved by mathematical smoothing^{24,25} of the digitised spectra, which were recorded at 1 nm intervals. Degradation of the original profile was avoided by using a five-point smoothing convolute.

Convolution coefficients may also be used to generate derivative spectra mathematically.²⁴⁻²⁶ The number and position of component bands of an observed spectrum may be elucidated by the analysis of the derivative functions of that spectrum. In particular, second- and fourth-derivative curves reach minimum and maximum values, respectively, at energies corresponding to the maximum absorbance of the component bands in a spectrum. Using the convolution pro-cedure of Savitsky and Golay^{24,25} the derivatives of observed and calculated spectra were obtained. The degree of noise in derivative spectra is increased as smaller sets of convoluting elements are used. However, the use of large sets in secondand fourth-derivative functions may result in a loss of resolution of closely overlapping bands.²⁶ Therefore, several convolutions were performed on each spectrum studied, to realise consistent results. This technique, applied to the spectrum of $HgBr_4^{2-}$ in water, is illustrated in fig. 1. The hidden band, seen as a weak shoulder around 270-280 nm, is now clearly resolved at 277 nm.

For resolving the spectra of the various mercury(II) halide species into their component bands, the conventional leastsquares fitting method requires an assumption concerning the type of band distribution involved. The usual functions considered are Gaussian, Cauchy (Lorentzian), or the product or sum functions of both. For the intramolecular charge-transfer transitions described here the commonly employed Gaussian function was found most suitable. The program was based on the least-squares minimization procedure of Fletcher and Powell,²⁷ and included matrix inversion²⁸ to increase the rate of convergence of fit.

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Fig. 1. Second- and inverted fourth-derivative curves superimposed on the ultraviolet absorption spectrum of $HgBr_4^{2-}$ in water at 20 °C. The numbers indicate the number of data points used in calculating the derivatives. The curves show that the maxima of the main band and the lower-energy hidden band are clearly resolved only when convolutes > ca. 19 are employed.

Calculation of Spectra

The reaction of mercury(II) halides with added halide, and many other reactions, proceed stepwise, viz.

$$HgX_2 + X^- \rightleftharpoons HgX_3^- \tag{1}$$

$$HgX_{3-} + X_{-} \rightleftharpoons HgX_{4}^{2-}.$$
 (2)

It has been shown^{29,30} that, for mercury(II), the tetrahalogeno species begins to form before all the dihalide is converted to the trihalogeno species. This may be seen in the spectral changes that occur as halide is successively added to the mercury(II) halide. A steady change in the spectra occurs until the spectrum of HgX_4^{2-} only is observed: the spectrum of HgX_3^{-} cannot be observed free of contributions due to either the di- or the tetra-halide. Here, general methods, some in combination, have been derived and examined, in order (in principle) to calculate HgX_3^{-} from both the above systems, and we therefore also discuss their various merits.

Use of known Formation Constants

For equilibrium (1), upon applying Beer's law and the law of mass action, it may be shown that, at any given wavelength,

$$A/M = (\varepsilon_a + K_3 X \varepsilon_b)/(1 + K_3 X)$$
(3)

where A is the observed absorbance, M is the total molar concentration of metal, X is the free-ligand concentration, K_3 is the stability constant for HgX₃⁻ [eqn (1)], and ε_a and ε_b are the molar absorbance of HgX₂ and HgX₃⁻, respectively. All

but K_3 and ε_b are experimentally observable. Thus by substitution of known values of K_3 into eqn (3) the molar absorbance of HgX₃, as a function of wavelength, *i.e.* the spectrum of HgX₃, may be found. This method requires an accurate knowledge of the three HgX₃ equilibrium constants, and that the experimental conditions be exactly the same as those used in the determination of the equilibrium constant. Van Eck⁸ has used the early data of Sillen²⁹ to obtain an approximate spectrum of HgX₃ in water.

This method may be extended to utilize the observable spectrum of HgX_4^{2-} by means of the comparable equation, *viz*.

$$A/M = (\varepsilon_{\rm b} + K_4 X \varepsilon_{\rm c})/(1 + K_4 X) \tag{4}$$

where ε_c is the molar absorbance of HgX₄²⁻ and K₄ is the stability constant for HgX₄²⁻ [eqn (2)]. For the three mercury halides in equilibrium ε_b (for HgI₃⁻) may be derived from

$$A/M = (\varepsilon_{a} + K_{3} X \varepsilon_{b} + K_{3} K_{4} X^{2} \varepsilon_{c})/(1 + K_{3} X + K_{3} K_{4} X^{2})$$
(5)

but with less accuracy owing to the increased number of parameters. We have shown earlier¹⁴ that the stability constants for HgX_3^- and Hg_4^{2-} are dependent on ionic strength. In our experiments here the ionic strength was not normally kept constant, as halide was progessively added to HgX_2 ; it was thus not appropriate in this study to use literature stability constants in the above equations with our molar absorbance data for HgX_2 and HgX_4^{2-} .

