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The Effects of Outer-Sphere Electron Transfer on the Vibrational Spectrum of Cs_2SbCl_6

H. W. Clark[1a] and Basil I. Swanson*[1b]

Contribution from the Department of Chemistry, University of Texas, Austin, Texas 78712, and The Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87545. *Received October 9, 1980*

Abstract: The previously unobserved $[Sb^{III}Cl_6]^{3-}$ infrared active modes in both Cs_2SbCl_6 and $Cs_2[Sn^{IV}_{1-2x}Sb^{V}_{x}Sb^{III}_{x}]Cl_6$ have been observed in the 77 K Fourier transform far infrared spectra of these mixed-valence compounds. The intensities of the $[Sb^{III}Cl_6]^{3-}$ modes decrease dramatically as the temperature is raised, however, and become unobservable at 373 K. It is proposed that this striking temperature dependence of the $[Sb^{III}Cl_6]$ is the result of the thermal charge transfer dynamics within the lattice. It has also been shown that the strong interionic forces in the Cs_2MCl_6 lattice can significantly affect the electron transfer process in both Cs_2SbCl_6 and $Cs_2[Sn^{IV}_{1-2x}Sb^{V}_{x}Sb^{III}_{x}]Cl_6$.

For several years, the peculiar properties of the compound Cs_2SbCl_6 have made it the object of a great deal of chemical interest and study. The early work on Cs_2SbCl_6 centered on finding an explanation for its characteristically intense color caused by a broad absorption in the visible region because other comparable Cs_2MCl_6 compounds are only slightly colored. In his pioneering work on mixed-valence solids, Peter Day proposed that the visible absorption was due to electron transfer between $[Sb^{III}Cl_6]^{3-}$ and $[Sb^{V}Cl_6]^{1-}$ sites in Cs_2SbCl_6.[2,3] Thus, Cs_2SbCl_6 could be more correctly written as $Cs_2[Sb^{V}_{0.5}Sb^{III}_{0.5}]Cl_6$. The visible absorption can then be described as the electronic excitation which involves the outer-sphere electron transfer between the two localized sites of Cs_2SbCl_6.

The suggestion of two localized antimony sites in Cs_2SbCl_6 provoked a number of attempts to verify the existence of two distinct $[SbCl_6]^{n-}$ ions in the Cs_2SbCl_6 lattice. In recent years, UV absorption,[4] Mössbauer,[5,6] photoelectron spectroscopy,[7,8] and conductivity[3] data have all been used to argue the existence of two distinct antimony oxidation states in Cs_2SbCl_6. The results of vibrational spectroscopy have, however, been more confusing. The conventional far-infrared spectrum of Cs_2SbCl_6 first reported by Day shows a strong, sharp absorption at 346 cm^{-1} and a broad absorption centered at 190 cm^{-1}.[9] The observation of only two bands is somewhat surprising in view of the fact that four internal modes are expected given the reported cubic *Fm*3*m* space group,[10] F_{1u} symmetry stretch, and deformation modes for each antimony site. While the absorption at 346 cm^{-1} is unquestionably the $[Sb^{V}Cl_6]^{1-}$ F_{1u} stretch, the absorption at 190 cm^{-1} cannot be definitely assigned to any of the remaining three modes of vibration. Day later proposed that the "missing" $[Sb^{III}Cl_6]^{3-}$ F_{1u} stretch and the two deformations were all contained in the broad, low-energy absorption.[4]

Donaldson and Silver, disputing the localized site theory for Cs_2SbCl_6, proposed that this "lack" of identifiable $[Sb^{III}Cl_6]^{3-}$ infrared absorption was evidence of only one antimony site.[11] They proposed that the $[Sb^{III}Cl_6]^{3-}$ 5s electrons were actually delocalized in a conduction band. They presented a low-temperature far-infrared spectrum which showed adsorptions not seen at room temperature, and proposed that these new absorptions (308 and 280 cm^{-1}) were due to $[Sb^{III}Cl_6]^{3-}$ because the 5s electrons had become localized at the liquid nitrogen temperature.

Part of the confusion concerning the vibrational spectra of Cs_2SbCl_6 was cleared up with Clark and Trumble's publication of the resonance Raman spectrum of Cs_2SbCl_6.[12] The presence of the broad $[Sb^{III}Cl_6]^{3-}$ A_{1g} stretch at 257 cm^{-1} indicated the presence of $[Sb^{III}Cl_6]^{3-}$ vibrations in Cs_2SbCl_6 at room temperature. The resonance Raman spectrum raised two other questions, however. The presence of the octahedral symmetry forbidden $[Sb^{V}Cl_6]^{1-}$ F_{1u} stretch in the Raman indicated a lower than *Fm*3*m* (O_h) symmetry and a loss of mutual exclusion between the IR and Raman. Previous powder X-ray results have been interpreted in terms of an *Fm*3*m* space group,[10] in which case mutual exclustion of IR and Raman bands would hold. This loss of symmetry was not visible in Day's IR spectrum of Cs_2SbCl_6. A second question is that of the resonance enhancement of a combination mode involving a lattice vibration at 60 cm^{-1} in the Raman spectrum. The resonance enhancement of this lattice mode indicates a strong but, as yet, poorly understood interaction between the Cs_2SbCl_6 lattice and the electron-transfer process.

