Correlation Between Structure and Phonon Spectra of Linear Polyiodide Chains in $Tl_6I_6M^{n+}_{2/n}(I_4)^{2-}$, [M = Pb, Ag, Au, $(Bi_{0.5}Tl_{0.5})$]

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Raman- and IR-spectra of four compounds of the general composition $Tl_6I_6M^{n+}_{2/n}(I_4)$ [n: formal valence of the M-atom, M = Ag, Au, Pb and $(Bi_{0.5}Tl_{0.5})$] were investigated in order to identify the polyiodide species present. In accordance with structural results comparable amounts of I_4^{2-} and I_3^-/I^--groups were found for M = Ag, Pb and $(Bi_{0.5}Tl_{0.5})$, while in $Tl_6I_6Au_2(I_4)$ I_3^-/I^--groups predominate.

I. Introduction

Hexagonal compounds of the general composition $Tl_6I_6M^{n+}_{2/n}(I_4)^{2-}$ (n being the valence of the metal atom) display channels along the crystallographic c-axis, accommodating linear chains of polyiodide ions [1]. For M = Ag [2], Pb [3, 4] and $(Bi_{0.5}Tl_{0.5})$ [5] the results of structure determinations suggest the presence of I_4^{2-} groups, while asymmetric I_3^- and I^--ions seem to predominate in $Tl_6I_6Au_2(I_4)$ [6]. However, the straightforward interpretation of the structure analyses is difficult due to the unusually large anisotropic temperature factors of the iodine atoms along the c-axis, a result which might be interpreted as positional disorder, permitting the presence of both I_4^{2-} and I_3^- in any of these compounds. Another complication arises from a yet unresolved superstructure for M = $Bi_{0.5}Tl_{0.5}$, which is very likely related to the arrangement of the iodine atoms within the channels.

In an effort to settle these questions, we tried to identify the different species of polyiodide ions by means of their Raman spectra which are an especially suitable tool due to the resonance enhancement of the polyiodide internal vibrations [7]. Raman spectra of polyiodide compounds with iodine groups ranging from I_2 up to I_5 have been recorded and assigned in some cases in the last years, especially by Marks and his group [7]. No data are yet available on I_4^{2-}-groups.

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II. Experiment

The compounds were prepared according to procedures given earlier [1–5]. Raman spectra were excited with laser lines from an Argon ion laser between 514.5 nm and 457.9 nm with a typical power of 50 mW and recorded with a double holographic grating monochromator, an RCA 31034 A02 photomultiplier plus associated photon counting electronics. The spectrometer slits were set for a resolution of 5 cm^{-1}. The samples were measured at 80 K in a liquid nitrogen cryostat to avoid sample heating and surface burning from the incident laser light. The IR spectrum of $Tl_6I_6Pb(I_4)$ was measured on a Beckmann IR Fourier spectrometer with a resolution of 4 cm^{-1} at room temperature.

III. Results and Discussion

The spectra of polycrystalline samples of the four different compounds, recorded at $\lambda_L = 488.0$ nm and $T = 80$ K are shown in Figure 1. The corresponding peak positions are collected in Table 1. The dependence of the spectrum on the excitation wavelength for $Tl_6I_6(Bi_{0.5}Tl_{0.5})(I_4)$ is shown in Figure 2. The unpolarized IR-reflectivity of $Tl_6I_6Pb(I_4)$ is given in Fig. 3, the peak positions are listed in Table 1.

In an attempt to identify the different possible I_x-groups in the polyiodine chains by referring to their known spectra from the literature one can immediately eliminate the presence of I_2- and I_5^--groups, the I_5^--group being built up by an I^- located symmetrically between two I_2-groups. Both of

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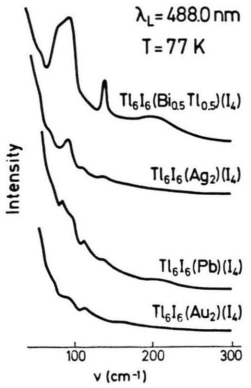

Fig. 1. Raman spectra of $Tl_6I_6M^{n+}_{2/n}(I_4)^{2-}$[M = Pb, Ag, Au, $(Bi_{0.5}Tl_{0.5})$].

