A CORRELATION BETWEEN VOLATILITY AND MOLECULAR STRUCTURE: SPECTROSCOPIC ESTIMATION OF THE TEMPERATURE FOR ONSET OF SUBLIMATION IN METAL β-DIKETONATES

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The MOCVD technique for deposition of thin films is based on the availability of volatile metalorganic compounds. It is, therefore, necessary to understand the factors that control the volatilisation of a single molecule from its neighbourhood. Although metalorganic compounds, e.g., metal β-diketonates (1), are widely employed in MOCVD, only a few studies have been carried out on the sublimation processes of these β-diketonate class of precursors (2).

We have developed a theoretical model for the sublimation of large molecules such as β-diketonates, based on the concept that sublimation temperature is a manifestation of internal energy, *viz.*, the vibrational-rotational and electronic energy, of the subliming molecule. This model follows the sublimation mechanism given by Hirth and Pound (3), which states that the dis-association of molecule from lattice position is followed by diffusion of atoms/molecules in clusters on the surface, until they evaporate. The model was modified by taking into account of the simultaneous vibrational-rotational mechanism of diffusion, as proposed by several research groups (4-7). We assume that diffusion activation energy is small enough to be provided by the vibrational-rotational motion of the molecule and constituent groups at high temperatures, such as the sublimation temperature.

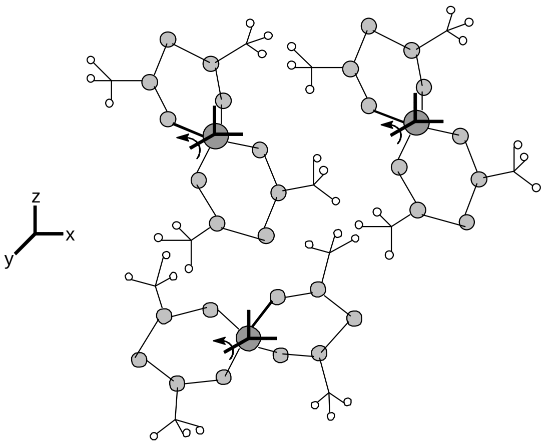

Fig.1: Schematic illustration of diffusion mechanism of $Co(pd)_2$ molecules in cluster: On detachment from their lattice positions, the molecules $Co(pd)_2$ are assumed to be physisorbed onto the surface of the crystalline lattice with the orientation of six-membered acetylacetonate ring parallel to the surface, *i.e.*, the xz plane. Individual molecules in the cluster undergo rotation around the y-axis, which passes through the centre of symmetry of each molecule and is normal to the plane of the paper. This in-plane rotation of individual molecules plays a role in shifting the positions of neighbouring molecules. This implies that diffusion activation energy is embodied in vibrational-rotational energy, as already noted above.

The following semi-theoretical equations were developed and used along with the IR, Raman, and UV-visible spectroscopic data, obtained at room temperature, in order to calculate the temperature for onset of sublimation, T_{onset} and the temperature for maximum rate of sublimation, T_{max} for tris(2,4-pentadionato)aluminium(III) [$Al(pd)_3$], tetrakis(2,4-pentadionato)zirconium(IV) [$Zr(pd)_4$], and bisaquo bis (2,4-pentadionato)cobalt(II) [$Co(pd)_2.2H_2O$].

$$(T_{onset}\alpha)^2 = hc/k_B*(iu_o/hc + n\sum\omega_i + \sum B_i + \sum\omega_r + 1/\lambda_{\pi\rightarrow\pi^*})$$

$$(T_{max.}\alpha - F)^2 = hc/k_B*(iu_o/hc + n\sum\omega_i + \sum B_i + \sum\omega_r + 1/\lambda_{\pi\rightarrow\pi^*}) + F^2$$

where α is a factor that is directly proportional to the number of molecules i in a cluster of molecules on the lattice surface at temperature T_{onset}, and inversely proportional to vib-rotational spectral broadening $\Delta\nu$, $\alpha = i/(\sum 17.26\Delta\nu_{i,\,298K})\ K^{-1/2}cm^{-1}$, u_o = lattice energy/molecule, h = Planck's constant, k_B = Boltzmann constant, c = velocity of light, n = number of pentadionate ligands per molecule, ω_i = IR band position, ω_r = band position in Raman spectra, B_i = rotational constant as determined from IR spectra, $\lambda_{\pi\rightarrow\pi^*}$ = wavelength associated with $\pi\rightarrow\pi^*$ electronic transition in the given molecule, and
$F = 10.422\times10^{-3}\sum(\Delta\nu_{i,\,298\,K})\ K^{1/2}cm^{-1}$.

It has been found that the values calculated for T_{onset} (based on the model described above) are in fairly good agreement with the experimental values obtained from thermogravimetric analysis. The results are summarised below:

Complex	T_{onset} (calc.)°C	T_{onset} (exp.)°C	T_{max} (calc.)°C
$Al(pd)_3$	113	100	139
$Zr(pd)_4$	143	130	168
$Co(pd)_2.2H_2O$	130	117	156

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