Resonance Raman Spectrum of the Mixed-valence Compound Cs_2SbCl_6

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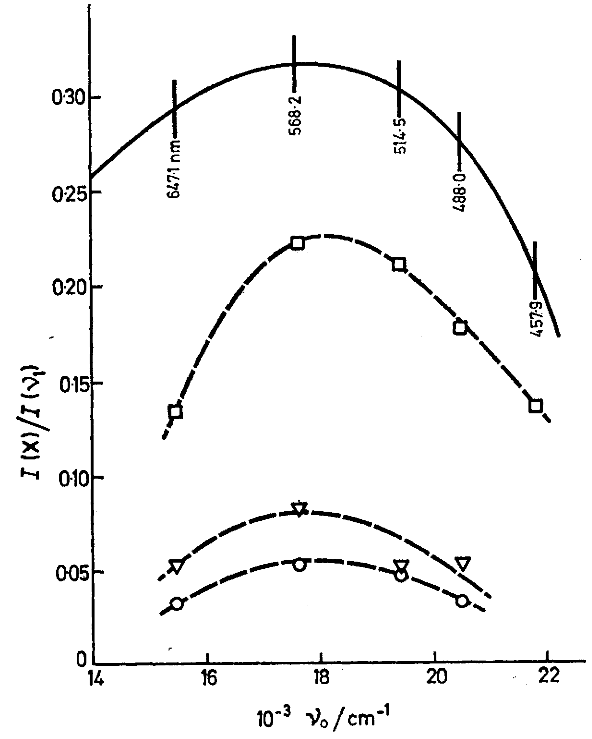
Summary The resonance Raman spectrum of the title compound exhibits four progressions, the progressing fundamental being ν_1 (a_{1g}) of the $SbCl_6^-$ ion; resonance is most effective using 568·2 nm excitation, close to the maximum of an allowed charge-transfer transition.

While much attention has been given to the resonance Raman (RR) spectra of simple inorganic compounds,[1] and of complex biological molecules,[2] an extensive and important category of materials having allowed electronic transitions in the visible region has as yet been neglected, namely mixed-valence compounds. It should be of considerable interest to discover the nature of the Raman spectrum of such compounds in the special circumstances of resonance with a mixed-valence electron-transfer band. At the same time, RR spectra may be informative regarding the assignments of the electronic spectra of mixed-valence compounds.

The dark blue solid Cs_2SbCl_6 is one of a group of similar compounds[3,4] containing antimony in oxidation states III and V, in the forms of the octahedral anions $SbCl_6^{3-}$ and $SbCl_6^-$ respectively. These substances are examples of Class II mixed-valence compounds, using the classification proposed by Robin and Day.[3] The electronic spectrum of Cs_2SbCl_6[5] shows a very broad, intense absorption in the visible region centred at 17,900 cm^{-1}, and assigned to the charge-transfer $5s \rightarrow 5s$ transition. Using the rotating sample technique,[6] excitation of this compound with several different lines of an Ar^+ or Kr^+ laser yields an RR spectrum. The charge-transfer absorption band is so broad that progressions are observed even using excitation some way off the band maximum.

Results are given in the Table. Vibrational spectra of mixed-valence compounds of this type are characteristically superpositions of the spectra of their constituents;[3,7] thus the Sb^{III}–Sb^{V} interaction in the ground state of Cs_2SbCl_6 must be small. The RR spectrum of Cs_2SbCl_6 is found to be dominated by bands arising from the $SbCl_6^-$ ion, with only one band due to the $SbCl_6^{3-}$ ion being observed (ν_1).

The analogous mixed-valence compound $Cs_4Sb^{V}Bi^{III}Cl_{12}$, whose corresponding $s \rightarrow s$ transition occurs at 24,000 cm^{-1}, gives a closely similar RR spectrum[8] to that of Cs_2SbCl_6;



the $\nu_1(a_{1g})$ fundamental of the constituent $BiCl_6^{3-}$ ion of the former occurs at 255 cm^{-1} [*cf.* for the $Co(NH_3)_6^{3+}$ and Cs^+ derivatives of this ion, this fundamental occurs at 259 cm^{-1} in each case[7]].