Table 1. Raman and IR spectra of $Tl_6I_6M^{n+}_{2/n}(I_4)^{2-}$.

M = Pb R:		93	103	120	145		225	
IR: 39, 46	57, 64	90	100					
M = Ag R:	80		102	120	146			
M = Au R:	80		101	123		167		
M = $Bi_{0.5}Tl_{0.5}$ R:		94	108		145		205	245

R: Raman; IR: Infrared reflectivity peaks.

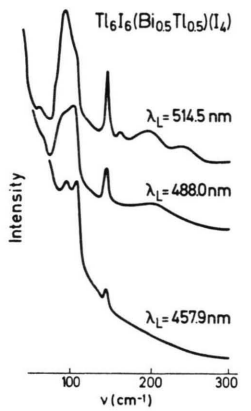

Fig. 2. Excitation energy dependence of the Raman spectrum of Tl_6I_6 $(Bi_{0.5}Tl_{0.5})$.

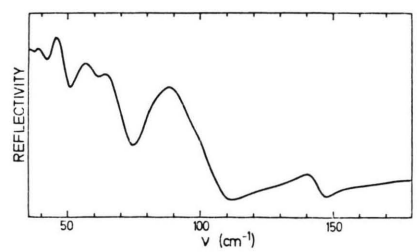

Fig. 3. IR reflectivity of $Tl_6I_6Pb(I_4)$.

them would imply the occurence of strong peaks from the I_2-stretching vibration at 209 cm^{-1} and 160 cm^{-1} for I_2 [8] and I_5^- [8], respectively. The remaining problem is how to separate out the possible coexistence of I_3- and I_4-groups. The symmetry types and activities of the internal phonons of the ideal linear molecules I_3^- and I_4^{2-} with symmetry $D_{\infty h}$ are listed in Table 2. Under the influence of lowered molecular symmetry due to changes in the atomic distances and of solid state effects the clearcut separation between IR- and Raman activity may break down, the frequencies may shift and degenerate modes may split. While thus the Raman spectrum of isolated *symmetric* I_3^--groups in polycrystalline $(C_6H_5)_4As^+I_3^-$ as well as that of $(C_6H_5)CONH_2)_2H^+I_3^-$, where I_3^- units are lined up in a linear chain, only shows the totally symmetric line at 118 cm^{-1} plus overtones [8], the same linear chain arrangement of *asymmetric* I_3^--groups in bis (1,2-benzoquinone dioximato) NiI [9] and in pyridinium triiodide [10] yields in addition to the strong totally symmetric line at 105 cm^{-1} a weaker line at 163 cm^{-1} assigned to the in-phase oscillation of the outer I atoms in the I_3^--group. An even stronger distortion of the I_3^--group is observed in CsI_3, where the molecules are no longer linear, but slightly bent ($\alpha = 178°$) [11], and strongly coupled to each other through a zig-zag chain arrangement, so that both stretching vibrations appear with equal strength in the Raman spectrum as factor group split doublets at 96, 105 cm^{-1} resp. 139, 150 cm^{-1} besides the bending and librational modes at 72,80 cm^{-1} and 56,63 cm^{-1} [11].

Based on these results and on the fact that iodine atoms are restricted to a linear chain structure in our compounds we can assign the line at 108 cm^{-1} and the weak structure at 163 cm^{-1} for $Tl_6I_6(Bi_{0.5}Tl_{0.5})(I_4)$ (see Figure 2) to the two stretching vibrations of I_3^-. Consistent with this assignment is our finding that the intensity of the 108 cm^{-1} line does not change much with the excitation energy as it is observed in all I_3^- containing compounds [8, 9]. Relative to the 108 cm^{-1} line the intensities of the peaks at 94 and 146 cm^{-1} drop when the excitation energy is changed from 2.41 eV (514.5 nm) to 2.71 eV (457.9 nm). We therefore identify them with the two Raman active stretching vibrations of I_4^{2-} (see Table 2).

