

also be mentioned that the effect of hydrogen bonding on the excited states is similar to the other perturbing effect due to the substituents<sup>3-5</sup>.

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### A METHOD FOR DETERMINING AN EXPLICIT VALUE OF CHEMICAL SHIFT IN $\gamma$ -RESONANCE ABSORPTION BY SOLIDS

In the  $\gamma$ -resonance absorption by solids, the relative change in the energy of the isomeric states (absorber and source) due to the charge distribution of S-electrons around the Mössbauer nucleus is measured along with the shift in  $\gamma$ -ray energy due to second order Doppler effect. The total shift is called as centre shift<sup>1</sup>. The independence of isomer shift with temperature is known from the work of Preston *et al.*<sup>2</sup>. So in the resonance absorption of gamma-rays, elimination of the contribution of second order Doppler effect to centre shift is possible, if there is a definite difference of temperatures between the source and absorber when the Mössbauer isotopes are located in different host lattices which then will give an explicit value for isomer shift (chemical shift).

The energy  $E_s$  of the emitted  $\gamma$ -ray by a Mössbauer source incorporated in a host lattice can be given as a sum of transition energy  $E_0$ , the chemical shift  $\Delta E_c$  and the second order Doppler shift  $\Delta E_D$ <sup>3</sup>

$$E_s = E_0 + \Delta E_c + \Delta E_D \quad (1)$$

and similarly for the absorbing nucleus in another environment

$$E_A = E_0 + \Delta E_c' + \Delta E_D' \quad (2)$$

Substituting values<sup>4</sup> for  $\Delta E_c$  and  $\Delta E_D$  the energy shift in the  $\gamma$ -rays emitted by the source relative to the absorber can be given as

$$\begin{aligned} E &= (E_A - E_s) \\ &= \frac{2\pi ze^2}{5} (R_{es}^2 - R_{ed}^2) \{ |\psi(0)|_A^2 - |\psi(0)|_S^2 \} \\ &\quad + \frac{E_0}{2c^2} (\langle v^2 \rangle_A - \langle v^2 \rangle_s) \end{aligned} \quad (3)$$

where  $\langle v^2 \rangle_s$  and  $\langle v^2 \rangle_A$  are the mean square velocities of the emitting and absorbing nuclei respectively and the rest notations are well known. Since the Mössbauer isotope forms an impurity in the host lattice, the values of  $\langle v^2 \rangle_s$  and  $\langle v^2 \rangle_A$  are not equal in general. Evaluation of the values of  $\langle v^2 \rangle_s$  and  $\langle v^2 \rangle_A$  are rather complicated at low temperatures but somewhat simpler at the high temperature limit<sup>5</sup>. For a cubic crystal, in harmonic approximation, at high temperature limit, we can write  $\langle v^2 \rangle$  as

$$\langle v^2 \rangle \cong \frac{3KT}{M'} \left\{ 1 + \frac{1}{20} \frac{M}{M'} \left( \frac{\theta_D}{T} \right)^2 \right\} \quad (4)$$

Here  $M$  is the mass of the host atom and  $M'$  is the mass of the impurity and other notations are well known. Thus relation (3) can be written as

$$\begin{aligned} \delta E &\cong \frac{2\pi ze^2}{5} (R_{es}^2 - R_{ed}^2) \\ &\quad \times \{ |\psi(0)|_A^2 - |\psi(0)|_S^2 \} \\ &\quad + \frac{E_0}{2c^2} \left[ \left( \frac{3K_B T'}{M'} - \frac{3K_B T}{M'} \right) \right. \\ &\quad + \left. \left\{ \frac{3K_B T'}{M'} \frac{1}{20} \frac{M''}{M'} \left( \frac{\theta_D^A}{T'} \right)^2 \right. \right. \\ &\quad \left. \left. - \frac{3K_B T}{M'} \frac{1}{20} \frac{M}{M'} \left( \frac{\theta_D^S}{T} \right)^2 \right\} \right] \end{aligned} \quad (5)$$

The second term in (5) gives the second order Doppler shift relative to the absorber and will be zero under two conditions.

(i) If the source and absorber are at the same temperature and are located in the same host lattices, then the second term in (5) will vanish. In this case the first term will also be zero and so the resonant absorption will occur exactly at zero velocity of the source relative to the absorber.

