The Electronic Spectra of the Mixed Mercury Dihalides. Part 2.† Identification, Equilibrium and Formation Constants, and Assignment of Transitions

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The electronic absorption spectra of HgXY (HgClI, HgBrI, and HgBrCl) in water at 20 °C are calculated over the complete wavelength range, and shown not to be the mean of those of $HgX_2 + HgY_2$. For the reaction $HgX_2 + HgY_2 \rightleftharpoons 2HgXY$ the spectra have been derived by two different techniques, which give the same profile. Equilibrium constants (log K), independent of added $Na[ClO_4]$, are: HgClI, 1.40 ± 0.15; HgBrI, 1.26 ± 0.10; HgBrCl, 0.70 ± 0.10. The reaction is exothermic. The replacement reaction $HgX_2 + Y^- \longrightarrow HgXY + X^-$ has not previously been studied spectroscopically to obtain the formation constants (log K), which are 0.98 ± 0.05, 0.52 ±0.09, and 0.23 ± 0.09, respectively. Accurate molar absorption coefficients could not be computed, but the spectral profiles are identical with the other results. The formation constants have been obtained by a new graphical method. The three independent methods have shown earlier incomplete spectra to be unreliable. Further, all the equilibrium and formation constants reported are the most accurate to date. The resolved spectral bands are discussed and assigned. The absence of the expected allowed transition $^1\Sigma^+ \rightarrow {}^1\Sigma^+(X)$ is explained as due to the proximity of $^1\Sigma^+(X)$ and $^1\Delta(Y)$ interacting by spin–orbit coupling to produce the representation $^1\Delta$, to which transitions are forbidden.

THE reaction in solution between two dissimilar dihalides of mercury(II) to form uncharged mixed halide species has been investigated by various workers [1–3] and their findings outlined in Part 1.[4] In this paper the identification of the spectra of the mixed mercury dihalides is established, and their formation constants computed, by the methods given previously.[4] Upon resolving the authenticated spectra into their component bands it is then possible to identify and assign the various transitions.

RESULTS AND DISCUSSION

Reaction between Neutral Mercury(II) *Dihalides in Water.—Experimental observations.* The spectra of a series of solutions containing various proportions of two mercury(II) dihalides, but constant total mercury concentration, were recorded at 20 °C and are shown in Figure 1. Isosbestic points were not observed at those wavelengths at which HgI_2 and $HgBr_2$, and $HgCl_2$ and $HgBr_2$, have the same molar absorbances, indicating that more than two species were present in solution. The reaction was complete because the spectra were not time-dependent.

Evidence for mixed-halide formation at wavelengths where spectra overlapped was obtained by assuming that no reaction had occurred, and that only HgX_2 and HgY_2 were present. For each solution the theoretical absorbance at all measured wavelengths was calculated and compared with the observed absorbances at the same wavelengths. The differences between the two were calculated and plotted using a computer program and the results are shown in Figure 2. It was previously shown [4] that the difference between the calculated and observed absorbance is zero when $\varepsilon(HgXY) = [\varepsilon(HgX_2) + \varepsilon(HgY_2)]/2$. The wavelengths at which this occurred, together with those derived from the diagrams in ref. 3, are given in Table 1. These difference plots now demonstrate conclusively the presence of the mixed halides and that HgXY spectra are not the average of those of the two constituent species.

TABLE 1

Wavelengths (nm) at which $\varepsilon(HgXY) = [\varepsilon(HgX_2) + \varepsilon(HgY_2)]/2$ in water at 20 °C

System	This work	Spiro and Hume [3]
$HgI_2 + HgBr_2$	190	
	208	210
	232	229
	248	247
$HgI_2 + HgCl_2$	202	202
	232	225
		238
$HgBr_2 + HgCl_2$	208	212

Calculation of spectra of mixed mercury dihalides. The spectra of the mixed dihalides were derived using the three methods given in Part 1.[4] First, for each mixed dihalide system, the displaced–equilibrium method was applied to a solution containing an excess of added HgY_2. For the $HgI_2 + HgCl_2$ system it was possible to observe directly when complete conversion of HgI_2 into HgClI had occurred by monitoring at 264 nm, where $HgCl_2$ does not absorb (Figure 1), and hence know which spectra to use in this calculation.

For the $HgI_2 + HgBr_2$ and $HgCl_2 + HgBr_2$ systems, however, no suitable wavelength was available. The mixed-dihalide spectra were thus calculated for a series of solutions containing various ratios of HgX_2 to added Y^-. The resulting calculated spectra for HgXY varied with increasing $[Y^-]$ until all the minor species were converted into the mixed dihalide, after which the spectra of the latter remained constant within experimental error. The spectra of HgBrI and HgBrCl so calculated were smoothed by a 15-point convolution and are shown, with HgClI, in Figure 3, along with the very limited and less precise spectra calculated by Spiro and Hume,[3] taken from the diagrams in their paper.

Secondly, the reference-point method (*a*) [4] was applied

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† Part 1 is the preceding paper (ref. 4).

to spectra of solutions containing neutral dihalides at equimolar concentrations, using the wavelengths at which $\varepsilon(HgXY) = [\varepsilon(HgX_2)]/2$, *i.e.* $\Delta\varepsilon = 0$, as reference points. However, the observed absorbances at these wavelengths could not be precisely determined because they were associated with steeply rising bands on one or both of the dihalide species. The use of $\Delta\varepsilon = 0$ reference points was therefore restricted to confirmatory evidence for previously calculated mixed-halide spectra, with which they agreed within experimental error.