Least-squares Method

Eqn (3) may be rearranged to give

$$\mathbf{I}' = -(1/K_3)(A' - \varepsilon_{\mathbf{a}})/X + \varepsilon_{\mathbf{b}}$$
(6)

where A' = A/M, the molar absorbance of the solution. This equation is now in the linear form y = mx + c and thus at any given wavelength, for a series of solutions with different ligand concentrations, a least-squares procedure may be applied to yield values⁸ of K_3 and ε_b . Repeating this at all recorded wavelengths will, in principle, yield the entire spectrum of HgX₃⁻. When tested, this method was here found to be very sensitive to the value of the free-ligand concentration. Also, the calculated K values varied widely with wavelength, and hence the spectrum of HgX₃⁻ thus derived was not meaningful.

Comparative Absorbance Plots

A graphical approach may be used. Comparative absorbance plots of $A' vs. (A' - \varepsilon_a)/X$, at various wavelengths, will have a slope of $-1/K_3$, and the intercept will be at ε_b . Currently this procedure is time-consuming and impractical for large numbers of wavelengths. However, it was useful in that, in the range of solutions for which eqn (6) held true, K_3 was readily determined and an accurate value of ε_b at any given wavelength could be found for use in the reference-point method (described below).

Eqn (4) may be treated similarly to yield the spectrum of HgX_3^- , utilising the spectrum of HgX_4^{2-} . Since eqn (5) is nonlinear with respect to the unknowns ε_b , K_3 and K_4 (with three species in equilibrium), a graphical approach is not applicable under these conditions. However, a least-squares minimisation may be applied to such spectra obtained as a function of ligand concentration. Van Eck⁸ has used an interative method in an attempt to determine the unknowns in eqn (5), but we chose not to develop the required computer programs for use with our data, on the basis of the limited success with the two species systems.

Reference-point Method

For a system of two absorbing species, A and B, in equilibrium, the molar absorbance at any given wavelength of the solution is given by $\varepsilon_d = f_a \varepsilon_a + f_b \varepsilon_b$, a variant of Beer's Law, where ε_d is the molar absorbance of the solution, ε_a and ε_b the molar absorbances and f_a and f_b the mole fractions of A and B, respectively, and further, $f_a + f_b = 1$. Upon employing solutions of different relative compositions we can obtain the molar absorbance of HgX₃⁻ as

$$\varepsilon(\mathrm{HgX}_{3}^{-}) = \beta[\varepsilon_{\mathrm{d}} - \varepsilon(\mathrm{HgX}_{2})] + \varepsilon_{\mathrm{d}}. \tag{7}$$

This method of calculating spectra requires a knowledge of the molar absorbance of HgX_3^- at a given reference wavelength. This may be obtained by one (or more) of five different methods.

(1) Known formation constants, such as those derived from eqn (3) or (4) [or, in principle eqn (5)], may be used. One (or more) wavelengths are chosen, and for several solutions of HgX_2 with added halide the molar absorbance of HgX_3^- is calculated. The average absorbance at one wavelength may then be used as the reference-point absorbance. If published constants are available then solutions employed must be of the same ionic strength, and at the same temperature, as the original study. Using our data the reference-point absorbance had too large an error to yield acceptable spectra for HgX_3^- .

(2) Using the least-squares method outlined above gives the absorbance at a given wavelength and the formation constant simultaneously. This approach has the same constraints as method (1).

(3) The comparative absorbance plots described above yielded reference-point absorbances at given wavelengths that compared well with those obtained independently by other methods. The reference wavelength chosen was normally that at which derivative spectra had shown there to be peaks attributable to the HgX_3^- species.

(4) The change in the spectra of solutions of an ion as a ligand is added can show initially the formation of say, HgX_3^- and then HgX_4^{2-} . If the spectrum of HgX_3^- differs considerably from that of HgX_4^{2-} , as is clearly the case for the mercury(II)-iodide system, this change with added halide may be extrapolated to give the molar absorbance of HgX_3^- . This method has limited use when considerable spectral overlap between, say, ML_3^- and ML_4^{2-} occurs, although an approximate value for ML_3^- can be obtained, which can then serve as a useful check of the other methods employed.

(5) When a set of spectra contain one (or more) isosbestic points this implies that only two species are in equilibrium, and the total, say, mercury(II) concentration is constant.^{31,32} Such solutions may contain HgX₂ and HgX₃⁻, or HgX₃⁻ and HgX₄²⁻, and the molar absorbance of HgX₃⁻ at the isosbestic point wavelength is thus accurately defined.

However, the HgX₂ spectrum cannot be used as the reference spectrum, in eqn (7), with the isosbestic point(s) as the reference-point absorbance(s) for the HgX₂ \rightleftharpoons HgX₃⁻ equilibrium, in the calculation of the spectrum of HgX₃⁻, as the mathematics now involve division by zero. But the isosbestic points formed in the second equilibrium, HgX₃⁻ \rightleftharpoons HgX₄²⁻, are valid as references points (and vice versa). In practice, only the iodo system contained clearly defined isosbestic points, and the calculated spectrum of HgI₃⁻ could be noisy if the original sample spectrum employed in the calculation had not been carefully smoothed. This arises because the method multiplies small differences between spectra. Also, an added complication with the mercury(II) complexes arises because the complexing halide ligand partially absorbs in the spectral region of interest, and this must be accurately computed and subtracted before true molar absorbances of HgX_3^- can be obtained in the overlap region. This iterative procedure is now described.

