A P P E N D I X

Computational method used for the determination of integrated band intensity.

The mathematical basis of the least square technique employed for fitting the experimental absorbance data in terms of gaussian curves described by eqn. (3.5) (Chapter-III) is a follows.

For convenience, let us write the calculated absorbance at a frequency ν, A_ν, as

$$A_\nu = f(x_1, x_2, \ldots x_k) \qquad \ldots \quad (A.1)$$

where $x_1, x_2 \ldots, x_k$ are the k adjustable parameters of eqn. (3.5).

The residual, S, is then given by

$$S = \sum_\nu (A'_\nu - A_\nu)^2 \qquad \ldots \quad (A.2)$$

where A'_ν is the experimental value of absorbance.

The minimisation of S with respect to the adjustable parameters then require each derivative of the type $\partial s/\partial x_i$ to be zero at the minimum. This leads to the following set of normal equations:

$$\sum_\nu (A'_\nu - A_\nu) \frac{\partial A_\nu}{\partial x_i} = 0 \; ; \; i = 1, 2, \ldots k \quad \ldots \quad (A.3)$$

The nonlinear set of equations given by eqn. (A.3) are difficult to handle and are solved in practice by an iterative procedure after linearization as described below.

Let $x_1^0, x_2^0 \ldots x_k^0$ be the initial approximations to $x_1, x_2, \ldots, x_k$, respectively.

Using Taylor's expansion and neglecting cubic and higher order terms we have:

$$S = S_o + \sum_i \left(\frac{\partial S}{\partial x_i}\right)_o \Delta x_i + \frac{1}{2}\sum_i \sum_j \left(\frac{\partial^2 S}{\partial x_i \partial x_j}\right)_o \Delta x_i \, \Delta x_j \quad \ldots \qquad (A.4)$$

where the subscript 'o' refers to the values calculated with initial values of the parameters x_k's and

$$\Delta x_i = x_i - x_i^o \quad \text{etc.} \quad \ldots \qquad (A.5)$$

Differentiating eqn. (A.4) and equating to zero we get,

$$\left(\frac{\partial S}{\partial x_i}\right)_o \neq \sum_j \left(\frac{\partial^2 S}{\partial x_i \partial x_j}\right)_o \Delta x_j = 0 \quad \ldots \qquad (A.6)$$

Differentiating eqn. (A.2) we get,

$$\left(\frac{\partial S}{\partial x_i}\right)_o = -2 \sum_\nu (A_\nu^o - A_\nu) \left(\frac{\partial A_\nu}{\partial x_i}\right)_o \quad \ldots \qquad (A.7)$$

$$\left(\frac{\partial^2 S}{\partial x_i \partial x_j}\right)_o = 2 \sum_\nu \left[\left(\frac{\partial A_\nu}{\partial x_i}\right)_o \left(\frac{\partial A_\nu}{\partial x_j}\right)_o - (A_\nu^o - A_\nu) \left(\frac{\partial^2 A_\nu}{\partial x_i \partial x_j}\right)_o \right] \ldots (A.8)$$

Substituting these values into eqn. (A.6) and neglecting the terms containing second derivatives which are usually small, we get,

$$\sum_j \sum_\nu \left(\frac{\partial A_\nu}{\partial x_i}\right)_o \left(\frac{\partial A_\nu}{\partial x_j}\right) \Delta x_j = (A_\nu^o - A_\nu) \left(\frac{\partial A_\nu}{\partial x_i}\right)_o \quad \ldots \qquad (A.9)$$

$$\text{for } i = 1, 2 \quad \ldots . \quad k$$

The set of linear simultaneous equations given by eqn. (A.9) can be easily solved by standard technique to obtain a better approximation to x_i's. The process is repeated till the output of two successive iterations agree within prescribed limit.

In many cases, eqn. (A.9) resulted in ill-conditioned set of simultaneous equations. The computational procedure was, therefore, modified and the residual, S, was minimised with respect to one parameter at a time and the process was repeated till desired convergence was obtained. When one of the parameters, say, x_i is varied keeping all the others constant minimisation condition leads to the equation

$$x_i = x_i^0 + \sum (A_\nu^0 - A_\nu) \ (\partial A_\nu / \partial x_i)_0 \Big/ \sum \left(\frac{\partial A_\nu}{\partial x_i}\right)_0^2 \quad \ldots \ (A.10)$$

In order to avoid the uncertainity with the solution of ill-conditioned set of equations, successive approximations to x_i's were obtained through eqn. (A.10).

The numerical computations were carried on DCM Microsystem 1121.