Application of quantum mechanical models to variable-temperature absorption spectra of nickel(II) complexes

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The use of mathematical quantum models to describe molecular absorption spectra is a relatively unexplored field. When electrons absorb a photon of light, they move between energy states. Absorption spectroscopy is very useful because it accurately shows the differences in energy of possible electronic states. These electronic transitions, under normal circumstances, are governed by selection rules. For example, transitions must take place between orbitals of different energies, and changes in electron spin are forbidden. Allowed absorption bands are theoretically curves with a single maximum, but in reality, there exist forbidden transitions that couple with the allowed bands. These forbidden bands steal intensity from the allowed bands to cause a dip in the absorbance, and a double peak formation in the spectra.

We use a curve-fit equation from the literature[1-3] which mathematically describes a two-band coupling system. To test the validity of the equation, different spectra of the same molecule were examined to see if the properties of the curve fit values change with respect to changes in the spectra. Four octahedral nickel(II) complexes were examined. Ni(imidazole)$_6$(NO$_3$)$_2$ and Ni(pyrazole)$_6$(NO$_3$)$_2$ have a forbidden band in between two allowed bands, while Ni(1,10-phenanthroline)$_3$(NO$_3$)$_2$ and Cs[Ni(H$_2$O)$_6$](PO$_4$) have a forbidden band off to the side of two allowed bands. One inadequacy of the model was found to be that the equation only takes into account coupling between one forbidden band and one allowed band. This was determined based on the fact that curve fits using the literature equation did not adequately re-create the spectra, or had a large margin of error when they did.

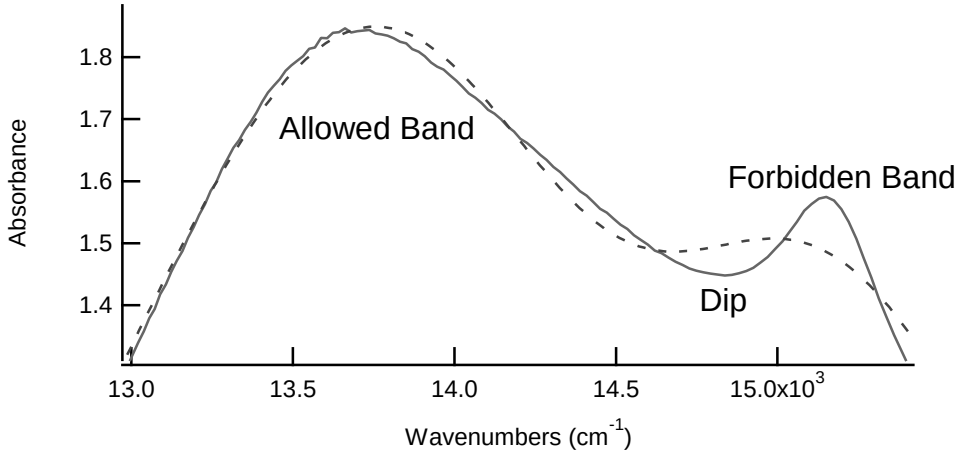

Figure 1: Room temperature absorption spectrum of Cs[Ni(H$_2$O)$_6$](PO$_4$) *(solid line)*, with curve fit *(dotted line)*.

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