We wish to report results of a vibrational spectroscopic study of $Cs[Sb^{III}_{0.5}Sb^{V}_{0.5}]Cl_6$ and related solids wherein the $(Sb^{III}Cl_6)^{3-}$ modes have been identified. The far-infrared spectrum of $(Sb^{III}Cl_6)^{3-}$ exhibites dramatic temperature dependence which we attribute to the lattice dynamics associated with thermal electron transfer. Comparison of results obtained for pure Cs_2SbCl_6 with those observed for the doped system $Cs_2[Sn^{IV}_{1-2x}Sb^{III}_{x}Sb^{V}_{x}]Cl_6$ helps to clarify the role that structure and lattice motions play in the electron-transfer process.

Experimental Section

Cs_2SbCl_6, $Cs_2[Sb^{V}_{0.5}In^{III}_{0.5}]Cl_6$, $Cs_2[Sn^{IV}_{0.66}Sb^{V}_{0.17}Sb^{III}_{0.17}]Cl_6$, and $Cs_2[Sb^{V}_{0.5}Sb^{III}_{0.1}In^{III}_{0.4}]Cl_6$ were synthesized by previously published methods from HCl solutions of the constituent ions.[4] $[Co(NH_3)_6][SbCl_6]$ was also synthesized by using Day's previously published synthetic method.[9]

The infrared spectra were obtained by using a Digilab FTS-20V vacuum Fourier transform infrared spectrometer and a 6.25 μm mylar beamsplitter. A triangular apodization function was used, and approximately 500 scans were averaged for each spectrum. All spectra were obtained from Nujol mulls between polyethylene plates. The room-temperature spectra were obtained by using the evacuated bench to eliminate water vapor. The high- and low-temperature spectra were obtained by using a N_2 purge system. The low-temperature spectra were obtained by using a liquid nitrogen cooled sample holder inside an evacuable cell

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Table I. Infrared Absorption Frequencies (cm^{-1})

	Cs_2SbCl			$(Co(NH_3)_6)$-$[SbCl_6]$	$CsSbCl_6$	$Cs_2[Sn^{III}_{0.66}Sb^{V}_{0.17}Sb^{III}_{0.17})Cl_6$			Cs_2SnCl_6
assignment	77 K	298 K	373 K	298 K	298 K	77 K	298 K	373 K	298 K
Sb^{V}–Cl str									
A_{1g}	327	326							
E_g	274	288							
F_{1u}	352	348	347		342	353	350	349	
Cl–Sb^{V}–Cl def									
F_{1u}	192	190	188		188				
F_{2g}	176 (sh)								
Sb^{III}–Cl str									
A_{1g}	256					258	256		
E_g									
F_{1u}	214	~210 (sh)		210		196			
Cl–Sb^{III}–Cl def									
F_{1u}	170 (sh)			172					
F_{2g}	118	117							
Sn^{IV}–Cl str									
F_{1u}						316	314	310	313
Cl–Sn^{IV}–Cl def									
F_{1u}						170	171	170	172
Cs F_{1u} trans	69	66	65			73	69	68	69

with polyethyelene windows. The high-temperature spectra were obtained by using a resistively heated metal sample holder and polyethylene plates.

The Raman spectra were obtained by using a Spex Ramalog spectrometer with Spectra-Physics 171 Ar^+ and Kr^+ gas lasers. All Raman spectra were taken with the use of a spinning cell arrangement to avoid sample decomposition in the laser beam.

Results

The severe limitations of conventional-grating far-infrared spectrometers may have been a cause for part of the confusion over the spectrum of Cs_2SbCl_6, and the relatively poor signal-to-noise ratio is most certainly a cause for missing weaker absorptions completely. The advantages of a Fourier transform infrared (FTIR) spectrometer have allowed significant improvement in both resolution and signal-to-noise ratio over conventional-grating far-IR spectra.

An essential first step in the vibrational analysis of Cs_2SbCl_6 is to know where to expect the vibrational modes of $[Sb^{V}Cl_6]^{1-}$ and $[Sb^{III}Cl_6]^{3-}$. The cubic solid $CsSbCl_6$ provides a well-characterized high-symmetry model for the $[Sb^{V}Cl_6]^{1-}$ ion, but the $[Sb^{III}Cl_6]^{3-}$ situation is more complex. The M_3SbCl_6 vibrational spectra reported by Martineau and Milne are not well suited for comparison because the $[Sb^{III}Cl_6]^{3-}$ lies in a very low symmetry site which makes identification of the F_{1u} modes in the resulting complex spectra difficult.[13] Clark has pointed out that antimony may not even be six-coordinate in such systems.[12] A much better system for comparison is that of $[Co(NH_3)_6][SbCl_6]$ which has been shown by single-crystal X-ray analysis to have $[Sb^{III}Cl_6]^{3-}$ in a high-symmetry site.[14] The frequencies obtained from the infrared spectra of Cs_2SbCl_6 and $[Co(NH_3)_6][SbCl_6]$ are lised in Table I. It should be noted that the previously published conventional IR spectrum of $[Co(NH_3)_6](SbCl_6]$ did not resolve the two critically important F_{1u} modes at 210 and 172 cm^{-1}.[4]

The infrared frequencies obtained for Cs_2SbCl_6 at various temperatures and as a dopant in a Cs_2SnCl_6 lattice are shown in Table I along with the frequencies for Cs_2SnCl_6 and $CsSbCl_6$. The room-temperature spectrum of Cs_2SbCl_6 shows three previously unreported weak absorptions at 326, 288, and 117 cm^{-1}. Comparison to $[Co(NH_3)_6][SbCl_6]$ and $CsSbCl_6$ shows that none of these three absorptions correspond to IR-active F_{1u} modes of either $[Sb^{V}Cl_6]^{1-}$ or $[Sb^{III}Cl_6]^{3-}$. The absorptions do, however, have a very good frequency correlation to gerade- or Raman-active modes of $[Sb^{V}Cl_6]^{1-}$ and $[Sb^{III}Cl_6]^{3-}$. Because of the already demonstrated breakdown of mutual exclusion in Cs_2SbCl_6 as evidenced by the presence of the IR-active F_{1u} stretch in the Raman, the absorption at 326 cm^{-1} has been assigned to the A_{1g} stretch of $[Sb^{V}Cl_6]^{-1}$, the absorption at 288 cm^{-1} to the E_g stretch of $[Sb^{V}Cl_6]^{1-}$, and the absorption at 117 cm^{-1} to the F_{2g} deformation of $[Sb^{III}Cl_6]^{3-}$.

