

Interpolation of Franck-Condon Factors

In recent years, much effort has been expended to provide arrays of Franck-Condon factors $q_{v'v''}$ for many molecular band systems, particularly those of astrophysical and aeronautical interest because of the rapid growth of quantitative spectroscopic activity in aerospace and related fields. Many different straightforward analytical and numerical methods have been used in the calculation of q -arrays of various sizes appropriate to a number of molecular potentials of which the Morse potential has been the most popular. The calculation of a $q_{v'v''}$ array is in principle a simple task, though often formidable if an electronic computer and appropriate programme are not available.

In spite of the activity, many band systems remain to be treated. Some potential users of $q_{v'v''}$ values whose need for the data are, for example, for definitive identification of bands or band systems, or for estimates of radiative heat transfer from hot gases, are often satisfied by order of magnitude estimates of $q_{v'v''}$. It would thus be valuable to have a simple means of making such estimates. To this end it is natural to consider whether some form of interpolation could be applied to the $q_{v'v''}$ arrays which have already been calculated. A transition parameter t which varies from band system to band system and which may be used for interpolation is therefore required in order that plots of $q_{v'v''}$ versus t can be made for each (v', v'') band of interest.

The steady and systematic change of Franck-Condon factor surfaces from a sharp diagonal ($v'=v''$) ridge to broad axially symmetric nested horseshoe-shaped ridges and valleys, as Δr_e (the change in equilibrium internuclear separation) steadily increases¹, implies that Δr_e will be incorporated in any transition parameter. $q_{v'v''}$ is the vibrational overlap integral square and is thus controlled by the extent of overlap Δr between the two potentials at v' and v'' respectively. If r_1 and r_2 are respectively the smaller and larger of the classical turning points of the molecular oscillator in the v' th vibrational level, Δr can take the four possible values $r_2''-r_1', r_2'-r_1'', r_2''-r_1'', r_2'-r_1'$, depending upon the relative position and widths of the two potentials. A 'gross' Δr which might be applied to a whole band system (rather than just to the $v'-v''$ band) is proposed to be the overlap between the two potentials at, say, the D/K height of each, where D is the dissociation energy and $1/K$ is any fraction. A non-dimensional transition parameter $t = \Delta r_e / \Delta r$ is then proposed. It is relatively easy to show that for each of the above four values of Δr , and apart from an arbitrary constant involving the choice of K , that $\beta \Delta r_e$ is a very good approximation to t . β is the harmonic mean of the coefficients β' and β'' of $(r-r_e)$ in the two Morse potentials involved. (This is similar to the parameter $\beta \Delta r_e$ which was suggested some years ago² on purely empirical grounds for interpolation of approximate q -arrays. β is the arithmetic mean of β' and β'' .)

The usefulness for interpolation purposes of $\beta \Delta r_e$ as a transition parameter has been tested in plots of $\log q_{v'v''}$ versus $\log t$ for many (v', v'') combinations using $q_{v'v''}$ values taken from the 85 arrays of 'Morse' Franck-Condon factors ($0.02 < t < 4.7$) which have so far been computed to high quantum numbers using a straightforward method which has been described in detail elsewhere³. The plots are smooth and undulating with remarkably little scatter. If the plots are themselves arranged in a $v'-v''$ Deslandres array, it is observed that along the rows and columns $v_i = n, v_i = n, n+1 \dots (v_i$ or $v_i = v'$ or v'' respectively), each of the plots exhibits n maxima each of which moves to larger t as n increases. The maxima occur where a Condon locus⁴ moves through (v', v'') as t increases. A provisional approximate q -array can be read from such plots for an uncomputed band system the transition parameter, t , of which has been evaluated.

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GEOCHEMISTRY

Genetic Type of the Source Material for Common Leads

RECENTLY the following formula was presumed^{1,2} to hold in general between the concentration (C_x) of minor element X in a liquid and the corresponding concentration (C_x^0) in an infinitesimal solid just separated from the liquid:

$$\frac{C_x'}{C_x} = \text{constant} = k_x \tag{1}$$

where k_x is defined as a partition coefficient of element X . Mathematical development of this general equation and application of its result to a triple combination of lead, thorium and uranium lead to³:

$$\log(C_U/C_{Pb}) = b \log(C_{Th}/C_{Pb}) + \log(C_U^0/C_{Pb}^0) - b \log(C_{Th}^0/C_{Pb}^0) \tag{2}$$

$$\log(C_U'/C_{Pb}') = b \log(C_{Th}'/C_{Pb}') + \log\{(C_U^0 k_U)/(C_{Pb}^0 k_{Pb})\} - b \log\{(C_{Th}^0 k_{Th})/(C_{Pb}^0 k_{Pb})\} \tag{3}$$

and

$$b = (k_{Pb} - k_U)/(k_{Pb} - k_{Th}) \tag{4}$$

where C^0 refers to concentration of subscripted element in the initial material for the Earth's oxide sphere. Equation (2) expresses the change of relative concentrations of the elements concerned in liquid, and equation (3) the corresponding change in solid, with the progress of crystallization of silicate melt. These equations indicate that the relative changes of logarithms of concentration in liquid and solid are expressed graphically by two straight lines running parallel with each other. In turn it is not only possible but also of much significance to decide whether a correlation observed for abundances of some elements represents liquid or solid.

The treatment of data on isotopic analyses of common leads in ores has brought about the relationship⁴ written by:

$$\log(C_U/C_{204}) = 0.503 \log(C_{Th}/C_{204}) + 0.231 \tag{5}$$

where C_{204} stands for the concentration of lead-204, not of whole lead. It was pointed out⁵ that introducing the relevant chondritic abundances into equation (2) gave a result in agreement with the empirical equation (5), a fact suggesting that the source material for common leads is of a liquid type, not solid.

According to our model^{1,2} based on the geochemistry of lanthanides, on the other hand, the rock of the mantle as a whole is inferred to be a solid-type material which represents the aggregate of crystals segregated from the liquid. The partial melting of the mantle material can