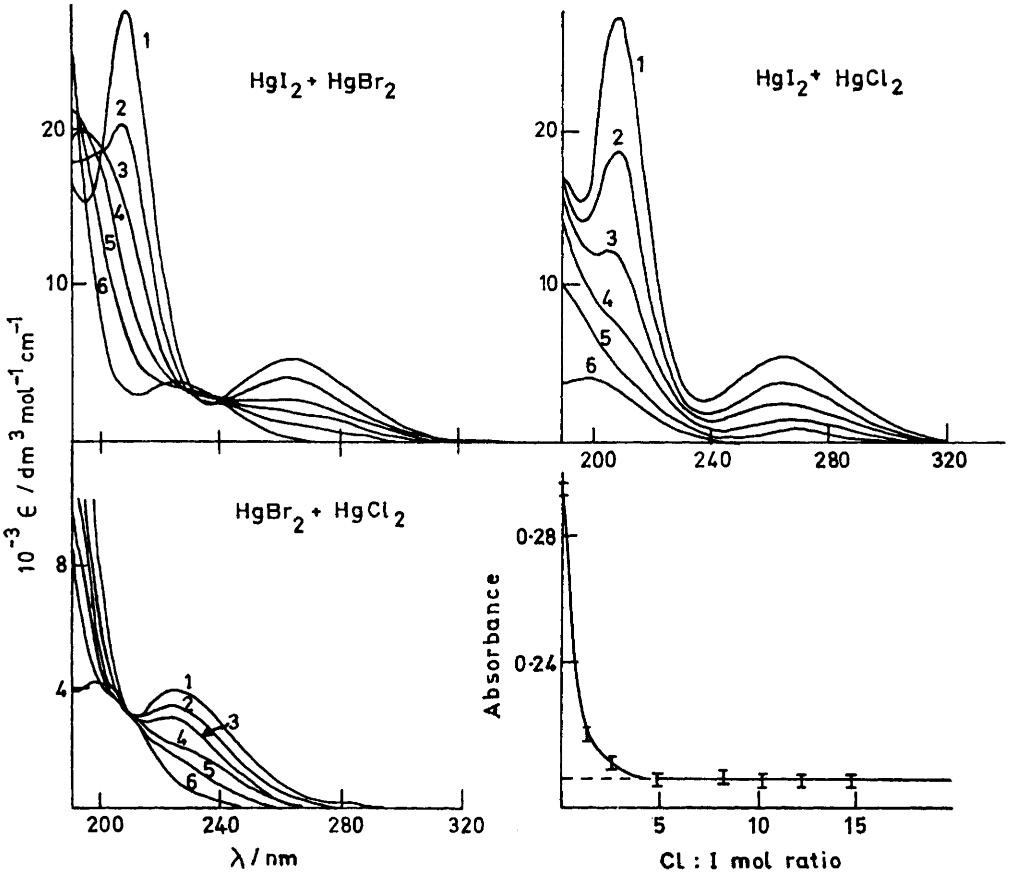

FIGURE 1 Spectra of aqueous solutions of $HgX_2 + HgY_2$ in varying proportions at 20 °C. Total mercury concentration constant at 8.0×10^{-5} mol dm^{-3}. Spectra: (1) and (6), HgX_2 and HgY_2, respectively; (2)—(5), X : Y mol ratios 4, 1.5, 0.67, and 0.25 : 1. Insert, plot of absorbance at 264 nm against Cl : I mol ratio for 5.0×10^{-5} mol dm^{-3} HgI_2 on addition of $HgCl_2$

The third method, reference-point method (*b*),[4] utilised the replacement of a less electronegative halogen in HgX_2 by a more electronegative one. The spectra calculated by this method agreed with those calculated by the other methods.

*Calculation of equilibrium and formation constants.** The spectra of aqueous solutions containing two dissimilar mercury(II) dihalides in mol ratios from 4 : 1 to 1 : 4 were recorded at 20 °C. The total concentration of mercury was maintained close to 10^{-5} mol dm^{-3}. Using the previously determined spectrum of HgXY, and the standard spectra of HgX_2 and HgY_2, the concentrations of the individual species in solutions were calculated[4] and the equilibrium constant of HgXY for each solution was computed, and the mean value found. Data points at 1 nm intervals were used over the range 200—300 nm for HgBrI and HgClI, and 200—260 nm for HgBrCl. The constants obtained are given in Table 2, together with other published data.

(*i*) *Effect of ionic strength.* The spectra of solutions of equimolar concentrations of $HgBr_2$ and HgI_2 in water and in solutions containing $Na[ClO_4]$ at concentrations 0.2, 0.4, 0.5, 0.8, and 1.0 mol dm^{-3} were recorded. Similar measurements were also made for $HgI_2 + HgCl_2$, and $HgCl_2 + HgBr_2$ solutions. In all cases no changes in the spectra were observed. The spectral profile of, for example, the $HgI_2 + HgCl_2$ mixture in water alone was exactly superimposed on that recorded in 0.5 mol dm^{-3} $Na[ClO_4]$. A series of solutions containing HgI_2 and $HgBr_2$ were prepared in 0.5 mol dm^{-3} $Na[ClO_4]$ and from their spectra the equilibrium constant of HgBrI calculated. The mean value obtained for K was 18.6 ± 3.2, in good agreement with that for HgBrI in water alone, 18.0 ± 1.5.