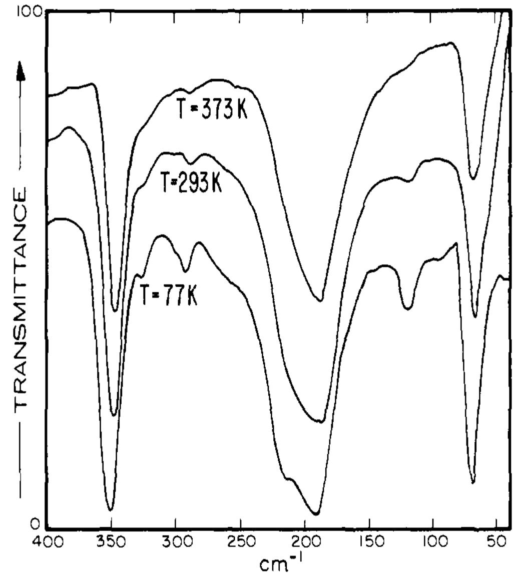

Figure 1. Top: Cs_2SbCl_6 at 373 K. Middle: Cs_2SbCl_6 at 293 K (room temperature). Bottom: Cs_2SbCl_6 at 77 K.

Examination of Figure 1 shows that at 77 K these three gerade modes at 326, 288, and 117 cm^{-1} have significantly increased in intensity, and at 373 K they have virtually disappeared. Thus, the symmetry change which allows these Raman-active modes in the IR seems to be temperature dependent. Unfortunately, temperature-dependent resonance Raman data are not yet available for comparison.

Figure 1 also shows that the broad low-energy band centered at 190 cm^{-1} changes as a function of temperature. This region has been expanded in Figure 2, and it can be seen that at 77 K there is a well-resolved absorption at 214 cm^{-1} and a slightly stronger absorption at 192 cm^{-1} which has a weaker low-energy shoulder at ca. 170 cm^{-1}. By comparison to the $[Co(NH_3)_6]$-$[SbCl_6]$ infrared spectrum, the absorption at 214 and 170 cm^{-1} can be assigned to the previously unlocated $[Sb^{III}Cl_6]^{3-}$ F_{1u} stretch and F_{1u} deformation, and the stronger absorption at 192 cm^{-1} must obviously be the $[Sb^{V}Cl_6]^{1-}$ F_{1u} deformation.

Figure 1 also shows that the absorption around 190 cm^{-1} changes significantly with temperature. At room temperature, the $[Sb^{III}Cl_6]^{3-}$ modes are significantly weaker and are poorly

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Table II. Frequencies (cm^{-1})

assignment	$Cs_2[Sb^{V}_{0.5}In^{III}_{0.5}]Cl_6$ IR	$Cs_2[Sb^{V}_{0.5}In^{III}_{0.5}]Cl_6$ Raman	$Cs_2[Sb^{V}_{0.5}Sb^{III}_{0.1}In^{III}_{0.4}]Cl_6$ IR	$Cs_2[Sb^{V}_{0.5}Sb^{III}_{0.1}In^{III}_{0.4}]Cl_6$ Raman	$[Co(NH_3)_6][InCl_6]$ IR	$[Co(NH_3)_6][InCl_6]$ Raman
Sb^{V}–Cl str						
A_{1g}	328	329	327	328		
E_g	290	289	290	288		
F_{1u}	348	350	348	350		
Cl–Sb^{V}–Cl def						
F_{1u}	184		185			
F_{2g}		178		177		
Sb^{III}–Cl str						
A_{1g}				255		
F_{1u}			203			
Cl–Sb^{III}Cl def						
F_{1u}			176			
F_{2g}						
In^{III}–Cl str						
A_{1g}	270	271	270	270		277
E_g						193
F_{1u}	248		253		253	
Cl–In^{III}–Cl def						
F_{1u}	161		160		160	
F_{2g}	150	153	150	153		149
Cs translation						
F_{1u}	73		73			
F_{2g}		52		53		

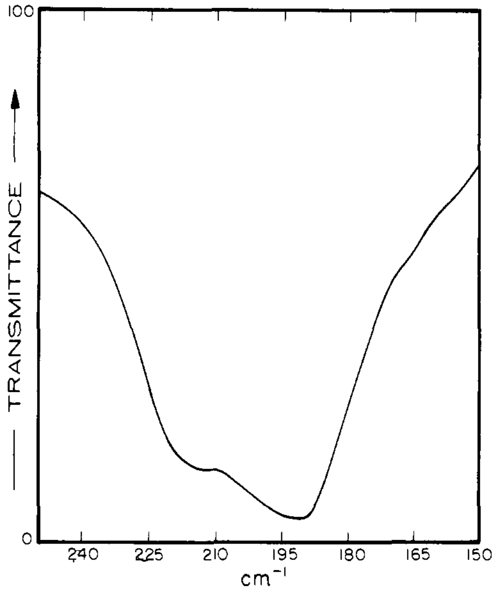

Figure 2. Expansion of low-energy region of Cs_2SbCl_6 at 77 K.

resolved. At 373 K the $[Sb^{III}Cl_6]^{3-}$ modes have nearly disappeared, with only a slight asymmetry to the 190-cm^{-1} band to indicate the presence of the $[Sb^{III}Cl_6]^{3-}$ F_{1u} stretch. Thus the entire Cs_2SbCl_6 IR spectrum shows significant changes as a function of temperature.

