Electronic Spectra and Geometries of HgX_3^- in Water

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Summary The electronic spectra, in the visible and u.v. regions, of HgX_3^- (X = Cl, Br, or I) have for the first time been obtained, by a computer technique, free from any contributions of HgX_2 or HgX_4^{2-}, and the resolved bands are assigned and permit identification of $HgCl_3^-$ as planar with D_{3h} symmetry, and HgI_3^- as pyramidal, with C_{3v} symmetry, which suggests that the solvated species are trigonal-bipyramidal and tetrahedral, respectively; $HgBr_3^-$ has possibly intermediate or pyramidal geometry.

Solids of formula $MHgX_3$ are known (M = univalent cation, X = Cl, Br, or I) but in the case of chlorides $HgCl_3^-$ is not present.[1] For bromides the structure is intermediate between $HgBr_3^-$ chains and individual ions having trigonal structure.[2] For iodides an approximately trigonal-planar structure is also found.[3] Attempts to elucidate the structure of the trihalides in aqueous solution are hampered[4] because these anions disproportionate, and addition of X^- to HgX_2 never yields exclusively HgX_3^-. Thus no definitive Raman studies have been performed on HgX_3^- in water. To date a tetrahedral species $[HgBr_3(OH_2)]^-$ has been postulated in solution to explain why the observed entropy of $HgBr_4^{2-}$ exceeds that of the tribromo species, when the calculated entropies show the reverse.[5] Gallagher and King[6] found the entropy of the trichloro species best explained by the configuration $[HgCl_3(H_2O)_3]^-$. *X*-Ray diffraction studies of the trichloro species suggests[4] a pentagonal bipyramid with the chlorine atoms co-planar $[HgCl_3(H_2O)_2]^-$, though this is uncertain since the solutions could not be obtained free from $HgCl_2$ or $HgCl_4^{2-}$.

We have measured the electronic spectra of the system HgX_2 with added halide. At X : Hg mole ratios of just over 2:1 to 20:1, HgX_2 and HgX_3^- were present; at greater ratios, HgX_4^{2-} was also present. Further halide addition soon resulted in a two-species equilibrium, between HgX_3^- and HgX_4^{2-}, up to a mole ratio of *ca.* 200:1 after which essentially only HgX_4^{2-} was present in solution. As isosbestic points were at times observed, we were able to compute, and then resolve, the discrete spectrum for each of the three HgX_3^- species (Figure 1), based on a procedure developed earlier.[7]

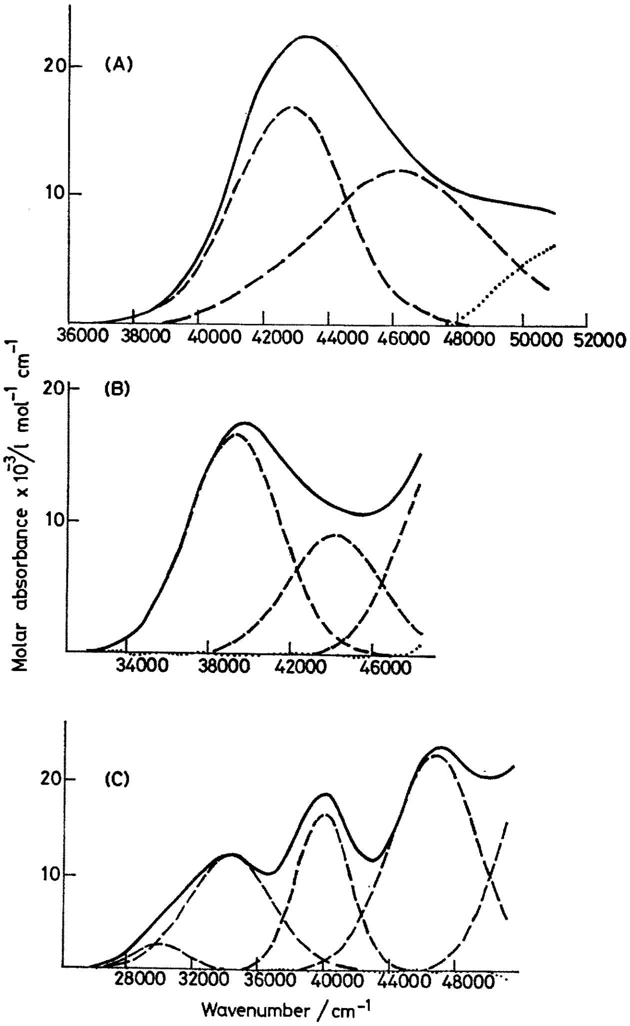

Figure 1. Electronic spectra of (A) $HgCl_3^-$ (B) $HgBr_3^-$, and (C) HgI_3^-.