(*ii*) *Precision of the data.* The accuracy of the cal-

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* Equilibrium constants refer to the equilibrium between HgX_2 and HgY_2, and formation constants to the reaction between HgX_2 and Y^-. Activities are not known in this case, but the dilute solutions used support activity coefficients of unity and hence these stoicheiometric constants are essentially equivalent to thermodynamic constants.

TABLE 2

Constants (log K) for the mixed mercury dihalides in water at 20 °C

Species	This work	Marcus [a]	Spiro and Hume [b]
(a) Equilibrium constants for the equimolar reaction $HgX_2 + HgY_2 \rightleftharpoons 2HgXY$			
HgClI	1.40 ± 0.15	1.75 ± 0.20	1.35 ± 0.17
HgBrI	1.26 ± 0.10 [c]	1.10 ± 0.20	1.07 ± 0.08
HgBrCl	0.70 ± 0.10	2.0 ± 0.5	1.14 ± 0.11
		1.20 ± 0.05 [d]	
(b) Formation constants for the reaction $HgX_2 + Y^- \longrightarrow HgXY + X^-$			
HgClI	0.98 ± 0.05		5.772 ± 0.009 [e]
HgBrI	0.52 ± 0.09	4.01 ± 0.04	
HgBrCl	0.23 ± 0.09		

[a] Ref. 1; 0.49 mol dm^{-3} Na[ClO$_4$] + 0.01 mol dm^{-3} HClO$_4$ at 25 °C. [b] Ref. 3; 0.001 mol dm^{-3} HClO$_4$ at 25 °C. [c] Same value obtained in 0.5 mol dm^{-3} Na[ClO$_4$]. [d] As corrected by Eliezer.[5] [e] Work of Belevantsev *et al.*[6]

culated K values depended on the accuracy of the recorded and calculated spectra. The error limits in Table 2 are therefore estimates by the authors, allowing for variations in the spectra, and not standard deviations. The standard deviations calculated from the scatter of the calculated K values within a given set of results were considerably less.

(*iii*) *Effect of temperature.* A qualitative study of the effect of temperature on the reaction between mercury dihalides was performed. The spectra of solutions, equimolar in HgX_2 and HgY_2, were recorded at 20 and 50 °C. Comparison of these spectra with those showing the effect of temperature on the dihalides alone indicated that, as the temperature rose, the equilibrium was displaced away from HgXY, *i.e.* the reaction $HgX_2 + HgY_2 \rightleftharpoons HgXY$ is exothermic.

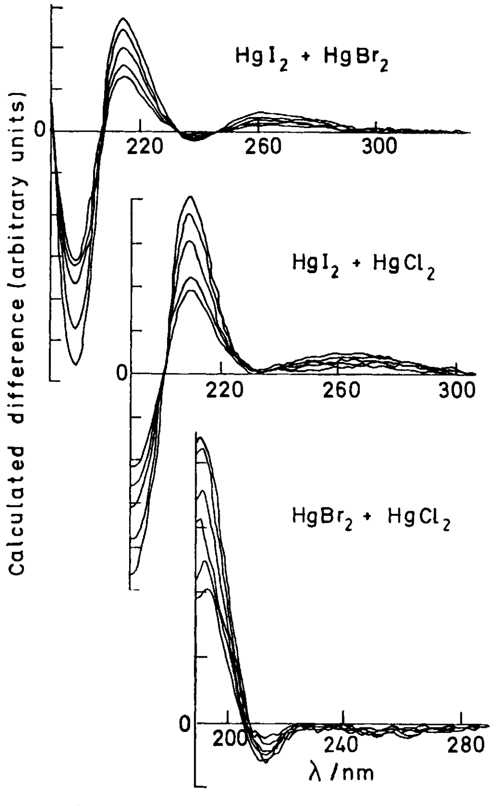

FIGURE 2 Calculated differences between observed and theoretical spectra for mixtures of the mercury(II) halides in water at 20 °C

(*iv*) *Comparison with other data.* We consider first the equilibrium constants calculated for the reaction of two neutral dihalides. Table 2 shows the large errors in all the equilibrium constants reported, and the poor agreement between the results obtained. Spiro and Hume[3] used spectra which this work (Figure 3) now shows to be incomplete and inaccurate, and thus their reported error limits, and hence their values, particularly for HgBrI and HgBrCl, must be considered unrealistic. Further, their reported molar absorbance values and those displayed in their spectra were often very different. The results of Marcus[1] were obtained by a solvent-distribution technique to measure the concentrations of species. Preferential distribution of one or more of the species would cause the equilibrium to be displaced, and hence to yield different results from those obtained by the method used here. His value for HgBrI (2.0 ± 0.5) has subsequently been corrected to 1.2 ± 0.5 by Eliezer,[5] although no reason was given. Spiro and Hume[3] pro-