The infrared spectrum of $Cs_2[Sn^{IV}_{0.66}Sb^{III}_{0.17}Sb^{V}_{0.17}]Cl_6$ at various temperatures is shown in Figure 3, and the frequencies are tabulated in Table I. The situation is very similar to that of Cs_2SbCl_6. Comparison with the Cs_2SnCl_6 spectrum shows that the $[Sn^{IV}Cl_6]^{2-}$ vibrational modes are relatively unaffected by the $[Sb^{V}Cl_6][Sb^{III}Cl_6]$ dopant. The $[Sb^{V}Cl_6]^{1-}$ and $[Sb^{III}Cl_6]^{3-}$ portion of the spectrum, however, shows essentially the same temperature dependence as in Cs_2SbCl_6. There are distinct absorptions due to $[Sb^{III}Cl_6]^{-3}$ at 77 K which disappear as the temperature is raised, and the presence of the $[Sb^{III}Cl_6]^{3-}$ A_{1g} stretch shows that the same temperature-dependent loss of mutual exclusion also occurs when Cs_2SbCl_6 is doped into Cs_2SnCl_6. It is also interesting to note that there is no evidence for any gerade modes for Cs_2SnCl_6 at any temperature in the doped system, and that the F_{1u} stretch for $[Sb^{V}Cl_6]^{1-}$ also shows an intensity change as a function of temperature.

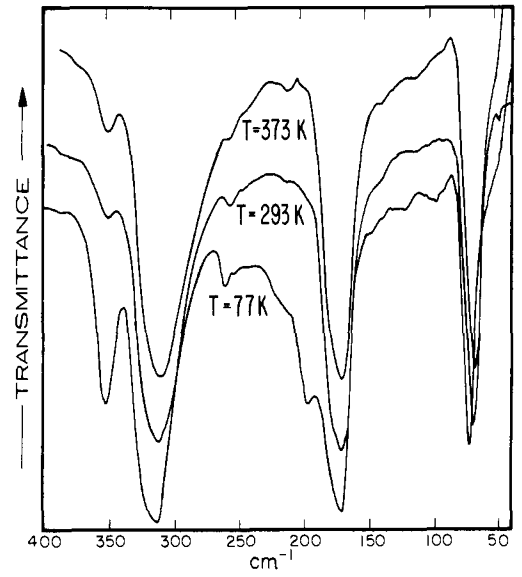

Figure 3. Top: $Cs_2[Sn^{IV}_{0.66}Sb^{V}_{0.17}Sb^{III}_{0.17}]Cl_6$ at 373 K. Middle: at room temperature. Bottom: at 77 K.

The infrared spectrum of $Cs_2[Sb^{V}_{0.5}In^{III}_{0.5}]Cl_6$ provides an interesting comparison to Cs_2SbCl_6. A comparison of the Raman frequencies with the IR frequencies in Table II indicates that the same loss of mutual exclusion which occurs in $Cs_2[Sb^{V}_{0.5}Sb^{III}_{0.5}]Cl_6$ also occurs in $Cs_2[Sb^{V}_{0.5}In^{III}_{0.5}]Cl_6$. The difference between the two systems is that the IR absorption of $Cs_2[Sb^{V}_{0.5}In^{III}_{0.5}]Cl_6$ does not change with temperature. In contrast to the behavior of $[Sb^{III}Cl_6]^{3-}$, the $[In^{III}Cl_6]^{3-}$ vibrational modes are clearly evident at all temperatures, and do not vary in intensity.

The vibrational frequencies for $Cs_2[Sb^{V}_{0.5}Sb^{III}_{0.1}In^{III}_{0.4}]Cl_6$ are also shown in Table II. A comparison of IR to Raman frequencies shows that inversion symmetry is also absent in this lattice. It is interesting to observe, however, that despite its relatively low concentration, the $[Sb^{III}Cl_6]^{3-}$ modes are evident at all temperatures, and do not vary in intensity as a function of temperature. This behavior is in strong contrast to the $[Sb^{III}Cl_6]^{3-}$ absorptions in Cs_2SbCl_6 and the doped system $Cs_2[Sn^{IV}_{0.66}Sb^{III}_{0.17}Sb^{V}_{0.17}]Cl_6$.

