CHAPTER I

INTRODUCTION

It is well known that the degree of interaction between solvent and solute is responsible for various solvent effects. Usually, more polar the solvent, the greater the interaction e.g. solvent shifts. Literature in organic compounds is extensive, but not so in inorganic compounds.

Also, the oxygen atoms of acetylacetonate complexes as well as the chelate rings themselves, can function as sites for H-bond formation. Literature on H-bond formation of some $M(AcAc)_{2,3}$ has only been reported by X-ray[1], solvation[2], UV and visible[4] spectral studies.

Therefore, we consider it desirable to study solvent effects of some bivalent and trivalent metal acetylacetonates in a variety of solvents in the UV region.

1.1 The Franck-condon Principle and Hydrogen Bonding[5]

Both McConnell,[6] Bayliss and McRae[7] have discussed the effect of solvent on an electronic transition. The equilibrium distances and orientations of solvent molecules around a solute molecule are dictated by the energies of solvation. If the solute molecule makes an electronic transition, the solvation arrangement of the initial state is not necessarily the most stable for the new electronic distribution and, indeed, could be energetically repulsive. Since the solvent molecules cannot re-orient fast enough during the transition, (Franck-Condon principle) such a change in solvation energies would result in a change in the energy separation of the two states and there would be a solvent shift.

In an H-bonding system, the interaction is localized at functional groups with either proton donor or acceptor properties. A solvent shift then indicates that the H-bonding properties of these functional groups in the initial state differ from the H-bonding properties of these same groups in the final state. The magnitude of the shift can be evaluated in terms of the Franck-Condon principle. The following theory, however, must not be regarded as definitive.

Figure 1 portrays potential functions for formation of an H-bond A-H. . . B where R is the H-bond length, A-H is the solvent molecule and B is the solute molecule.

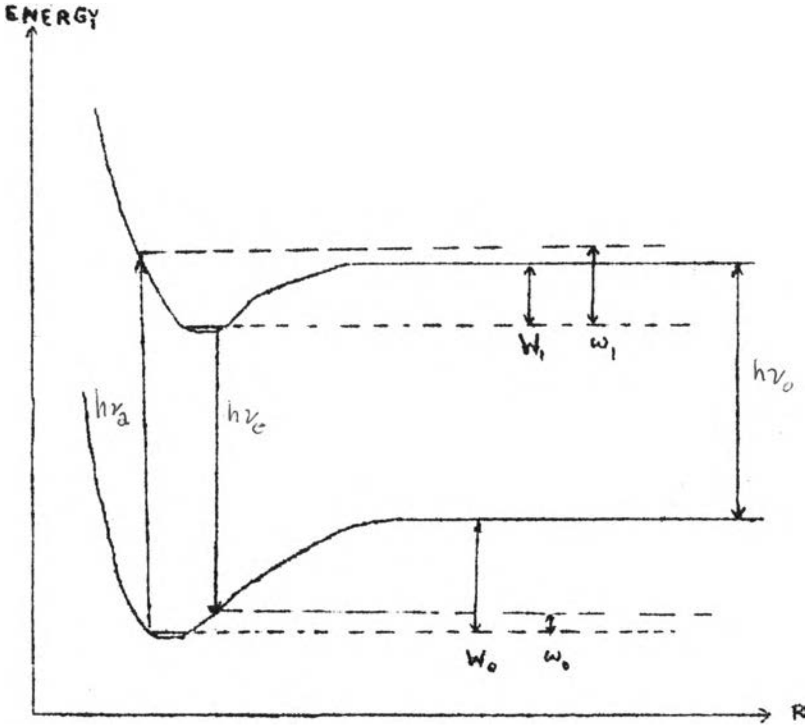

Fig.1a ($W_o > W_1$)

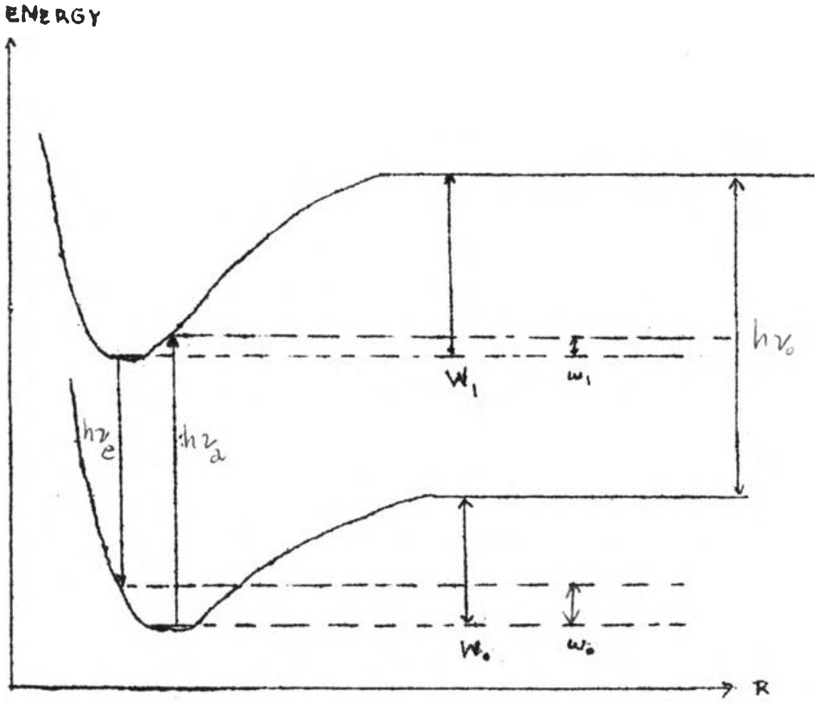

Fig.1b ($W_o < W_1$)