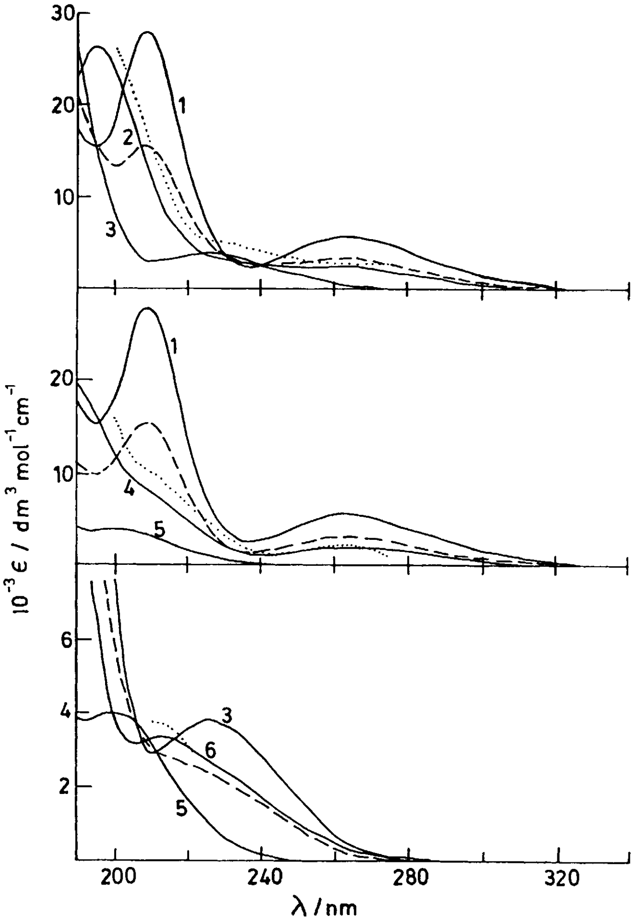

FIGURE 3 Spectra of the dihalides and mixed halides of mercury in water at 20 °C. Species: (1) HgI$_2$, (2) HgBrI, (3) HgBr$_2$, (4) HgClI, (5) HgCl$_2$, (6) HgBrCl. (— — — —), Median line of the dihalides; (· · · ·), mixed-halide spectra from ref. 3

pose that equilibrium constants in 0.5 mol dm^{-3} Na[ClO$_4$] solutions are increased by 0.11 log units owing to the effect of ionic strength on the activity coefficients of HgX_2 and HgY_2. We found no increase, but they assumed [3] the activity of HgXY did not change. Should all activities change then log K could only be constant if $\gamma(HgXY)^2 \sim \gamma(HgX_2)\cdot\gamma(HgY_2)$.

Replacement Reactions between HgX_2 *and* Y^- *in Water.*—*Experimental observations.* The replacement of chlorine in $HgCl_2$ by Br^- and I^-, and of bromine in $HgBr_2$ by I^-, has not previously been studied spectroscopically. Spectra, in water at 20 °C, were recorded against a reference containing the same quantity of added alkali-metal halide as the sample solution, Figure 4, maintaining $R < 2$ (R = mol ratio Y : Hg), to eliminate the possibility of addition reactions.

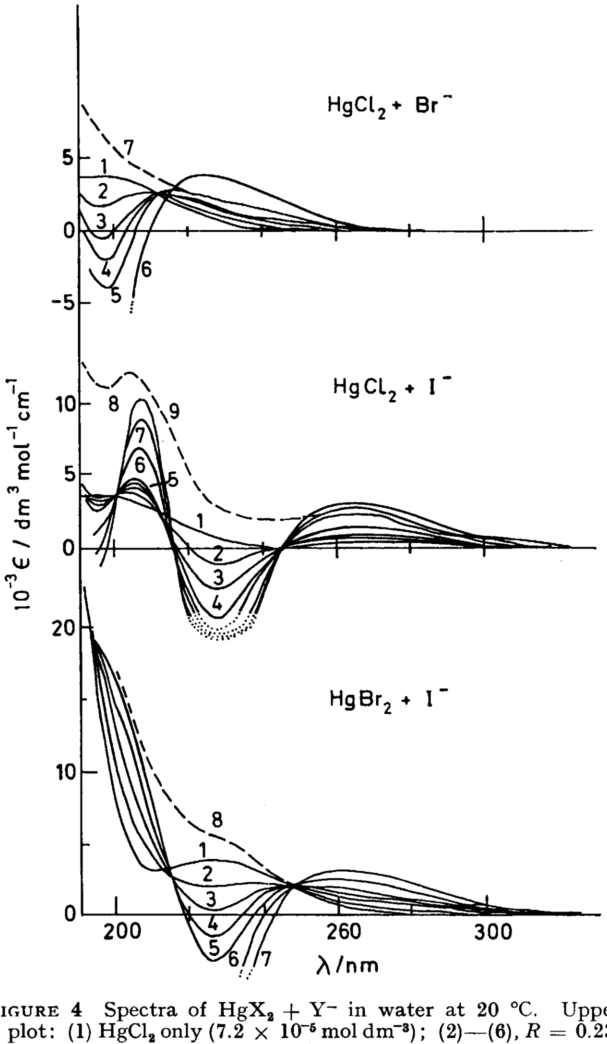

FIGURE 4 Spectra of $HgX_2 + Y^-$ in water at 20 °C. Upper plot: (1) $HgCl_2$ only (7.2 × 10^{-5} mol dm^{-3}); (2)—(6), R = 0.23, 0.5, 0.7, 1.0, and 2.3 : 1 respectively; (7), R = 1.0 : 1, but with only water in the reference cell. Middle plot: (1) $HgCl_2$ only (7.2 × 10^{-5} mol dm^{-3}); (2)—(8), R = 0.17, 0.34, 0.5, 0.61, 0.67, 1.22, and 1.35 : 1 respectively; (9), R = 1.22 : 1, but with only water in the reference cell. Lower plot: (1) $HgBr_2$ only (8.8 × 10^{-5} mol dm^{-3}); (2)—(7), R = 0.14, 0.28, 0.41, 0.55, 0.82, and 1.1 : 1 respectively; (8), R = 0.41 : 1, but with only water in the reference cell