The low energy and close proximity of the two $[Sb^{III}Cl_6]^{3-}$ F_{1u} modes indicate some fundamental changes occur in the Sb–Cl bonds in going from $[Sb^{V}Cl_6]^{1-}$ to $[Sb^{III}Cl_6]^{3-}$. In order to get

Table III. Force and Compliance Constants[a]

	$[Sb^{III}Cl_6]^{3-}$	$[Sb^{V}Cl_6]^{1-}$
$F_{11}(A_{1g})$, mdyn/Å	1.35	2.19
$F_{22}(E_g)$, mdyn/Å	0.86	1.73
$F_{33}(F_{1u})$, mdyn/Å	0.71	1.50
$F_{44}(F_{1u})$, (mdyn Å)/rad^2	1.28	1.33
$F_{34}(F_{1u})$, mdyn/rad	0.40	0.05
$F_{55}(F_{2g})$, (mdyn Å)/rad	0.51	0.94
f_{rr}^{cis}, mdyn/Å	0.082	0.077
f_{rr}^{trans}, mdyn/Å	0.31	0.38
f_r, mdyn/Å	1.02	1.88
C_{rr}^{cis}, Å/mdyn	−0.070	−0.020
C_{rr}^{trans}, Å/mdyn	−0.68	−0.13
C_r, Å/mdyn	1.02	0.54
$(r)_r^{cis}$	−0.069	−0.037
$(r)_r^{trans}$	−0.67	−0.24

[a] F_{11} etc. represent symmetry force constants, f_r and C_r represent valence force and compliance constants.

a rough quantitative idea of these changes, a simple force constant calculation has been carried out, and the results are shown in Table III. In order to determine the force constant values for the two by two F_{1u} block, it was necessary to include a nonzero off-diagonal interaction force constant. It was not possible, of course, to exactly determine the three F_{1u} force constants because only two vibrational frequencies were available. Thus, the F_{1u} block force constants were refined to get the best fit to the frequency data by using the smallest interaction force constants which would produce reasonable primary force constants. Despite the uncertainty in their exact values, it is obvious that the $[Sb^{III}Cl_6]^{3-}$ F_{1u} interaction symmetry force constant has to be an order of magnitude larger than the $[Sb^{V}Cl_6]^{1-}$ F_{1u} interaction force constant to allow a reasonable refinement of the two F_{1u} blocks. The Sb^{V}–Cl bond length was approximated to be 2.43 Å, and the $[Sb^{III}Cl_6]^{3-}$ E_g stretch was approximated to be at 203 cm^{-1}. These approximations make the calculated force constants of value only as relative representations of the bonding trends in the two ions. It is obvious, however, that there are significant differences in the force and compliance constants of the two ions.

Discussion

The rationale for studying mixed valece materials with the Cs_2MCl_6 antifluorite structure is to better understand how lattice forces and structure perturb the electron-transfer process. Structural instabilities in R_2MX_6 systems with the antifluorite arrangement have been extensively studied.[15-19] In general, the materials undergo structural phase transformation from the cubic high-temperature form to tetragonal and, eventually, monoclinic structures at reduced temperatures. The instabilities are directly related to the relative sizes of the $(MX_6)^{2-}$ and R^+ ions;[18-20] larger cations stabilize the cubic form. In particular, hexachloride salts with Cs^+ counterion are stable in the cubic phase to very low temperatures thereby constraining the $(MCl_6)^-$ complex ion to octahedral sites.[20] In the case of Cs_2SbCl_6, the interionic forces constrain both $(Sb^{V}Cl_6)^{1-}$ and $(Sb^{III}Cl_6)^{3-}$ ions to be more similar structurally than they would otherwise be in the absence of strong lattice forces.

The lattice forces are particularly strong for Cs_2SnCl_6 by virtue of the smaller complex ion size; Cs_2SnCl_6 does not undergo the cubic tetragonal phase transformation characteristic of the antifluorite structural instability even at low (10 K) temperatures. When Cs_2SbCl_6 is doped into Cs_2SnCl_6, the electron-transfer absorption drops 4500 cm^{-1} as Cs_2SbCl_6 goes from 0% to 91% of the doped complex. Thus, it is clear that the lattice forces in these systems can significantly perturb the energy of the electron-transfer process between Sb^{III} and Sb^{V}. The observation of resonance Raman enhancement of a combination mode involving a lattice vibration in pure Cs_2SbCl_6[12] indicates that the solid state structure is also dynamically involved in the electron-transfer process. Further, the observation[21] that $(SnCl_6)^{2-}$ vibrations are resonance enhanced when the excitation frequency is tuned to the Sb^{III}–Sb^{V} intervalence charge-transfer absorption in the doped system $Cs_2[Sb^{IV}{}_{1-2x}Sb^{III}{}_xSb^{V}{}_x]Cl_6$ also points to the importance of the lattice structure in the dynamics of electron transfer in solids.

The Fourier transform infrared spectra have resolved many of the questions concerning the vibrational nature of Cs_2SbCl_6. The resolution and assignment of the two F_{1u} modes in $[Co(NH_3)_6][SbCl_6]$ has removed the past uncertainly concerning the frequency of the IR-active $[Sb^{III}Cl_6]^{3-}$ modes of vibration and allowed the location and assignment of the previously unlocated $[Sb^{III}Cl_6]^{3-}$ modes in Cs_2SbCl_6. Thus, Day's prediction that the $[Sb^{III}Cl_6]^{3-}$ modes in Cs_2SbCl_6 were in the region of the broad 190-cm^{-1} low-energy band has been shown to be correct. Donaldson and Silver were also correct, however, in stating that the IR absorptions of Cs_2SbCl_6 change as a function of temperature. The diverse responses to temperature variations by the various mixed-valence systems of antimony must be explained if we are to understand the vibrational nature of Cs_2SbCl_6.