Halide Imbalance

The iodide ion, with a strong absorbance peak in water at 226 nm, overlaps most with the spectra of the iodo mercury(II) species. In preparing the various solutions equal quantities of alkali-metal halide were added to the sample and reference solutions. In the former some free halide, the amount as yet unknown, reacted with HgX_2 . The reference solution thus had a net excess free halide absorbance compared with the sample solution and, for iodide, this effectively reduced the true absorbance below 250 nm.

The compensation procedure was as follows. The HgI₃ spectrum was calculated over the whole wavelength employed, and from this the concentration of HgI₃ (apparently) present was obtained. The concentration of free iodide ions was found by difference, the absorbance imbalance of the original sample spectrum then calculated, and a new corrected sample spectrum derived. This process was repeated until the difference between successively amended spectra (below 250 nm) was less than a predetermined amount (normally <0.01%). The set of corrected spectra now exhibited two new isosbestic points in place of the original one.

In the case of reference spectra containing chloride and bromide ions the above procedure may be applied, and for our mercury(II) complexes the imbalance contribution in the far ultraviolet was tested but not found significant enough to warrant its implementation.

We now present our findings for the definitive spectra of HgI_3^- , $HgBr_3^-$ and $HgCI_3^-$ in water.

Results

Reaction of Mercury(II) Iodide with Added Iodide

The changes in absorption spectra obtained upon addition of I⁻ to aqueous HgI₂ at 20 °C, to form HgI₃⁻ and HgI₄²⁻, are shown in fig. 2. Initially, as HgI_3^- formed, the 209 nm HgI_2 peak decreased and a shoulder formed around 290 nm, on the side of the 264 nm peak, and simultaneously this peak moved to 240 nm. An isosbestic point appeared at 232 nm up to a mole ratio of 5 of iodide to mercury, defined as R in this study. Above this ratio the UV cut-off in the 1 cm cells prevented spectral measurements below 240 nm. As R was further increased, peaks formed at 287 and 252 nm, due to HgI₃, and a shoulder arose at 320 nm, indicating the presence of HgI_4^{2-} . For 25 < R < 50, the 290 nm region remained effectively constant as HgI₃ was steadily converted to HgI_4^{2-} , and its continued formation is shown by the rising peak at 322 nm. For R > 50 the absorbance at 290 nm dropped to a minimum and isosbestic points appeared at 286 and 306 nm. The 322 nm peak continued to rise rapidly with increase in R to 500, after which the rise slowed, but did not cease until $R \approx 30\,000$, which corresponded to complete conversion to HgI_4^{2-} . Thus a three-species equilibrium occurred with 4 < R < 50.

An isosbestic point also indicates internal linearity in a system, and such sets of spectra show a linear dependence in plots of absorbance at one wavelength vs. that at a different

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Fig. 2. Ultraviolet absorption spectra changes obtained upon addition of iodide to aqueous HgI_2 (6.2×10^{-5} mol dm⁻³) at 20 °C. Iodide/mercury mole ratios (R) are, progressively: (i) 2.0(HgI_2), (ii) 2.4, (iii) 2.8, (iv) 4.0, (v) 8, (vi) 12, (vii) 18, (viii) 25, (ix) 40, (x) 80, (xi) 200, (xii) 40000(HgI_2^{-1}). Arrows indicate isosbestic points, that at 232 nm belongs to the equilibrium $HgI_2 + I^- = HgI_3^-$, and those at 286 and 306 nm to the equilibrium $HgI_3 + I^- = HgI_4^{-2}$. Both equilibria are present when the spectra do not pass through any of these isosbestic points [curves (v)-(vii)].

wavelength. Fig. 3 shows plots of the absorbances of solutions at a wavelength on one side of an isosbestic point vs. absorbances at a wavelength on the other side. Straight lines resulted for solutions with 2 < R < 5 and 50 < R < 30000,



Fig. 3. Internal linearity plots for HgI_2 with added iodide in water at 20 °C. Wavelength pairs are taken from wavelengths above and below an isosbestic point associated with the equilibria described: (a) $HgI_2 \rightleftharpoons HgI_3^-$, (b) $HgI_3 \rightleftharpoons HgI_4^{2-}$, (c) $HgI_3 \rightleftharpoons HgI_4^{2-}$.

confirming internal linearity and two-species equilibria in these ranges.

Calculation of the Spectrum of Hgl₃

At an isosbestic point the molar absorbances of the two species in equilibrium are the same. For the reasons given above the molar absorbances of HgI_3^- at 286 and 306 nm, derived from the observed spectra, were used in the referencepoint method for 2 < R < 5 to calculate the full spectrum of HgI₃. The experimental molar absorbances were 12400 ± 50 and $10500 \pm 50 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively. All the calculated spectra, using either value, passed through both isosbestic points, and also the non-usable, but observed, isosbestic point at 232 nm. However, these calculations did not allow for halide absorption imbalance, and when this was included the HgI_3^- spectrum no longer passed through the 232 nm isosbestic point, but did pass through the isosbestic points at 207 and 216 nm in the corrected spectra (fig. 4). The spectrum of HgI₃⁻ had absorbance maxima at 291 nm ($\varepsilon = 12400 \pm 200$ dm³ mol⁻¹ cm⁻¹) and 250 nm ($\varepsilon = 18800 \pm 300$ dm³ mol⁻¹ cm⁻¹). When the molar absorbances of the isosbestic points were varied by up to 250 dm³ mol⁻¹ cm⁻¹ the calculated peak position at 291 nm did not change position, and varied in intensity by only 200 dm³ $mol^{-1} cm^{-1}$.

