



Fig. 1. Infrared spectra in the region $350\text{--}150\text{ cm}^{-1}$ for the isotopic $\text{ZnCl}_2 \cdot (2,2'\text{-DTDP})$ and $\text{ZnBr}_2 \cdot (2,2'\text{-DTDP})$ complexes.

For the $\text{ZnCl}_2 \cdot (2,2'\text{-DTDP})$ complex it may be observed that the absorption at 293 cm^{-1} is metal-sensitive and halogen-sensitive (disappears in $\text{ZnBr}_2 \cdot (2,2'\text{-DTDP})$). Therefore, the absorption must be associated with a zinc-chlorine stretching mode. Its frequency position is normal for a terminal zinc-chlorine stretching mode associated with a tetrahedral environment for the zinc atom [28–35]. The selection rules predict a symmetrical and an asymmetric vibration in molecules of this type. A second zinc-chlorine stretching vibration in complexes of this stereochemistry has been assigned in related complexes in the region of $310\text{--}330\text{ cm}^{-1}$. A band was observed at 320 cm^{-1} in both the chloride and bromide complexes, and was found to be only slightly metal-sensitive. A ligand band was observed at 345 cm^{-1} , and thus the band at 320 cm^{-1} may involve both a ligand mode and the other zinc-chlorine stretching mode. The absorption at 222 cm^{-1} is metal-sensitive and halogen-insensitive. Thus, this band must involve the zinc-nitrogen stretching mode. Pressure sensitivities allow us to determine the nature of the two zinc-chlorine stretching modes. Under pressure, the absorption at 293 cm^{-1} shows a significant decrease in peak intensity relative to the band at 320 cm^{-1} . From previous high-pressure studies we have determined that the symmetrical metal-halogen stretching vibration is more

[28] R. J. H. CLARK and C. J. WILLIAMS, *Inorg. Chem.* **4**, 350 (1965).

[29] R. J. H. CLARK, *Spectrochim. Acta* **21**, 955 (1965).

[30] G. B. DEACON, J. H. S. GREEN and F. B. TAYLOR, *Australian J. Chem.* **20**, 2069 (1967).

[31] G. E. COATES and D. RIDLEY, *J. Chem. Soc.* 166 (1964).

[32] J. BRADBURY, K. P. FOREST, R. H. NUTTALL and D. W. A. SHARP, *Spectrochim. Acta* **23A**, 2701 (1967).

[33] C. POSTMUS, J. R. FERRARO and W. WOZNAK, *Inorg. Chem.* **6**, 2030 (1967).

[34] C. W. FRANK and L. B. ROGERS, *Inorg. Chem.* **5**, 615 (1966).

[35] J. R. FERRARO, W. WOZNAK and G. ROCH, *Ric. Sci.* **38**, 433 (1968).