The mixed-valence compound Cs_2SbCl_6 is a complex solid-state system, and the perturbations caused by the interaction of the two antimony sites in the lattice make Cs_2SbCl_6 more than a simple superposition of $[Sb^{V}Cl_6]^{1-}$ and $[Sb^{III}Cl_6]^{3-}$. To understand the temperature dependence of the vibraitonal spectra of Cs_2SbCl_6, one must consider the individual nature of the two ions, the electronic interaction between the two ions, and the dynamics within the lattice. While the vibrational and electronic nature of the $[Sb^{V}Cl_6]^{1-}$ ion are relatively straightforward, $[Sb^{III}Cl_6]^{3-}$ is more complex. According to valence-shell electron-pair repulsion theory, $[Sb^{III}Cl_6]^{3-}$ should have a stereoactive electron pair and thus be significantly distorted from octahedral symmetry. However, the only reliable X-ray single-crystal structure, that of $[Co(NH_3)_6][SbCl_6]$, has shown the $[Sb^{III}Cl_6]^{3-}$ ion to be essentially octahedral.[14] It is possible that in a lattice with strong interionic interactions such as $[Co(NH_3)_6][SbCl_6]$ or Cs_2SbCl_6 that the "lone pair" of electrons actually occupies an a_{1g} antibonding orbital, thus giving the "lone pair" a spherical rather than directional distribution. This same occupation of a totally symmetric antibonding orbital by the two "outermost" valence electrons has been proposed for other $MS_6{}^{n-}$ ions with "lone pairs" which show octahedral symmetry.[22]

It is obvious from an examination of the primary valence stretching force constants (f_r) in Table III that the Sb^{V}–Cl bond is considerably stronger than the Sb^{III}–Cl bond. The Sb^{V}–Cl bond is stronger, in part, because of the increased ionic attraction which results from the higher charge on antimony. However, it is likely that the occupation of an $a_{1g}{}^*$ antibonding orbital in $[Sb^{III}Cl_6]^{3-}$ must certainly further weaken the Sb^{III}–Cl bond in comparison to the Sb^{V}–Cl bond.

The observed $[Sb^{III}Cl_6]^{1-}$ vibrational frequencies are unusual in that the F_{1u} symmetry stretch is low relative to the A_{1g} stretch. Indeed, the close proximity of F_{1u} Sb^{III}–Cl stretch and Cl–Sb^{III}–Cl deformation modes leads to extensive mixing of these motions in the normal modes. Further, by virtue of the low frequency of the F_{1u} stretch the cis and trans valence interaction force constants (f_{rr}^{cis} and f_{rr}^{trans}) are much larger in comparison to the primary valence force constant (f_r) for $[Sb^{III}\text{–}Cl_6]^{3-}$ than for $[Sb^{V}Cl_6]^{1-}$. This is also the case for the interaction valence compliance constants C_{rr}^{cis} and C_{rr}^{trans}. This has a more direct physical meaning in the compliance constant formalism, however. The interaction

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displacement coordinates, $(j)_i$, are related to the compliance constants, $(j)_i = C_{ij}/C_{ii}$. These interaciton displacement coordinates measure the change in coordinate j required to minimize the potential energy following a fixed unit distortion of coordinate i.[23] The valence interaction displacement coordinates $(r)_r^{cis}$, which represent the response of an Sb–Cl bond to a cis bond unit distortion, and $(r)_r^{trans}$, which represents the response of an Sb–Cl bond to a trans bond distortion, are listed in Table III. The negative sign of the interaction displacement coordinates for both ions indicates that as one bond is extended, the other bonds become stronger. The much larger interaction displacement coordinates for $[Sb^{III}Cl_6]^{3-}$ indicate that this ion is much less stable to perturbations than $[Sb^VCl_6]^{1-}$. The relatively large stretch–stretch interactions and the low values for the primary Sb^{III}–Cl stretch force constant are, no doubt, a direct manifestation of the inherent instability of the $[Sb^{III}Cl_6]^{3-}$ ions. The fact that $[Sb^{III}Cl_6]^{3-}$ dissociates to $[Sb^{III}Cl_5]^{2-}$ and even $[Sb^{III}Cl_4]^{1-}$ in solution suggests that the solid-state lattice forces of the Cs_2MCl_6 structure stabilize an otherwise unstable ionic species.[24]

The appearance of gerade modes in the IR and ungerade modes in the Raman spectra of the mixed valence solids has two possible explanations. First, a breakdown in mutual exclusion may occur by virtue of phonon dispersion and electron–phonon interactions. Essentially, modes of vibration away from the zone center ($K \neq 0$) need not obey the selection rules consistent with a space group possessing an inversion center. Alternatively, the true space group may be of lower symmetry than the previously reported $Fm3m$. It is noted that the $Fm3m$ space group assignment was based on powder X-ray data[10] in which large-angle diffraction lines were weak and diffused. In such cases, powder X-ray studies are not sensitive to small distortions and can indicate higher symmetry than is actually present. The observation that breakdown in mutual exclusion for Cs_2SbCl_6 is temperature dependent (above) supports the latter explanation, since electron–phonon interactions should also be important at high temperature. The observed mutual exclusion of the IR and Raman modes for Cs_2SbCl_6 at higher temperatures could result from a ferroelectric phase change as temperature is raised.