A check on the accuracy of the calculated HgI₃⁻ spectrum was made using a comparative absorbance plot (fig. 5). The wavelength chosen was that of the peak at 291 nm. The intercept, which gives the molar absorbance at that wavelength, was obtained from a least-squares fit of the data points, and gave a value of $12400 \pm 200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, identical with the value obtained in the calculated spectrum.

A further check used the calculated spectrum of HgI₃⁻ to evaluate the formation constant for the reaction in eqn (1). In conjunction with the amended spectra for 2 < R < 5 consis-



Fig. 4. Calculated spectra for HgI_2 in water at 20 °C with added iodide, obtained after an iterative procedure to remove halide imbalance (see text). Iodide/mercury mole ratios (R) are, progressively: (i) 2.0(HgI_2), (ii) 2.4, (iii) 2.8, (iv) 3.4, (v) 4.0. Curve (vi) is HgI_3, and (vii) is HgI_3 before halide correction. Note that, in comparison with curves (i)-(iv) in fig. 2, the original well defined but now recognised as fortuitous) isosbestic point, at 232 nm, is now replaced by two excellent isosbestic points, at 207 and 216 nm, in the corrected spectra. Curves (vi) and (vii) in this plot illustrate the magnitude of the molar absorbance change needed to correct for halide imbalance in this system.



Fig. 5. Comparative absorbance plot, employing 14 different R values, for HgI₂ in water at 20 °C with added iodide, using absorbance data at 291 nm in eqn (6). The intercept and slope were obtained from a least-squares fit to the relevant data. The molar absorbance (ϵ) for HgI₃⁻ at 291 nm and the log K₃ value so obtained are within experimental error of these data determined independently. Intercept, ϵ (HgI₃⁻) = 12400 ± 200; slope log K₃ = 3.67 ± 0.02.

tent K_3 values were obtained for all spectra and at all wavelengths in the range 230–300 nm.

Reaction of Mercury(II) Bromide with added Bromide

The main features of the reaction in water at 20 °C between mercury(II) bromide and added potassium bromide are illustrated in fig. 6. For R < 4 an isosbestic point appeared around 200 nm, but as this was close to the cut-off point it could not be accurately observed. As R was increased, a peak rose at *ca.* 250 nm, indicating the formation of HgBr₃⁻: with R > 500 this peak shifted to 248 nm and continued to rise as



Fig. 6. Ultraviolet absorption spectra changes obtained upon addition of bromide to aqueous $\text{HgBr}_2(1.1 \times 10^{-4} \text{ mol dm}^{-3})$ at 20 °C. Bromide/mercury mole ratios (R) are, progressively: (i) 2.0(HgBr_2), (ii) 10, (iii) 25, (iv) 30, (v) 50, (vi) 60, (vii) 70, (viii) 100, (ix) 300, (x) 500, (xi) 1000, (xii) 5000, (xiii) 15000, (xiv) 30000(HgBr_4^2). Note that, compared with the iodide system, much greater R values are required to produce observable changes, and that there are no isosbestic points identifying two species equilibria (however, see text).

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 $HgBr_4^{2-}$ was formed. Complete conversion to $HgBr_4^{2-}$ occurred with $R = 20\,000$, and no other change in the spectrum was observed on further addition of bromide up to a maximum mole ratio of 60 000.

Calculation of the Spectrum of HgBr₃

The bromomercury(II) system has no isosbestic point to indicate when the equilibrium between HgBr₃⁻ and HgBr₄⁻⁻ occurs, and so the previous best approach for the iodo system could not here be used. A least-squares analysis of spectra of solutions at constant ionic strength did not give consistent results, and could not be used to determine the molar absorbance of HgBr₃⁻ at any wavelength. However, second- and fourth-derivative analyses of the spectra of solutions with 4 < R < 500 indicated a peak at around 252 nm, attributed to HgBr₃⁻ (fig. 7). The spectrum of HgBr₃⁻ was therefore calculated using a combination of the comparative absorbance and reference-point methods.

A comparative absorbance plot at 252 nm was made for a series of spectra, which yielded a molar absorbance value of 17300 ± 300 (fig. 8). This value was used as the reference point in the reference-point method to calculate the complete spectrum of HgBr₃⁻ from solutions having with 4 < R < 40. The calculated spectra were not significantly different from each other, and all had a peak at 253 nm ($\varepsilon = 17300 \pm 300$ dm³ mol⁻¹ cm⁻¹).

The validity of this calculated spectrum was tested in two ways. First, different reference points and R values were used. Spectra calculated using solutions with R > 100 gave a peak at 248 nm, showing the presence of HgBr₄²⁻ in the sample solutions; irregular molar absorbances also indicated this. Solutions of lower R values also yielded inconsistent results, for example, a reference point of 9000 dm³ mol⁻¹ cm⁻¹ at 233 nm for R = 4, 16 and 30 gave peak absorbances of 8000, 12 500 and 14 500 dm³ mol⁻¹ cm⁻¹, respectively.