No fewer than four weak progressions are observed, the progressing fundamental being invariably $\nu_1(a_{1g})$ of the

$SbCl_6^-$ ion (324 cm^{-1}) in accordance with the selection rule derived by Peticolas and his co-workers.[9] Overtones of ν_1 are seen as far as $4\nu_1$. The next strongest progression is $\nu_L + n\nu_1$, as far as $n = 2$, where ν_L is a lattice mode centred at *ca.* 60 cm^{-1}. The lattice band was not observed directly because of its proximity to the exciting line, but the value deduced for its frequency is a very reasonable one for a compound containing ions of this type;[5,10] for example, an i.r.-active lattice mode occurs at 68 cm^{-1}.[5] Progressions involving lattice modes have not previously been observed. The observation is intuitively reasonable in the case of resonance with a charge-transfer transition between two ions. The distinction between 'internal' and 'external' modes in crystals is in any case an approximation, since appreciable mixing occurs between low-frequency vibrations of both types.

TABLE

Raman spectral data for Cs_2SbCl_6 (568·2 nm excitation)

Assignment (X)[a]	ν/cm^{-1}	$\Delta\nu_{\frac{1}{2}}$/cm^{-1}	$I(X)/I(\nu_1)$[b]
ν_5	175	—	0·05
$\nu_1(SbCl_6^{3-})$	257	23	0·25
ν_2	286	—	0·02
ν_1	324	7·5	1·0
$\nu_1 + \nu_L$	384	20	$0{\cdot}08_2$
$\nu_1 + \nu_5$	501	—	<0·01
$\nu_1 + \nu_1\ (SbCl_6^{3-})$ ..	584	18	$0{\cdot}05_5$
$2\nu_1$	650	12	0·22
$2\nu_1 + \nu_L$	703	—	<0·01
$2\nu_1 + \nu_1\ (SbCl_6^{3-})$ ..	904	—	<0·01
$3\nu_1$	974	16	$0{\cdot}05_3$
$4\nu_1$	1300	—	<0·01

[a] Unless otherwise indicated assignments refer to the $SbCl_6^-$ ion. The 286 cm^{-1} band is assigned by comparison with spectra of $Rb_2(Tl,Sb)Cl_6$, and $Rb_2(In,Sb)Cl_6$ (ref. 7) and of the NMe_4^+ salt and HCl (12M) solution of $SbCl_6^-$ (unpublished work). The 257 cm^{-1} band is assigned by comparison with the spectrum of the $Co(NH_3)_6^{3+}$ salt (ref. 7); the assignments of ref. 10(a) in this respect are believed to be incorrect. [b] Determined by cut-and-weigh procedure, and corrected for spectral response.

The remaining progressions observed are $\nu_1\ (a_{1g})(SbCl_6^{3-}) + n\nu_1$ up to $n = 2$, and what appears to be the first member of the series $\nu_5\ (t_{2g})(SbCl_6^-) + n\nu_1$. As n increases, the members of each progression show characteristically[1] (a) a decrease in intensity, and (b) an increase in half-band width.

In the Figure are plotted the intensities of the stronger overtone and combination bands, relative to that of the $\nu_1\ (a_{1g})$ band of the $SbCl_6^-$ ion, for several exciting lines. For all progressions the excitation profile measured by this criterion is at a maximum near 568·2 nm, *i.e.* close to the maximum in the visible charge-transfer absorption band. The intensity of the $\nu_1\ (SbCl_6^{3-})$ band was *ca.* 28% of the intensity of $\nu_1\ (SbCl_6^-)$ for all exciting frequencies used.

On the assumption that charge migration from one anion to the other would lead to changes in the bond lengths of each anion in Cs_2SbCl_6,[†] one might have anticipated the observation of RR progressions associated with both the tervalent as well as the quinquevalent anion. However, as indicated above, only ν_1 of the quinquevalent anion is observed to act as the progressing fundamental. Whether this reflects merely the superior Raman scattering activities of the quinquevalent ion (on account of the greater degree of covalent character in M^V–Cl than M^{III}–Cl bonds),[11] or whether irradiation into the mixed-valence transition selectively influences modes involving the $SbCl_6^-$ ion, remains to be ascertained.

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[†] In $(NH_4)_2SbBr_6$, the Sb–Br bond length is 2·80 Å for the $SbBr_6^{3-}$ ion and 2·56 Å for the $SbBr_6^-$ ion (*cf.* ref. 3).

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