It is not likely, however, that a phase change is responsible for the most striking experimental result: the virtual disappearance of the $[Sb^{III}Cl_6]^{3-}$ vibrational absorption bands above room temperature. In this light, we propose the following explanation to fit the experimental observations. On the basis of thermal conductivity studies, Day concluded that the charge carrier in the lattice is an Sb^{IV} hole formed by the reaction

$$Sb^{III}_A + Sb^{V}_B \rightarrow Sb^{IV}_A + Sb^{IV}_B$$

Day futher concluded that the carrier migration involves "hopping" of the Sb^{IV} hole through the Sb^{III} ion sites.[25] Thus, except for the initial formation of the Sb^{IV} carrier, the Sb^V ions are not directly involved in the thermally activated charge migration, and the electron-transfer reaction can be written as

$$Sb^{IV}_A + Sb^{III}_B \rightarrow Sb^{III}_A + Sb^{IV}_B$$

More importantly, Day has calculated that the "hopping" frequency for the charge-transfer reaction in Cs_2SbCl_6 occurs on the far infrared time scale for Cs_2SbCl_6.[4] It is surprising, at first, that the thermal charge migration occurs on such a rapid time scale. This can be rationalized, however, by considering the previously mentioned interionic forces in the Cs_2SbCl_6 lattice which constrain the two antimony ions into the same tightly cubic site. This lowers the energy needed to transform one antimony site into the other and makes the electron motion more rapid than would be expected in the absence of these solid-state forces. It should be noted that the electron hopping frequency for $[Co(NH_3)_6][PbCl_6]$, which is a mixed-valence compound involving $[Pb^{II}Cl_6]^{4-}$ and $[Pb^{IV}Cl_6]^{2-}$, is two orders of magnitude slower than that for Cs_2SbCl_6.

Brüesch, Strasser, and Zeller[25] have observed temperature-dependent disappearance of infrared vibrational modes in ionic conductors such as AgI which appear to be similar to that observed in the Cs_2SbCl_6 compounds. Similar changes have been observed for Raman spectra of more complex ionic conductors such as Ag_2HgI_4, where broadening and new features for both Ag^+ and Hg_4^{2-} motion appear. In their theoretical treatment, Brüesch, Strasser, and Zeller explain the temperature dependence of the infrared modes of vibration in terms of diffusive modes.[24] A diffusive mode lacks a short-term restoring force, thus allowing the ion to translate through the lattice. When a vibrational mode of a system changes from oscillatory to diffuse, the short-term oscillatory motion for that vibration is lost and that vibrational mode becomes broadened and may even disappear completely.[25] Nitzan, Ratner and Shriver developed a coupled mode model to explain Raman results for Ag_2HgI_4[26] wherein a diffusion translation of the Ag^+ ion mode broadens higher energy modes such as the symmetric HgI_4^{2-} stretch by direct coupling.[27]

Although the conduction mechanism in Cs_2SbCl_6 is not ionic, a similar explanation is possible. On the molecular scale, the transfer of an electron in and out of the $[Sb^{III}Cl_6]^{3-}$ ion requires distortion along certain $[Sb^{III}Cl_6]^{3-}$ vibrational modes. When these vibrational motions result in thermal electron transfer, the $[Sb^{III}Cl_6]^{3-}$ vibrational motions can become diffusive in the sense that the electron transfer in and out of the A_{1g} antibonding orbital destroys the short-term restoring force of the $[Sb^{III}Cl_6]^{3-}$ vibrations. It has been shown that the $[Sb^{III}Cl_6]^{3-}$ ion is particularly unstable to perturbations. Essentially, the $Sb^{III}Cl_6$ ion structure will be strongly perturbed by the electron-transfer process. When this electron-transfer event occurs on the far infrared time scale, the vibrational modes of the $[Sb^{III}Cl_6]^{3-}$ ions will be dynamically broadened.

It is the temperature dependence of the Sb^{IV} charge-carrier concentration that may cause the temperature-dependent changes in the $[Sb^{III}Cl_6]^{3-}$ vibrations. At 77 K there are almost no Sb^{IV} holes migrating through the lattice to perturb the $[Sb^{III}Cl_6]^{3-}$ vibrational modes. As the temperature is raised, the number of charge carriers goes up rapidly, and an increasing number of $[Sb^{III}Cl_6]^{3-}$ vibrations would be preturbed. At 373 K there appear to be enough Sb^{IV} holes to affect a significant number of $[Sb^{III}Cl_6]^{3-}$ ions on the vibrational time scale.

This explanation can also account for other experimental results. The vibrational modes of $Cs_2[Sb^V{}_{0.5}In^{III}{}_{0.5}]Cl_6$ show no temperature dependence because the charge-carrier-formation reaction

$$Sb^V + In^{III} \rightarrow Sb^{IV} + In^{IV}$$

is highly endothermic. Thus, the small number of charge carriers in $Cs_2[Sb^V{}_{0.5}In^{III}{}_{0.5}]Cl_6$ results in low thermal conductivity and little perturbation of the vibrational modes. Day has also shown that when the $[Sb^{III}Cl_6]^{3-}$ concentration drops below 10%, the thermal charge transfer drops dramatically because the concentration is too low to allow the hole migration mechanism. Thus, $Cs_2[Sb^V{}_{0.5}Sb^{III}{}_{0.1}In^{III}{}_{0.4}]Cl_6$ shows no temperature dependence of the $[Sb^{III}Cl_6]^{3-}$ vibrational modes because the $[Sb^{III}Cl_6]^{3-}$ concentration is too low to allow thermal charge transfer via the Sb^{IV} hole migration. The fact that the $[Sb^{III}Cl_6]^{3-}$ vibrations do not show temperature dependence in $Cs_2[Sb^V{}_{0.5}Sb^{III}{}_{0.1}In^{III}{}_{0.4}]Cl_6$ also indicates that these temperature changes are not the result of internal dynamics of the $[Sb^{III}Cl_6]^{3-}$ ion but a result of the interaction of the $[Sb^{III}Cl_6]^{3-}$ ion with the other ions in the lattice.

