



Fig. 12 Effect of pressure on d levels Ni^{++} in $[Ni(NH_3)_6]Cl_2$.

which covalent forces enter in, and to which molecular orbital theory is necessary for a complete explanation.

The rare earths form an interesting group of ions in that they have a partially filled 4f shell, although the 5p and 5s shells are filled. Their characteristic pastel colors are due to weak transitions from one state to another within the 4f shell. The "radius" of the 4f shell is of the order of 0.5 Å. The ionic radius is about 1.5 Å. The study of pressure effects on these transitions gives a measure of the degree to which external pressure penetrates the inner shells through ionic interaction. There are indeed definite pressure effects which will be discussed in detail elsewhere. One which can be mentioned briefly is the large increase in intensity. The transition occurs because of mixing of the 4f and 5d levels. The increase of intensity, then, is a measure of the increased mixing of levels due to increased overlap of neighboring ions.

(c) Charge Transfer. In addition to the transitions discussed above, a type of electronic interaction occurs wherein there is transfer of an electron from one entity to another. This may be a transfer from one part of a molecule to another, as in organic dyes such as fluorescein or the cyanines and porphyrins or as in the permanganate and chromate ions, or it may be between adjacent molecules or ions.

These are usually very intense transitions. As a matter of fact the absorption edge discussed earlier is a special example wherein both the ground state and excited state belong to the crystal as a whole, rather than to specific molecules or ions. These