The second test compared the variation caused by different assumed spectra of $HgBr_3^-$ on the calculation of formation constants. Spectra for $HgBr_3^-$ were calculated assuming molar absorbances at 252 nm of 12000, 14500, 17300, 20000, 22000 and 24000 dm³ mol⁻¹ cm⁻¹. Reliable formation constants were obtained only with the 17300 dm³ mol⁻¹ cm⁻¹ molar absorbance, as shown by the standard errors and correlation coefficient of the minimisation, and also consistency over a range of sample spectra at constant ionic



Fig. 8. Comparative absorbance plot, employing 15 different R values, for HgBr₂ in water at 20 °C with added bromide, using absorbance data at 252 nm in eqn (6). (a) corresponds to the equilibrium HgBr₂ + Br \Rightarrow HgBr₃⁻, and the value of the intercept, for α (HgBr₃⁻) at 252 nm, is required in order to calculate the complete spectrum of HgBr₃ by the reference-point method [intercept, α (HgBr₃⁻) = 17 300 \pm 300, from slope log $K_3 = 2.25 \pm 0.06$]. (b) corresponds to the equilibrium HgBr₃⁻ + Br⁻ = HgBr₄²⁻, and the value of α (HgBr₄²⁻) at 252 nm so determined is within experimental error of that measured for HgBr₄²⁻ in fig. 6 [intercept, α (HgBr₄²⁻) = 36 500 \pm 500, from slope log $K_4 = 1.87 \pm 0.02$].

strength. Similarly, calculated spectra with peak absorbances of 17 000 and 17 600 dm³ mol⁻¹ cm⁻¹ were within experimental error of the spectrum calculated using 17 300 dm³ mol⁻¹ cm⁻¹. It is therefore concluded that the spectrum of HgBr₃⁻ has a peak absorbance of 17 300 dm³ mol⁻¹ cm⁻¹ at 253 nm (fig. 9).

Although halide imbalance occurred, as in the iodide system, the excess bromide absorption was not significant above 210 nm, and the spectrum of $HgBr_3^-$ was not calculated using data recorded below 215 nm.

Reaction of Mercury(II) Chloride with added Chloride

The reaction between $HgCl_2$ and added Cl^- in water, monitored spectrophotometrically, is shown in fig. 10. The absorp-



Fig. 7. Second- and fourth-derivative curves of the spectra of aqueous $HgBr_2$ with added KBr at various R values, using 9 and 13 point convolutes. At intermediate R values a peak is indicated at around 252 nm, attributed to $HgBr_3^-$.



Fig. 9. Calculated electronic spectrum of $HgBr_3^-$ in water at 20 °C (a), compared with those of $HgBr_2$ (b) and $HgBr_4^{2-}$ (c). Since these spectra do not overlap the absence of isosbestic points under conditions when two species are present in varying concentrations (but with total mercury concentration constant) may now be understood.

tion maximum of HgCl₂ at 204 nm ($\varepsilon = 4000 \pm 50$ dm³ mol⁻¹ cm⁻¹) increased as HgCl₃⁻ formed, and a shoulder appeared at 230 nm. As *R* was increased from 2 to 200 this shoulder became a peak, which continued to increase in intensity until *R* was 4000. With further increase in *R* to 40 000 the peak grew further, but also shifted steadily to 228 nm, due to the formation of HgCl₄²⁻. It then remained stationary but continued to increase in height until complete conversion of all the mercury to HgCl₄²⁻ occurred at $R = 200\,000$. No further changes in the spectrum were observed for larger *R* values.

Calculation of the Spectrum of HgCl₃

No isosbestic points were observed for this system, and attempts to apply a least-squares analysis to the spectra recorded at constant ionic strength to obtain values of the molar absorbance of $HgCl_3^-$ at any wavelength were unsuc-



Fig. 10. UV absorption spectra changes obtained upon addition of chloride to aqueous $\text{HgCl}_2(2.9 \times 10^{-4} \text{ mol dm}^{-3})$ at 20 °C. Chloride/mercury mole ratios (*R*) are, progressively: (i) 2.0(HgCl₂), (ii) 50, (iii) 100, (iv) 200, (v) 300, (vi) 500, (vii) 600, (viii) 10000, (ix) 50000, (x) 400 000(HgCl₄²). Much higher *R* values are again required to produce observable changes. As with the bromide system, no isosbestic points are seen, or can be expected due to the shape of the HgCl₃ profile.



Fig. 11. Plot of formal molar absorbance at 233 nm as a function of concentration of added chloride for solutions of $HgCl_2 + Cl^-$ in water at 20 °C. Straight-line sections correspond to concentrations with two chloromercury species in equilibrium. Intercept of line (iii) gives $\epsilon(HgCl_3^-)$ at 233 nm as 22 000 \pm 300 dm³ mol⁻¹ cm⁻¹. (i) Formation of HgCl_3^- from HgCl_2, (ii) formation of HgCl_3^- and HgCl_4^- from HgCl_2 (three species in equilibrium), (iii) formation of HgCl_4^- from HgCl_3^-.

cessful. The peak at 230 nm was firmly attributed to HgCl₃⁻ upon inspection of the fourth-derivative curves of the spectra of a series of solutions. A comparative absorbance plot for 233 nm was prepared, but resulted in a curve from which the molar absorbance of HgCl₃⁻ at this wavelength could not be reliably derived. However, a plot of formal molar absorbance against added chloride concentration yielded a value of $22\,000 \pm 300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for the molar absorbance of HgCl₃⁻ at 233 nm (fig. 11). On using this value in the reference-point method the spectrum of HgCl₃⁻ was obtained over the whole wavelength range, giving a spectrum with a peak at 230 nm and $\varepsilon_{\text{max}} = 22\,400 \pm 300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