AB_3 molecules may have a pyramidal or planar structure, corresponding to C_{3v} and D_{3h} symmetry, respectively, and the order of the molecular orbitals, after Walsh,[8] is given in Figure 2. The HgX_3^- ions have 24 valency electrons and these fill the orbitals up to and including $1a_2$. The $(1a_2)^2$ ground state for both planar and pyramidal molecules is $^1A_1$. The allowed transitions are also included in Figure 2.

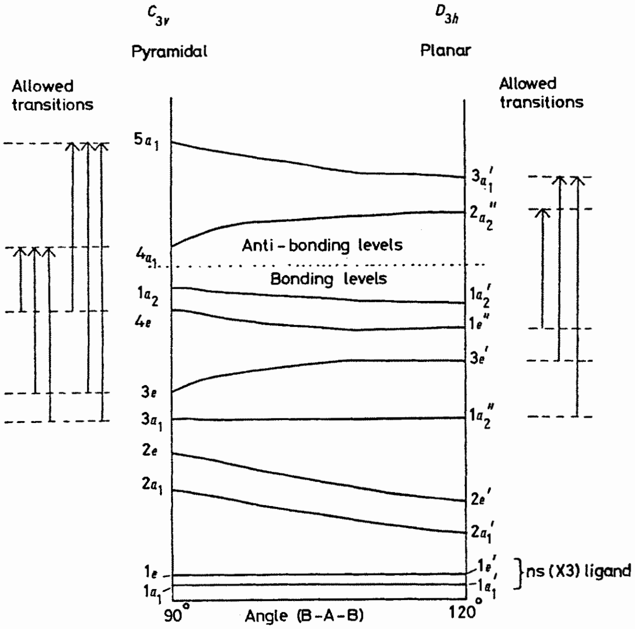

FIGURE 2. Order of the molecular orbitals and allowed transitions in HgX_3^-.

The band structure of HgI_3^- shows five transitions and may be interpreted in terms of a pyramidal structure, but not with the 90° bond angle of the extreme case of C_{3v} (Figure 2); an angle nearer the tetrahedral angle is expected. The peaks at 34300, 40000, and 46700 cm^{-1} are assigned to the electron excitations to the $4a_1$ orbital from the $4e$, $3e$, and $3a_1$ orbitals, respectively. The lowest transition corresponds to $^1A_1 \rightarrow {}^1E$. The spin forbidden $^1A_1 \rightarrow {}^3E$ of this configuration is made partially allowable by the mixing of the ^3E and ^1E states *via* spin–orbit coupling, giving the small low energy peak at 30000 cm^{-1}. The high energy band at 53400 cm^{-1} is attributed to $4e \rightarrow 5a_1$. An alternative theoretical explanation is considered unlikely.

The spectrum of $HgCl_3^-$ resolves into one main intense band, a lower intensity band, and an absorption edge. None of the complexities of the HgI_3^- system occur here, and 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 $(^1A_1' \rightarrow {}^1E')$. Spin-orbit coupling of the $^3E'$ state with $^1E'$ is not expected. The other two excitations to $2a_2''$ from $3e'$ and $1a_2'$, corresponding to those from $3e$ and $3a_1$ to $4a_1$ in HgI_3^-, are forbidden in D_{3h} symmetry and are not observed. The high energy band is identified as $3e' \rightarrow 3a_1'$ $(^1A_1 \rightarrow {}^1E')$, being much wider than the main band, as expected for excitation to a higher anti-bonding orbital.

The spectrum of $HgBr_3^-$ is of intermediate complexity and could be explained as having an intermediate structure, or possibly a pyramidal structure with C_{3v} symmetry. The three resolved bands are tentatively identified, as in HgI_3^-, as excitations from the $4e$, $3e$, and $3a_1$ orbitals to the $4a_1$ orbital. Similar results were obtained from the computed and resolved spectra of HgX_3^- in methanol.

It is therefore reasonable to suppose that $HgCl_3^-$ is solvated by two axial solvent molecules to give a trigonal-bipyramidal species, and HgI_3^- is solvated by one solvent molecule, yielding a slightly distorted tetrahedral species; $HgBr_3^-$ probably has the latter structure.

T.R.G. thanks the Royal Society for a travel grant and Michigan State University, East Lansing, Michigan, for facilities and assistance during the preparation of this communication.

(*Received*, 23*rd August* 1978; *Com.* 928.)

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