

The two extreme viewpoints concerning this absorption are:

(1) that it is an electron transfer or sharing between the Tl^+ and neighboring halide ions, and (2) that it is an internal transition localized on the Tl^+ ion and perturbed by the crystal field imposed by its nearest neighbors. Actually, there are limitations on either viewpoint as discussed by Knox and Dexter ⁽⁴⁾.

One can say that if the first viewpoint were essentially correct, the nature of the state, and the shift of the absorption peak with pressure should depend strongly on the halide ion (Cl^- , Br^- or I^-) and only in second order on the symmetry of the lattice. On the other hand, the second approach would predict a pressure shift which would be essentially independent of the halide ion, but might depend strongly on the lattice involved. Williams and his co-workers ⁽⁵⁾ have developed a semi-quantitative formulation of the second viewpoint as applied to KCl in particular. To summarize his results, the theory predicts a shift to lower energies with increasing pressure. This should be true for all alkali halides with the face centered cubic structure, but not necessarily for the simple cubic (cesium chloride) structure. Figure 1 ⁽⁶⁾ shows the low pressure shift for a series of these compounds. Energy shifts are shown in wave numbers (1000 cm^{-1} equal 2.88 kilocalories). Indeed, it can be seen that the predicted red shift prevails for all the fcc structures quite independent of the halide ion involved. Williams calculations tell nothing explicit about the simple cubic structure, but one can see from the initial blue shift that there is a marked effect of crystal symmetry. KCl has a transition at 19 kilobars to the simple cubic structure. Based on the low pressure results and Williams theory one would expect a discontinuous shift to higher energy for the absorption peak at the transition. Figure 2 shows