This method was used on several spectra containing only $HgCl_2$ and $HgCl_3^-$, and the resultant spectra all had peaks at 230 nm with maximum absorbance values of 22 300 \pm 600 dm³ mol⁻¹ cm⁻¹. This derived spectrum for $HgCl_3^-$ was thus less reliable than those calculated for HgI_3^- and $HgBr_3^-$. However, use of this spectrum in the calculation of formation constants gave reasonably consistent results, and the spectrum was therefore considered acceptable. The charge transfer to solvent spectrum of the chloride ion is well below 200 nm and therefore corrections for halide imbalance were not necessary.

Discussion

Having established, for the first time, the electronic absorption spectra of HgI_3^- , $HgBr_3^-$ and $HgCl_3^-$ in water, and noted that their profiles are not all similar, their structure in solution must be investigated. The only Raman study of aqueous systems is still the 1950s work of Delwaulle,^{33,34} and she was able to obtain only weak lines in the presence of the strong lines due to the tetrahedral tetrahalogeno species. Although we have now essentially defined more precisely the mercury(II)/halide mole ratio required for optimum concentration of HgX_3^- in aqueous media the basic equilibrium problem remains. We have therefore analysed the electronic transitions of HgX_3^- . We first resolved each spectrum into its composite bands, and then derived their structure using Walsh diagrams.³⁵

Analysis of the Spectra of the Trihalides

Our procedures have been described in detail elsewhere.¹⁵

The spectrum of HgI_3^- in water displays three main peaks, but its second- and fourth-derivative spectra show a fourth peak around 330 nm (fig. 12), and there must be a contribution from a band with a maximum in the far-ultraviolet, beyond our experimental range. The resolution of the $HgI_3^$ spectrum into Gaussian bands is shown in fig. 13.

The analysis of the spectrum of $HgBr_3^-$ showed two bands, one corresponding to the observed peak, and one at higher energy; a third band with maximum outside the measured range was again needed to fit the data (fig. 14).

The bands present in the spectrum of $HgCl_3^-$ corresponded to one main spectral peak and a second band at higher energy. No evidence for underlying peaks in the main band was found, and the contribution due to a third band at yet higher energies could be deduced from the spectra, but could not be computed with sufficient accuracy, and thus no estimate could be obtained for its peak maximum.

The parameters for the observed peaks and resolved bands are given in table 1.



Fig. 12. Second- (b) and inverted fourth-derivative (c) curves (17 and 19 point convolutes, respectively) of the spectrum of HgI_3^- (a), identifying its four component bands.



Fig. 13. Resolution of the spectrum of the calculated HgI_3^- spectrum in water at 20 °C into its component Gaussian bands. Upper difference plot (calculated HgI_3^- spectrum – sum of Gaussian bands) shows the excellence of the fit.



Fig. 14. Resolution of the spectrum of the calculated $HgBr_3^-$ spectrum in water at 20 °C into its component Gaussian bands. Upper difference plot (calculated $HgBr_3^-$ spectrum – sum of Gaussian bands) shows the excellence of the fit.

Interpretation of the Spectra of the Trihalides

The trihalogenomercurates may have a pyramidal or planar structure, corresponding to C_{3v} and D_{3h} symmetry, respectively. The order of the molecular orbitals, after Walsh,³⁵ is given in fig. 15 for MX₃ molecules, of structures from planar to pyramidal. The HgX₃⁻ species have 24 valence electrons, and these will fill the orbitals up to and including 1a₂. The $(1a_2)^2$ ground state for both planar and pyramidal molecules is ¹A₁.

In $C_{3_{v}}$ symmetry, the following electron excitations are allowed: $a_{1} \leftrightarrow a_{1}$, $a_{2} \leftrightarrow a_{2}$, $a_{2} \leftrightarrow e$, $e \leftrightarrow e$ and $e \leftrightarrow a_{1}$. In D_{3h} symmetry, there are allowed $a'_{1} \leftrightarrow a''_{2}$, $a'_{1} \leftrightarrow e'$, $a'_{2} \leftrightarrow a''_{1}$, $a'_{2} \leftrightarrow e'$, $a''_{1} \leftrightarrow e''$, $a''_{2} \leftrightarrow e''$, $e' \leftrightarrow e''$, $e' \leftrightarrow e'$ and $e'' \leftrightarrow e''$. The transitions relating to HgX₃⁻ are included in fig. 15(a). Excitation to the highest filled orbital is forbidden. Excitation to the $4a_{1}$ - $2a''_{2}$ orbital would favour a pyramidal excited state, whereas excitation to the $5a_{1}$ - $3a'_{1}$ orbital would favour a planar configuration.

