Raman Spectrum and Structure of Molten Indium Dichloride

J. H. R. CLARKE and R. E. HESTER*

(*Department of Chemistry, University of York, Heslington, York*)

PHASE studies of the indium–chlorine system have been interpreted as indicating the existence in the solid state of a compound $InCl_2$[1,2] of suggested[1] structure $In^{I}In^{III}Cl_4$, though no conclusive evidence for this is available. The related gallium–chlorine system similarly yields a compound $GaCl_2$, whose structure has unambiguously been established as $Ga^{I}Ga^{III}Cl_4$ in both solid[3] and liquid[4] states. We have obtained Raman spectra of the $InCl_2$ system, by use of He–Ne laser excitation techniques to avoid problems arising from the straw-yellow colour of the molten salt.

The structural information represented by these spectra parallels that obtained previously for molten $GaCl_2$.

This study was supported by a grant from the Office of Saline Water, U.S. Department of the Interior.

Raman spectra of $InCl_4^-$

Raman bands, cm.$^{-1}$				
Molten $InCl_2$ (350°)	Molten $InCl_3$,KCl (350°)	$InCl_4^-$ in ether[5] (*ca.* 25°)	Assignments for T_d symmetry	Approximate description
317s,p	320s,p	321s,p	$\nu_1(a_1)$	ν_s(In-Cl)
91m,dp	87m,dp	89m,dp	$\nu_2(e)$	δ (ClInCl)
349w,dp	346w,dp	337w,dp	$\nu_3(f_2)$	ν_a(In-Cl)
116m,dp	114m,dp	112m,dp	$\nu_4(f_2)$	δ (Cl_3In)

s = strong, m = medium, w = weak, p = polarised, dp = depolarised.

The spectrum of $InCl_2$ was found to be invariant from just above the melting point (268°) up to 500°, indicating a definite and thermodynamically stable chemical species. The appearance of the molten salt spectrum (Figure) is characteristic of tetrahedral species, the strongest band at 317 cm.$^{-1}$ being polarised and all other bands being much weaker and depolarised. These polarisation properties also enabled the strongly overlapping 317 and 349 cm.$^{-1}$ bands to be resolved (see Figure). The spectrum is effectively identical with that given by a molten equimolar mixture of $InCl_3$ and KCl, which is expected to have the structure $K^+InCl_4^-$, and with that found for $InCl_4^-$ in ether solution.[5] From the comparison of spectra made in the Table and Figure it is clear that the same species is responsible for each of them, namely the tetrahedral $InCl_4^-$ ion. The band assignments given in the Table follow from this. The Figure also shows the strongest Raman band given by solid $InCl_2$, at room temperature and just below its melting point. This band frequency, at 313 cm.$^{-1}$, is close to that of the strongest $InCl_4^-$ band, suggesting that this species persists in the solid state.

In conclusion, the Raman evidence establishes that $InCl_2$ in the liquid state, and probably also in the solid, has the structure $In^+InCl_4^-$.

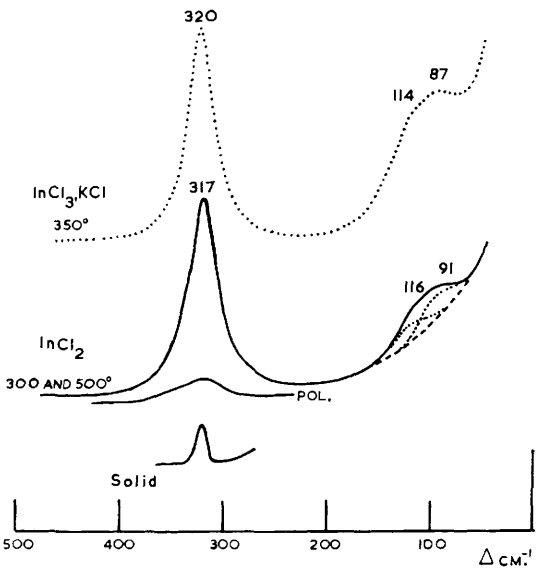

FIGURE. *Raman spectra of the* $InCl_4^-$ *ion in molten* $InCl_3$,KCl, *molten* $InCl_2$, *and solid* $InCl_2$.

(*Received, June 18th,* 1968; *Com.* 807.)

[1] J. R. Chadwick, A. W. Atkinson, and B. G. Huckstepp, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1021.
[2] V. N. Fadeev and P. I. Fedorov, *Zhur. neorg. Khim.*, 1964, **9**, 378.
[3] G. Garton and H. M. Powell, *J. Inorg. Nuclear Chem.*, 1957, **4**, 84.
[4] L. A. Woodward, G. Garton, and H. L. Roberts, *J. Chem. Soc.*, 1956, 3723.
[5] L. A. Woodward and M. J. Taylor, *J. Chem. Soc.*, 1960, 4473.