The minimum at 225 nm arising when I^- is present is due to free iodide, which has a maximum at this wavelength, being in excess in the reference cell, a consequence of the iodide in the sample cell reacting to form HgXI. The displaced Cl^- or Br^- in the sample cell caused an absorbance imbalance at lower wavelengths.

A comparison between spectra recorded against water and against alkali-metal halide solution showed that, at wavelengths greater than 220 nm for $HgCl_2 + Br^-$, and 260 nm for $HgBr_2$ or $HgCl_2 + I^-$, no imbalance occurred (Figure 4).

Reaction sequence. The reaction sequence $HgX_2 \longrightarrow HgXY \longrightarrow HgY_2$ was monitored by plotting the absorbance at a given wavelength against the added halide concentration. Sample plots are given in Figure 5.

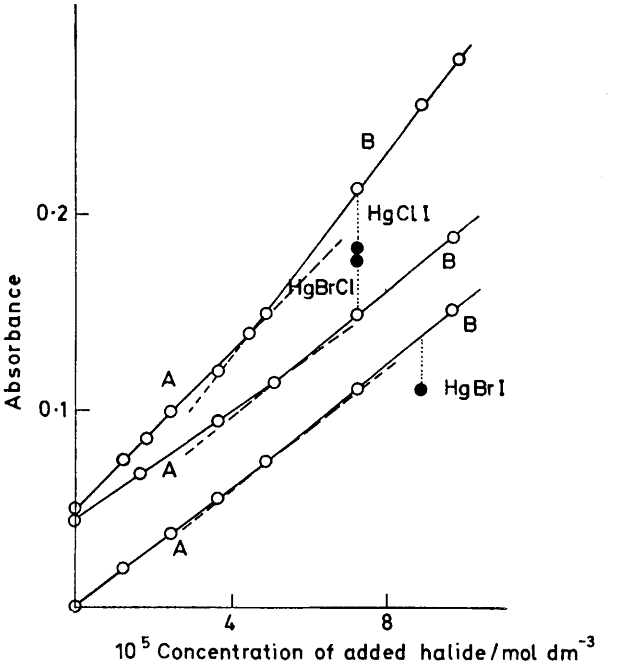

FIGURE 5 Plot to identify the appearance of HgY_2 in the reaction sequence $HgX_2 \longrightarrow HgXY \longrightarrow HgY_2$ on addition of Y^-. Lines: A, formation of HgXY; B, formation of HgY_2. Upper plot, $HgCl_2 + I^-$ at 265 nm (displaced by +0.05 absorbance unit for clarity); middle plot, $HgCl_2 + Br^-$ at 230 nm; lower plot, $HgBr_2 + I^-$ at 285 nm. Full circles, calculated values for the mixed halides at Y^- : Hg mol ratios of unity, demonstrating incomplete conversion into exclusively HgXY

For each system, two intersecting straight lines are apparent, corresponding to the successive formation of HgXY (line A) and HgY_2 (line B). The relative increase in absorbance on forming HgY_2 resulted from its molar absorbance being greater than that of HgXY at the wavelengths chosen.

The point of intersection of the two lines for the $HgCl_2 + I^-$ system occurred at [I^-] = *ca.* 4.8 × 10^{-5} mol dm^{-3} and when [Hg] = 7.22 × 10^{-5} mol dm^{-3}. Thus the formation of HgClI is not quantitative before formation of HgI_2 occurs. Figure 5 also includes the appropriate data from the calculated HgXY spectra, from the preceding section, which shows this phenomenon is characteristic of the formation of all mixed mercury dihalides by this route.

Calculation of the spectra of HgXY. The reference-point method (*b*)[4] was used to obtain the spectra of HgXY. In the region where free halide ions do not absorb, the calculated spectra were found to agree with those calculated for the interaction between the neutral dihalides, previous section (Figure 3).

Calculation of formation constants of HgXY *and* HgY_2. (*i*) *Computer method.* From the known spectra of the HgX_2, HgXY, and HgY_2 species it is possible, in principle, to calculate the concentrations of the individual species in a solution containing only these species, and hence the formation constants of HgXY and HgY_2, using the computer program described in the preceding paper.[4] However, inconsistent and inaccurate results were obtained using this method, due to the small number of data points available as a result of halide imbalance, which gave mercury species concentrations of low accuracy, and also due to the errors in the calculated free-halide concentrations which were derived from the calculated concentrations of the mercury species. A graphical method was therefore adopted.