Solvation of the mercury(II) halide increases from HgI_2 to $HgCl_2$, as the size of the halogen atom decreases. Addition of a halide ion to $[HgX_2(H_2O)_4]^\circ$ to form trigonal-bipyramidal $[HgX_3(H_2O)_2]^-$ will occur more readily for a strongly solvated HgX_2 molecule containing small halogen atoms than for a weakly solvated molecule with large halogen atoms. For large ligands and weak solvation, a more stable configuration would be pyramidal, with one solvent molecule occupying

Table 1. Absorption band parameters for HgX $_3$ in water at 20 °C

observed peaks		resolved bands				
Emax	 ٤ _m	E _{max}	ε _m	W	A	O.S.
			Hgl ₃			
34.36	12 420	30.00	2630	3.67	2.06	1.89
40.00	18853	34.32	12 200	6.10	15.9	6.87
46.95	23 7 50	40.00	16 700	3.86	13.7	5.92
		46.70	23 000	6.28	30.8	13.3
		53.42	25 000	5.87	31.3	13.5
			HgBr ₁			
39.53	17 420	39.20	16 500	5.25	18.5	7.99
		44.10	9000	5.25	10.1	4.36
		49.70	16 500	5.25	18.5	7.99
			HgCl			
43.48	22 3 50	42.80	17 000	4.03	14.6	6.30
		46.20	12 000	6.28	16.1	6.95

 $E_{\text{max}} = \text{peak}$ maximum (10³ cm⁻¹); $e_{\text{m}} = \text{molar}$ absorbance (dm³ mol⁻¹ cm⁻¹); W = band width at half-height (10³ cm⁻¹); A = band area (dm³ mol⁻¹ cm⁻¹ × 10⁻⁴); O.S. = oscillator strength.



Fig. 15. (a) Walsh diagram for AB₃ molecules with D_{3b} and C_{3v} symmetry, (b) spin-forbidden transition made partially allowed (see text),

the fourth tetrahedral position. Thus HgI_3^- is expected to be pyramidal and $HgCI_3^-$ planar; however, a bond angle in HgI_3^- of 90°, the extreme case of C_{3v} in fig. 15(*a*), is unlikely; an angle nearer the tetrahedral angle is expected. The structure of $HgBr_3^-$ will become clearer once band assignments have been made.

Band Assignments

Of the five transitions in the band structure of HgI₃⁻, those at 34 300, 40 000 and 46 700 cm⁻¹ are assigned to the electron excitations to the 4a₁, orbital from the 4e, 3e and 3a₁ orbitals, respectively. The lowest excitation, $4e \rightarrow 4a_1$, corresponds to the transition ${}^{1}A_{1} \rightarrow {}^{1}E$. The corresponding spin-forbidden transition, ${}^{1}A_{1} \rightarrow {}^{3}E$, of this configuration is made partially allowed by the mixing of the ${}^{3}E$ and ${}^{1}E$ states *via* spin-orbit coupling, and gives a small low-energy peak at 30 000 cm⁻¹, as indicated in fig. 15(b). The high-energy band at 53 400 cm⁻¹ is probably due to excitation from the 4e orbital to 5a₁.

An alternative explanation for the HgI₃⁻ spectrum is theoretically possible. Excitation of an electron from the 4e orbital to the 4a₁ orbital (for C_{3v}) gives rise to the transition ${}^{1}A_{1} \rightarrow {}^{1}E$, a spin-allowed transition. Spin-orbit coupling causes this ${}^{1}E$ state to mix with the ${}^{3}E$ state of the same configuration, which leads to splitting of ${}^{3}E$ into A_{1} , A_{2} and two E states. For a small spin-orbit coupling (as in HgBr₃⁻) only two transitions could be seen, but for large coupling (as expected for HgI₃⁻) spin-forbidden transitions to E, E and A_{1} would lead to three bands in addition to the spin-allowed transition to ${}^{1}E$ (fig. 16).

However, such an explanation requires that the three lowenergy bands are spin-forbidden and of low intensity. Transitions to the two E states would also lead to similar intensities for the two lowest-energy bands. This is not observed, since the lowest band, at $30\,000 \text{ cm}^{-1}$, has a molar absorbance of $2630 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ while the second band at $34\,320 \text{ cm}^{-1}$ has a much higher molar absorbance of $12\,200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The band at $30\,000 \text{ cm}^{-1}$ is thus here considered to be spin-forbidden, and the other an allowed transition, and the former explanation is therefore preferred.

The spectrum of $HgCl_3^-$ is very different from that of HgL_3^- and has none of its complexities. The band structure is best

explained in terms of a planar structure with D_{3h} symmetry. The excitation $1e'' \rightarrow 2a''_2$, corresponding to $4e \rightarrow 4a_1$ in C_{3v} symmetry, is allowed and explains the observed intense band; this is the ${}^{1}A'_{1} \rightarrow {}^{1}E'$ transition. Spin-orbit coupling of the ${}^{3}E'$ state with ${}^{1}E'$ is not expected to occur. The two other excitations, to $2a''_2$ from 3e' and $1a''_2$ (corresponding to those from 3e and $3a_1$ to $4a_1$ in HgI₃), are forbidden in D_{3h} symmetry and are not observed. The additional band noted at high energies is probably due to the transition $3e' \rightarrow 3a'_1$ (${}^{1}A_1 \rightarrow {}^{1}E'$). It is much wider than the main band, and this is expected for excitation to a higher antibonding orbital.