Their lowered frequencies with respect to those of I_3^- are in agreement with the expectations. The remaining broad structures at 205 and 245 cm^{-1} would then be an overtone of the I_3^- symmetric stretch vibration and a combination of the two I_4^{2-}-fundamentals respectively, whereas the weaker peaks at 70 – 80 cm^{-1} could be associated with bond-bend-

Table 2.

I_4^{2-} Internal modes ($D_{\infty h}$)

I — I — I — I		
→ → ← ←	Σ_g^+ }	Raman
→ ← → ←	Σ_g^+ }	Raman
→ → ← →	Σ_u^+	IR z-polarizsed
↑ I — I — I — I ↑	Π_u	IR x, y-polarised
↑ I — I — I — I	Π_g	Raman

I_3^- Internal modes ($D_{\infty h}$)

ν_1	I — I — I	Σ_g^+	Raman
ν_2	I — I — I	Π_u	IR
ν_3	I — I — I	Σ_u^+	IR

ing and/or librational modes [11]. The corresponding IR active bending and stretching modes are found in the IR reflectivity spectrum of $Tl_6I_6Pb(I_4)$ see Fig. 3 and Table 1).

On the ground of this mode assignment for $Tl_6I_6(Bi_{0.5}Tl_{0.5})(I_4)$ we can now try to correlate the observed Raman spectra of our compounds with the structural results (1 – 5) (see Figure 1). Starting at the bottom with $Tl_6I_6Au_2(I_4)$ the absence of peaks at 95/146 cm^{-1} and the relative prominence of the structures at 101/167 cm^{-1} can easily be reconciled with the structural result: prevailing presence of I_3^-, I^--groups and virtual absence of I_4^{2-}-groups. The so far neglected influence of the I^- could then be associated with a local mode of I^- between two I_3^- groups giving rise to the band at 120 cm^{-1}. The assignment of this band to the totally symmetric stretching mode of a *symmetric* I_3^- would be in contradiction to the structural results. However, it is still an open question why this mode is missing in the spectrum of $Tl_6I_6(Bi_{0.5}Tl_{0.5})(I_4)$. Concerning $Tl_6I_6Pb(I_4)$, the peaks at 93/145 cm^{-1} plus the weak shoulder at 103 cm^{-1} suggest the predominant existence of I_4^{2-}-ions besides a small number of I_3^-, I^--groups, the structure at 120 cm^{-1} again being interpreted as in the case of $Tl_6I_6Au_2(T_4)$. The same line of arguments can be applied to $Tl_6I_6Ag_2(I_4)$, except for the fact that instead of the usual 95/108 cm^{-1} doublet only one peak at 102 cm^{-1} with a FWHM of 10 cm^{-1} is observed, possibly due to a slight down shift of the I_3^- symmetric stretch vibration together with an upshift of the I_4^{2-}-stretch vibration.

Conclusion

Starting from structural results on $Tl_6I_6M^{n+}_{2/n}(I_4)^{2-}$, [M = Ag, Au, Pb, $(Bi_{0.5}Tl_{0.5})$] compounds suggesting different arrangements of the I_4-group in linear chains, the Raman spectra of these compounds have been interpreted to yield a predominant existence of I_3^-, I^--groups in $Tl_6I_6Au_2(I_4)$ whereas a coexistence of I_4^{2-}- and I_3^-, I^--groups is found in the other three cases. This result can be correlated again with the structural findings. In contrast to the other three compounds, in $Tl_6I_6Au_2(I_4)$ only 13% of the Au atoms occupy approximately the center of an I_6-octahedron, whereas the other 87% are located in the faces of the octahedron in a trigonal planar arrangement with the surrounding I atoms [6]. This relative change of the z-coordinates of the Au atoms with respect to the I_4-groups acts back on the Tl_6I_6 lattice and induces the formation of asymmetric I_3^--groups.

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