Fig.1 Hypothetical potential curves: energy vs. H-bond length.

A-B...B; R= Hydrogen bond length

Fig. 1a portrays the situation when the excited state forms a weaker H-bond and in Fig. 1b the excited state forms the stronger H-bond. In each case the energy separation of the non-H-bonded species ($R = \infty$) is assumed to be identical to $h\nu_0$ the energy separation in a non-H-bonding solvent of the same refractive index. The H-bond energy is designated W (W = $-\Delta H$) and the excitation energy implied by the Franck-Condon principle is labeled ω. (By these definitions, W and ω are always positive numbers. Of couse either W_0 or W_1 could be zero.)

There are three quantities of interest which might be experimentally accessible, ν_a, ν_e and ν_{o-o}, the frequencies appropriate to maximum absorption, maximum emission, and the 0-0 transition, respectively. These frequencies are related to the quantity ν_o by the relations

$$h(\nu_a - \nu_e) = h\Delta\nu_a = W_0 - W_1 + \omega_1 \qquad (1)$$

$$h(\nu_e - \nu_0) = h\Delta\nu_e = W_0 - W_1 - \omega_0 \qquad (2)$$

$$h(\nu_{0-0} - \nu_0) = h\Delta\nu_{0-0} = W_0 - W_1 \qquad (3)$$

The most interesting quantity is $W_0 - W_1$, which gives directly the difference in H-bond energies of ground and excited states. In Fig. 1a ($W_0 > W_1$) we see that the usual expectations of the potential form predict that $W_0 > \omega_0$ and $\omega_1 > \omega_0$. No upper limit can be sey on ω_1 , since the steep side of the potential function could rise sufficiently fast to make $\omega_1 > W_1$ (Fig. 1a).

In any event, it will only be a coincidence if $\omega_1 = W_1$ and we see that $h\Delta\nu_a$ can be expected, a priori, to measure W_0. Since ω_1 is positive, eq. 1 predicts that if $W_0 > W_1$ then $h\Delta\nu_a > 0$, i.e., a blue-shift which exceeds the difference $W_0 - W_1$ by ω_1 will be observed in absorption. Similarly, in emission, a shift will be observed which is less than $W_0 - W_1$ by ω_0 (i.e., either a red shift or blue shift may be observed; in either case, the shift will be small compared to W_0). If $W_1 = 0$, no shift will be observed in emission since then $W_0 = \omega_0$.

In Fig. 1b ($W_0 < W_1$) the anharmonicity expectations predict that $W_1 > \omega_1$ and $\omega_0 > \omega_1$. Now the absorption spectrum will show a shift which is less by ω_1 than the red shfft implied by the negative value of $W_0 - W_1$. The emission spectrum will show a red shift exceeding $|W_0 - W_1|$ by ω_0.

If a blue shift absorption is observed Fig. 1a is applicable and the blue shifts exceeds the difference by $W_0 - W_1$. If a red shift is observed in absorption then Fig. 1b is applicable ($W_0 < W_1$) and the red shift is less than the difference $W_1 - W_0$. If only a small blue shift is observed in absorption, either of Figs. 1a or 1b could be applicable. Similarly, in emission, a blue shift implies Fig. 1a, a large red shift implies Fig. 1b, and a small red shift is ambiguous. Under any circumstances, $h\Delta\nu_a$ and $h\Delta\nu_e$ contain the quantity $h\Delta\nu_{0-0} = W_0 - W_1$.

The blue shift phenomenon has been used to characterize $n \rightarrow \pi^*$ transitions and to distinguish them from $\pi \rightarrow \pi^*$ transitions (red shifts).[8,9,10]

$\underline{n \rightarrow \pi^*}$. In the $n \rightarrow \pi^*$ transition, one of the electrons is promoted from the non-bonding orbital to an empty anti-bonding π-orbital. The one non-bonding electron remaining on the oxygen atom (for example, as in the carbonyl group) is not adequate to sustain the hydrogen bond and the excited state is de-stabilized. Hence the hydrogen bond is weakened in the process of promotion and the energy of transition is increased, (i.e. blue shift).

$\underline{\pi \rightarrow \pi^*}$. Again using the carbonyl group as an example. This transition further stabilizes the excited H-bonded state due to delocalization of the π electrons. Hence the transition energy is decreased i.e. a red shift is recorded.