The spectrum of HgBr₃⁻ in water appears initially to resemble that of HgCl₃⁻ (fig. 9 and 10), but on consideration of the resolved bands (table 1) we find that the data are adequately explained by assuming a pyramidal structure with C_{3v} symmetry. The resolved structure of the HgBr₃⁻ spectrum consists of three bands: similar studies on HgBr₃⁻ in methanol³⁶ have revealed an additional low-intensity band at 35 000 cm⁻¹. These bands are here identified, as in HgI₃⁻, as excitation from the 4e, 3e and 3a₁ orbitals to the 4a₁ orbital. The first main transition is thus ${}^{1}A_{1} \rightarrow {}^{1}E$. The band not resolved in the aqueous spectrum of HgBr₃⁻ arises from the spin-orbit coupling of the ${}^{1}E$ state and the ${}^{3}E$ state of the (4e)³(4a₁)¹ excited state.

Sandström and Johansson³⁶ have reported X-ray diffraction studies for concentrated aqueous solutions of HgBr₃ and HgI₃, which indicated pyramidal structures, probably



Fig. 16. Effect of the magnitude of spin-orbit coupling on spinforbidden transitions. Full lines, allowed transitions; dashed lines, forbidden transitions. (a) No spin-orbit coupling, (b) small spin-orbit coupling, (c) large spin-orbit coupling.

with one coordinated water molecule. While this conveniently supports our interpretation of our spectra of these species we would point out that the concentrations they used were much in excess of ours and, since they used R < 4, our fig. 4 shows that less than half of the mercury(II) species in solution would be in the form HgI_3^- , and fig. 6 and 9 show that the concentration of $HgBr_3^-$ would be negligible (with [Hg] $\approx 10^{-4}$ mol dm⁻³). A study of the chloro species in aqueous solution would be instructive; however, Sandström³⁷ has examined dimethyl sulphoxide solutions by X-ray diffraction, which indicated a planar structure for HgCl₃, probably with two interacting DMSO solvent molecules giving overall trigonal-bipyramidal coordination.

Waters et al.¹⁰ have noted an interesting feature of $HgCl_3^$ and $HgBr_3$ in amide solvents, that of the presence of two configurational isomers, one of D_{3h} symmetry (considered unsolvated) and the other possessing essentially C_{3v} symmetry (having one coordinated solvent molecule). The Raman spectra also show that at R = 3 only the tri-species is present. The two isomers were in equilibrium, and their Raman spectra showed an isosbestic point as the temperature was changed. In this case a study of HgI_3^- would be salutary, as would further work by us to expand the table of the resolved band parameters as a function of temperature, to see if this phenomenon persists in aqueous solution; X-ray diffraction studies probably do not have sufficient precision to follow this equilibrium. We note, however, that our results for HgBr₃⁻ may indicate both D_{3h} and C_{3h} symmetry in water; we based our proposal for the latter symmetry on the additional resolved band in the HgBr₃ spectrum in methanol which we did not clearly resolve in water, but, contrariwise, the resolved-band half-widths and oscillator strengths in table 1 do not show a consistent trend.

We therefore conclude that, in aqueous solution, HgI_3^- and $HgBr_3^-$ are essentially tetrahedral species, with one water molecule coordinated to mercury. For HgCl₃, the four atoms are largely coplanar and two water molecules are additionally coordinated, one above and one below the plane, producing essentially a trigonal-bipyramidal species.

In more general terms we stress that the applicability of the various methods we have described for calculating the spectra of 'hidden' species must not be judged on their effectiveness within this study; in other systems a method we could not usefully use here may yield the most accurate results. Further, with many modern spectrophotometers displaying data on interactive VDU screens other calculation methods can become viable. For example, the data we display in fig. 7 could be displayed directly on a screen instead of, in our case, being the result of a composite of many charts produced overnight in the Computing Centre. In addition, multiple applications of the approach in fig. 8 could provide the spectra of $HgBr_3^-$, and other species. In fig. 8 the data were obtained manually from the absorbance at 252 nm of 15 different spectra, manipulated, plotted, and the two least-squares fits calculated for appropriate data. This could be automated and performed progressively at all recorded wavelengths, and the extrapolated molar absorbances plotted to yield the required spectrum. Also the formation constants simultaneously obtained could be plotted as a function of wavelength, and constancy (or otherwise) with wavelength would provide an important check on the validity of this approach to the system under study. For two-line plots as in fig. 8 it would still be necessary to examine each plot on the VDU to decide which data sets are to be combined in a straight-line fit, but this would not be tedious.

We further point out that the main merit of this approach is that it produces spectra, from which thermodynamic³⁸ and other parameters can be derived, often with better precision

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than previously. For example, good, statistically averaged formation constants can be obtained as a function of ionic strength.¹⁴ Such constants have previously been obtained by a variety of techniques, including electrochemistry and spectroscopy, but generally at some fixed ionic strength. The former technique often assumes the nature and identity of the species in solution, and the latter uses data at one or more wavelengths considered optimal. It is not surprising that the formation constants thereby derived are at times dissimilar. Belevantsev and Shoovayev¹⁷ have claimed a 'large disagreement' between their data and ours for the formation of HgXY in aqueous media, but their data were obtained from absorbance changes at a fixed wavelength; we used spectra, and our computer programs gave very acceptable residual and regression sums of squares, F ratios, multiple correlation coefficients, and degrees of freedom of the F ratio.15 We are therefore confident that our continuing approach for the spectra of HgX_3^- has again provided accurate data, and the resolved band data and oscillator strengths given in table 1 are reliable.

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