(*ii*) *Graphical method.* For the reaction $HgX_2 + Y^- \rightleftharpoons HgXY + X^-$, the formation constant (*K*) is given by $K = [HgXY][X^-]/[HgX_2][Y^-]$. Since $[HgXY] = [X^-]$, the total mercury concentration $c_T = [HgX_2] + [HgY_2]$ and the total added halide concentration $c_L = [HgXY] + [Y^-]$, then the absorbance at all wavelengths where only HgX_2 and HgXY absorb is given by $D = \varepsilon_a[HgX_2] + \varepsilon_b[HgXY]$, where ε_a and ε_b are the molar absorbance of HgX_2 and HgY_2 respectively. It can be shown that $K = [HgXY]^2/(c_T - [HgXY])(c_L - [HgXY])$ and $D = \varepsilon_b[HgXY] + \varepsilon_a(c_T - [HgXY])$. Combining these equations and rearranging we obtain (1). This is of the form $y = mx + c$, and thus a

$$(c_L + c_T)(D - c_T\varepsilon_a)/c_L = \frac{[1 - (1/K)](D - c_T\varepsilon_a)^2}{c_L(\varepsilon_b - \varepsilon_a)} + c_T(\varepsilon_b - \varepsilon_a) \quad (1)$$

plot of the left-hand side against $(D - c_T\varepsilon_a)^2/c_L(\varepsilon_b - \varepsilon_a)$ should be linear, with slope $[1 - (1/K)]$, from which *K* may be evaluated, for a system described by equation (1). Plots for the systems $HgCl_2 + I^-$, $HgCl_2 + Br^-$, and $HgBr_2 + I^-$ are given in Figure 6, and the derived formation constants are included in Table 2.

(*iii*) *Consideration of other published data.* The present formation constants are several orders of magnitude different from those reported elsewhere. Here the mercury concentration was approximately that of the added halide ions (Y^-), and no excess of halide (X^-) was present. Marcus,[1] investigating HgBrI, used a medium containing 0.5 mol dm^{-3} perchlorate and halide and an excess of Br^- up to 10^4 times that of I^-. Similarly, Belevantsev *et al.*,[6] investigating HgClI, used a 50-fold excess of Cl^- in the form of HCl, plus some HNO_3. Spectral data[7] for systems with halide ion in large excess show the presence of $[HgX_2Y]^-$ and $[HgX_2Y_2]^{2-}$, and thus the previous formation constants are incorrect.

Interpretation of the Resolved Spectra.—We now discuss the band structure in terms of electronic energy levels and simple molecular-orbital (m.o.) theory.

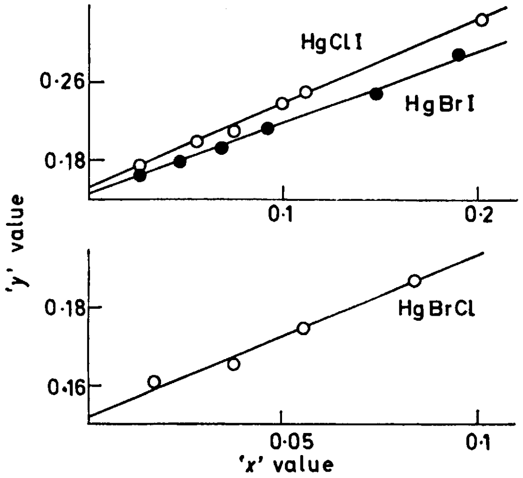

FIGURE 6 Comparative absorbance plots for deriving the formation constant *K* for HgXY from equation (1)

The dihalides have been shown to be linear in solution with $D_{\infty h}$ symmetry,[8] and we therefore consider the mixed mercury dihalides are also linear, and with $C_{\infty v}$ symmetry. The m.o. scheme (Figure 7) is similar to that for HgX_2 molecules[8] except that the *s* and *p* orbitals of the ligands are no longer the same and the resulting π orbitals are thus not degenerate. The

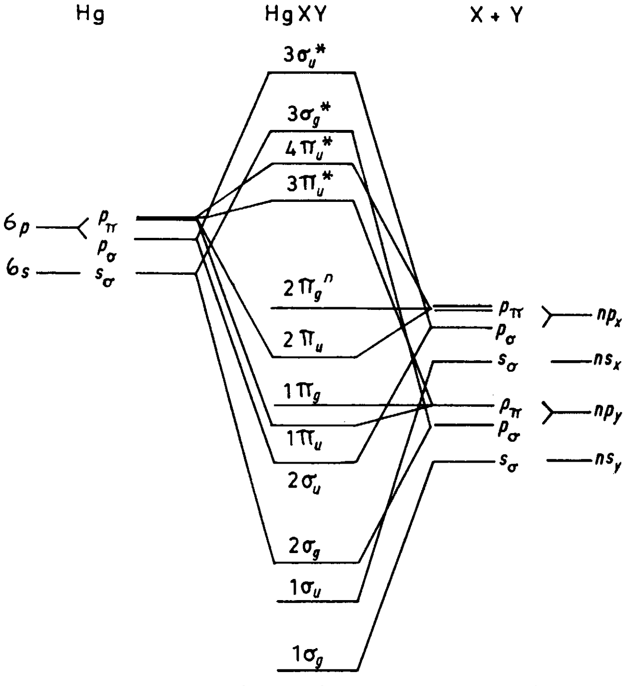

FIGURE 7 Correlation diagram for the orbitals of HgXY molecules with $C_{\infty v}$ symmetry. Superscripts: *, antibonding; *n*, non-bonding orbitals

introduction of the Y atom causes the degeneracy of the π orbitals to be lifted. The non-bonding orbital ($2\pi_g$) and the first antibonding orbital ($3\pi_u$) are of the same energy as in HgX_2 (corresponding to $1\pi_g$ and $2\pi_u$ in HgX_2, respectively).