The temperature-dependent spectra of Cs_2SbCl_6 doped into Cs_2SnCl_6 are shown in Figure 3. The situation is similar to that of pure Cs_2SbCl_6, but several differences also emerge. At 77 K all of the vibrational modes are observable, but at room temperature the $[Sb^{III}Cl_6]^{3-}$ vibrations are completely absent. Thus,

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the disappearance of the $[Sb^{III}Cl_6]^{3-}$ modes occurs at a much lower temperature than in pure Cs_2SbCl_6. A second difference is that the $[Sb^VCl_6]^{1-}$ F_{1u} stretch also seems to be temperature dependent at higher temperatures.

Both of these observations can be explained as results of the effects of the interionic forces of the host Cs_2SnCl_6 lattice. It has already been shown that the interionic forces of the Cs_2SnCl_6 lattice cause the optical electron-transfer energy in the doped system to be significantly lower than that for pure Cs_2SbCl_6. This is because the Cs_2SnCl_6 lattice is even more tightly cubic than the Cs_2SbCl_6 lattice (above). Thus, the $[Sb^{III}Cl_6]^{3-}$ and $[Sb^VCl_6]^{1-}$ ions are even more strongly constrained in the doped system, and this results in an even larger reduction of the energy needed to convert one antimony site into the other within the doped system. The result is that a significant number of Sb^{IV} holes can appear in the doped system at a lower temperature, and the frequency of electron migration may also increase because of the reduced distortions necessary to effect electron transfer. Thus, $Cs_2[Sn^{IV}{}_{0.67}Sb^V{}_{0.17}Sb^{III}{}_{0.17}]Cl_6$ shows the same temperature effects of the $[Sb^{III}Cl_6]^{3-}$ vibrations as Cs_2SbCl_6, but at a lower temperature because the solid-state forces of the host Cs_2SnCl_6 have lowered the energy barrier to thermal electron migration in the doped system.

The $[Sb^VCl_6]^{1-}$ F_{1u} vibration may show temperature dependence in the doped system for several reasons. It may be that the equilibrium for the hole-formation reaction has been shifted because of the lower energy barrier to Sb^{IV} hole formation in the doped system. In this way, the number of $[Sb^VCl_l]^{1-}$ ions would be reduced at high temperature because a larger number of the $[Sb^VCl_6]^{1-}$ ions have become involved in the Sb^{IV} hole-formation reaction. A second possibility is that the tight Cs_2SnCl_6 lattice may have changed the minimum-energy pathway for electron migration so that the $[Sb^VCl_6]^{1-}$ ions could become directly involved in the charge-migration process, and thus may be perturbed by the same mechanism as the $[Sb^{III}Cl_6]^{3-}$ ion.

It has been previously shown that the Cs_2SnCl_6 host lattice modes are strongly coupled to the dopant $Sb^{III}Sb^V$ electron transfer in $Cs_2[Sn^{IV}{}_{1-2x}Sb^V{}_xSb^{III}{}_x]Cl_6$.[21] In this light, the resonance enhancement of the combination mode involving a lattice vibration in Cs_2SbCl_6 and $Cs_2[Sb^V{}_{0.5}In^{III}{}_{0.5}]Cl_6$ means that a lattice distortion must be involved in the dynamics of the electron-transfer process. The 62-cm^{-1} lattice mode is somewhat high in energy to be the Cs^+ translation, but several temperature-dependent Raman studies of other Cs_2MCl_6 compounds have shown rotational modes near 60 cm^{-1}.[28] The interionic forces of the simple antifluorite structure have been shown to cause mutual rotation of the octahedra of R_2MCl_6 systems (R = Li, Na, and K) so that the M–Cl···Cl–M vectors no longer align. This distortion is caused by the relatively small size of the cations which occupy the tetrahedral sites in the lattice.[28] It is possible that Cs_2SbCl_6 has undergone a similar rotational distortion because of the different sizes of the $[Sb^{III}Cl_6]^{3-}$ and $[Sb^VCl_6]^{1-}$ ions in the same lattice site. A rotational mode would then be coupled to the electron-transfer process, and thus become resonance enhanced because it may be necessary for the octahedra to rotate back into alignment in order to facilitate electron transfer.

An important question that must be addressed by those concerned with the study of mixed-valence compounds is why these dramatic temperature effects for Cs_2SbCl_6 were not apparent in the other experimental techniques. The major reason is that with three exceptions, the published experimental data were obtained at a single temperature. Those exceptions are the previously mentioned Donaldson and Silver far-IR study[11] and a temperature-dependent Mössbauer study done in Russia[29] and later repeated by Longworth and Day.[30] Experimental difficulties and incorrect conclusions obscured Donaldson and Silver's essentialy correct observation of absorption changes in Cs_2SbCl_6 as a function of temperature. The Russian Mössbauer data shows that at liquid-nitrogen temperature there are two signals assigned to Sb^{III} and Sb^V, but when the temperature is raised to only 140 K they report that a new intermediate signal grows in as the two Sb^{III} and Sb^V signals decrease. However, Longworth and Day's subsequent study of the temperature dependence of the ^{121}Sb Mössbauer spectrum shows no evidence for any new intermediate signal.[30] Unfortunately, the Mössbauer spectrum could not be followed to higher temperatures by vitrue of poor statistics.[30] It is important to note that the other reported Mšsbauer studies as well as the photoelectron studies were all carried out only at 77 K where the thermal electron-transfer effects are virtually nonexistent. UV–visible studies are not sensitive to the reported temperature effects because they concern the optical rather than thermal electron transfer and are relatively insensitive to local dynamic effects. Thus, it should be concluded that more care must be taken in the future to obtain temperature-dependent experimental data on mixed-valence systems.

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