(ii) If the source and the absorber are located in different host lattices and the Mössbauer experiment is performed at high temperature and the condition

$$\begin{aligned} T' \left[ 1 + \frac{M''}{20M'} \left( \frac{\theta_D^A}{T'} \right)^2 \right] \\ = T \left[ 1 + \frac{M}{20M'} \left( \frac{\theta_D^S}{T} \right)^2 \right] \end{aligned} \quad (6)$$

is satisfied, then the contribution in energy shift due to second order Doppler effect will be zero in the resonant absorption spectrum. In

this case we will have only the chemical shift. Table I shows the source temperature and the

TABLE I

Source and absorber temperatures for elimination of second order Doppler shift for  $\text{Co}^{57}$  in Pd host and  $\text{Fe}^{57}$  absorber in Fe

Source temperature (° K)	Absorber temperature (° K)
300	286.5
320	307.5
340	328.4
360	349.2
380	369.8
400	390.4

corresponding absorber temperature for the zero contribution of the second order Doppler effect in the centre shift. We have made the calculations using relation (6). The source is  $\text{Co}^{57}$  diffused in the Pd matrix and the absorber is  $\text{Fe}^{57}$ . We have used the values<sup>6</sup>  $\theta_D^s = 275^\circ \text{K}$  and  $\theta_D^a = 467^\circ \text{K}$ .

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### ADDUCTS OF COBALT ACETYLACETONATE WITH THIOUREA AND N-METHYL THIOUREA

DIVALENT cobalt ion having a  $3d^7$  non-bonding shell can form tetra-, penta-, or hexa-coordinated complexes depending on the polarisability of the ligand and experimental conditions. Adducts of acetylacetonates of  $\text{Co(II)}$ <sup>1</sup>,  $\text{Zn(II)}$ <sup>2</sup>,  $\text{Cd(II)}$ <sup>3</sup>,  $\text{Ni(II)}$ <sup>4</sup> and  $\text{Mn(II)}$ <sup>5</sup> with nitrogen donor ligands were reported earlier by previous workers. But adducts with sulphur donor ligands do not appear to have been reported earlier. In the present communication, two hexa-coordinated complexes of the

type  $\text{Co(acac)}_2\text{L}_2$ , where L is thiourea and N-methyl thiourea are reported.

The starting material diaquo bis-acetylacetonato cobalt(II) was prepared by adding ethanolic solution of acetylacetonate in stoichiometric ratio to an ethanolic solution of hydrated cobalt(II) chloride followed by dropwise addition of ammonia. The precipitated compound was suction filtered, washed with alcohol, ether and dried *in vacuo*. The mixed ligand complexes were prepared by refluxing cobalt acetylacetonate in ethanolic medium with the respective ligands in 1:2 ratio for about thirty minutes. On cooling the solution, the compounds separated which were suction filtered, washed with alcohol, ether and dried *in vacuo*. The purity of the compounds was established by estimating metal and sulphur. Conductance measurements were carried out in M/1000 acetone solution using a Toshniwal conductivity bridge. Magnetic susceptibility was determined on solid specimens using Gouy method. Infra-red spectra were recorded on Nujol mulls using a Unicam SP-200 spectrophotometer. Electronic spectra in the visible range were recorded in M/100 acetone solutions using SP-500 spectrophotometer. Analyses, conductance, magnetic susceptibility, infra-red and electronic spectral data are given in Tables I and II.

The octahedral stereochemistry of diaquo bis-acetylacetonate cobalt(II) has been confirmed<sup>6</sup> by X-ray analysis. The compounds reported in this communication are fairly soluble in acetone in which medium they are non-electrolytes. The compounds are paramagnetic indicating the presence of three unpaired electrons,  $\mu_{eff}$  values being 4.91 and 4.95 B.M. Figgis and Nyholm indicated<sup>7</sup> that  $\mu_{eff}$  values of octahedral cobalt(II) complexes lie between 4.8 and 5.2 B.M. The infra-red spectra reveal that  $\nu(\text{C}-\text{S})$  is shifted to lower frequency range indicating that thiourea is bonded through sulphur. The introduction of the additional heteroligand molecules may disturb the electron distribution round the metal atom resulting in shifts of  $\nu(\text{C}-\text{C})$  and  $\nu(\text{C}-\text{O})$  since they are involved in a resonating ring system<sup>8</sup> of acetylacetonate. The broad absorption band at  $3450 \text{ cm}^{-1}$  due to co-ordinated water molecules which appeared in diaquo bis(acetylacetonate) cobalt(II) is absent in the adducts indicating that the water molecules have been completely replaced by the heteroligands forming high spin octahedral complexes having the formula