The ground-state configuration is . . . $(2\pi_u)^2(2\pi_g)^2$, giving a $^1\Sigma^+$ term, and the first excited state . . . $(2\pi_u)^2(2\pi_g)^1(3\pi_u)^1$, giving the excited terms $^1\Sigma^+$, $^1\Sigma^-$, and $^1\Delta$ (neglecting multiplicity changes). In contrast with HgX_2, the transition to $^1\Sigma^+$ is allowed and expected to be intense. Transitions to $^1\Sigma^-$ and $^1\Delta$ are forbidden, but, as in HgX_2, transitions to $^1\Delta$ are considered to occur.[8] Promotion to the second antibonding orbital, giving the configuration . . . $(2\pi_u)^2(2\pi_g)^1(4\pi_u)^1$, can also occur, yielding the same terms and transitions. The splitting of the $2\pi_u$ orbital of HgX_2 to the $3\pi_u$ and $4\pi_u$ orbitals in HgXY will determine the order of the excited states, as shown schematically in Figure 8.

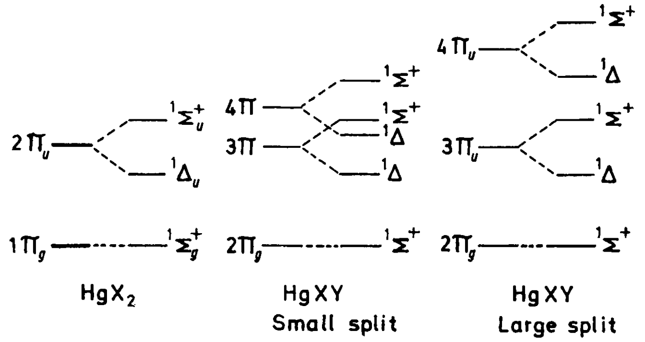

FIGURE 8 Splitting of the $2\pi_u$ orbital of HgX_2 on replacement of one X by Y

Since the $1\pi_g - 2\pi_u$ energy difference in HgX_2 increases from HgI_2 to $HgCl_2$,[8] this difference is sufficient in water for $HgCl_2$ to make the $^1\Delta_u$ transition (at 50×10^3 cm^{-1}) of greater energy than the $^1\Sigma^+{}_u$ transition of HgI_2 (48×10^3 cm^{-1}). This is shown schematically in Figure 9.

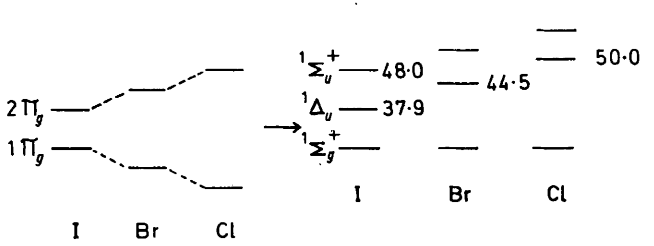

FIGURE 9 Separation of the $1\pi_g$ and $2\pi_u$ energy levels in HgX_2 and the observed transitions in HgX_2 spectra

However, in HgXY molecules the $2\pi_g$ orbital (corresponding to $1\pi_g$ in HgX_2) does not change in energy from, for example, HgBrI to HgClI; the non-bonding level corresponds to the p_π orbital of the least electronegative halogen atom. The order of states thus deduced for the mixed neutral species in water is given in Figure 7, together with the band analysis from Part 1.[4]

The two low-energy transitions in HgBrI and HgClI have low intensity and indicate transition to a forbidden Δ^1 state. In both species the third transition is intense and is expected to be due to excitation to a $^1\Sigma^+$ state. The order of the low-intensity transitions should be $^1\Delta$(I), $^1\Delta$(Br),$^1\Delta$(Cl), as shown in Figure 10. The lowest transition in HgBrI and HgClI should correspond to the transition to $^1\Delta_u$ in HgI_2, and have the same energy: this is found, the energy being 37.8×10^{-3} cm^{-1}.

The second transition of HgBrI corresponds to the transition to the $^1\Delta_u$ state in $HgBr_2$, but should be of lower energy since the ground state of HgBrI is derived from the $2\pi_g$ orbital from the iodine atom (level 3 in Figure 10), whereas in $HgBr_2$ it is derived from the lower energy $1\pi_g$ orbital from the bromine atom (level 2). This is observed, the transition is at 44.2×10^3 cm^{-1} in $HgBr_2$ but 43.2×10^3 cm^{-1} in HgBrI.

The third, and intense, band of HgBrI was found at 51.2×10^3 cm^{-1}. This would be expected for an allowed transition to the $^1\Sigma^+$ state, corresponding to that in $HgBr_2$, found [7] at *ca.* 53.0×10^3 cm^{-1}, and a decrease to this value is expected because the $^1\Sigma^+$ ground state in HgBrI is derived from the iodine and not from the bromine atom. However, this leaves the $^1\Sigma^+$ state derived from iodine unused, and an intense transition at *ca.* 48.0×10^3 cm^{-1} would therefore be expected. No such transition is observed, and the intense band at 51.2×10^3 cm^{-1} could not be assigned to this transition, its energy being too high. The non-appearance of the transition to $^1\Sigma^+$(I) is explained thus: The $^1\Sigma^+$(I) and $^1\Delta$(Br) lie close together and interact under the influence of spin–orbit coupling. The direct product of the $^1\Sigma^+$ and $^1\Delta$ representations (species) in $C_{\infty v}$ symmetry is $^1\Delta$ and hence transitions to this are forbidden. The transition found at 43.2×10^3 cm^{-1} in HgBrI thus represents transition to this resultant state rather than simply to $^1\Delta$(Br).

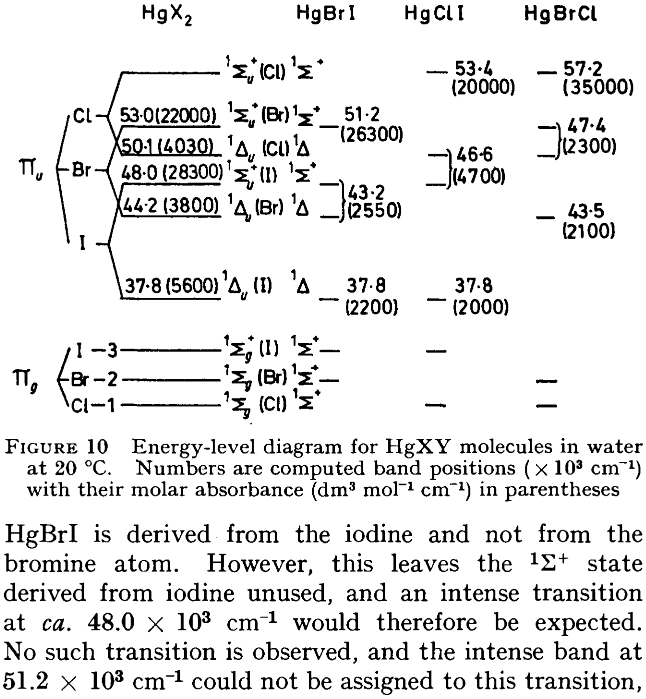

FIGURE 10 Energy-level diagram for HgXY molecules in water at 20 °C. Numbers are computed band positions ($\times 10^3$ cm^{-1}) with their molar absorbance (dm^3 mol^{-1} cm^{-1}) in parentheses

A related argument is required to explain the second and third bands found for HgClI. The intense band at 53.4×10^3 cm^{-1} is at too high an energy to correlate with $^1\Sigma^+$(I) and must therefore be due to transitions to $^1\Sigma^+$(Cl). The $^1\Sigma^+$(I) state interacts with the $^1\Delta$(Cl) state and gives a new $^1\Delta$ state, at 46.6 × 10^3 cm^{-1}, which, correlating mainly with $^1\Delta$(Cl), is expected to be at lower energy than that due to excitation to the $^1\Delta_u$ state in $HgCl_2$, since the ground state of HgClI is derived from the $^1\Sigma^+$(I) ground state (level 3). The intensity of this transition is greater than the corresponding transition to a $^1\Delta$ state in HgBrI and is attributed to the large difference in the energies of the chlorine and iodine atomic orbitals, causing the coupling of $^1\Sigma^+$(I) with $^1\Delta$(Cl) to be less effective.

The band structure of HgBrCl is explained along similar lines to that for HgBrI and HgClI. The lowest-energy band at 43.5 × 10^3 cm^{-1} is attributed to the transition from the $^1\Sigma^+$(Br) ground state (level 2) to $^1\Delta$(Br) excited state, and correlates with the low-energy transition in $HgBr_2$, at 44.2 × 10^3 cm^{-1}. The intense band at 57.2 × 10^3 cm^{-1} has too high an energy to be due to transition to $^1\Sigma^+$(Br), which would be at *ca.* 53.0 × 10^3 cm^{-1}, and is therefore assigned to transition to $^1\Sigma^+$(Cl). This band is expected to have a higher energy than the corresponding transition to $^1\Sigma^+$(Cl) in HgClI (at 53.4 × 10^3 cm^{-1}) because the ground state in HgBrCl, $^1\Sigma^+$(Br), is at a lower level than $^1\Sigma^+$(Br), the ground state in HgClI. The second low-intensity band at 47.0 × 10^3 cm^{-1} is then assigned to the $^1\Delta$ resultant state derived from interaction of $^1\Sigma^+$(Br) and $^1\Delta$(Cl).

Conclusions.—Three independent methods have yielded complete and essentially identical calculated spectra for HgXY in water and Na[ClO_4] solutions. The earlier spectra[3] are thus unreliable and the equilibrium and formation constants reported here are the most accurate to date. The spectra of these mixed mercury dihalides in aqueous solutions derive from transitions of electrons from ligand-localised molecular orbitals to mercury-localised molecular orbitals. The forbidden transitions observed in HgXY have approximately half the intensity shown[8] for corresponding transitions in HgX_2, as expected for a reduction of the populations of the ground state by half. The allowed transitions are relatively unaffected.

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