Chapter-IV

FRANCK-CONDON FACTORS & r-CENTROIDS

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4.1 Introduction:

Franck-Condon Factors are useful in determining the relative transition probabilities of bands in different band systems of molecule. The problem of transition probabilities needs careful study as they differ for the same system from one excitation condition to other. According to quantum mechanics, the transition probabilities and the intensities of transitions can be calculated by evaluating the integral of the product of the electric moment and the wave functions of initial and final states, where the integration is carried out over all co-ordinates of the electrons and nuclei. But as the wave-functions and the electric moments cannot be given uniquely, different methods and approaches are suggested by different workers.[1to14] Here, we have selected a few of them to calculate F.C. factors in a number of band systems of different diatomic molecules.

4.2 Different Methods for Computation of F.C.Factors:

4.2.1 Hutchisson Method:[1,2]

Hutchisson calculated the intensity of special line in the new quantum mechanics by evaluating the integral of the product of electric moment and the wave-functions of intial and final state. The integration is carried out using harmonic oscillator wave functions, whose origins are shifted due to change of the nuclear separation during the electronic transition.

According to Condon,[15] the measure of intensity is given by the expression:

$$I = \int\int m(x_1 r)\psi_{e'n'}(x_1 r)\psi_{e''n''}(x_1 r)\, dx\, dr \quad \ldots (4.1)$$

where m = the instantaneous electric moment, $\psi_{e'n'}$ and $\psi_{e''n''}$ are the wave functions of initial and final state, $x_1 r$ are the total coordinates of the electron and the nuclei respectively, $e_1 n$ are the electronic and vibrational quantum numbers.

According to Born and Oppenheimer,[16] the complete wave function ψ_{en} can be expressed as a product of an electronic wave function $\Phi_e(x)$ and an oscillatory wave function $\psi_{en}(r)$. The oscillatory wave function $\psi_{en}(r)$ corresponds to the motion of nuclei moving under an effective force arising from the moving electrons and the repulsion of the nuclei. Hence,

$$I = \int\int m(x_1 r)\Phi_{e'}(x)\psi_{e'n'}(r)\Phi_{e''}(x)\psi_{e''n''}(r)\, dx\, dr \quad \ldots (4.2)$$

The electric moment is defined as the vector sum of the coordinates of the electrons times their charge and coordinates of nuclei times their charge. This may be expressed as:

$$M(x_1 r) = A(x) + B(r) \quad \ldots (4.3)$$

The first term will be a constant because during electron transition, nuclei remain practically fixed. The second term will be a function of only the nuclear coordinates, because the heavy nuclei cannot respond immediately to the changes in the electronic arrangement.

Hence,

$$I = \int A(x)\Phi_{e'}(x)\Phi_{e''}(x)dx \int \psi_{e''n''}(r)\, dr +$$

$$\int \Phi_{e'}(x)\Phi_{e''}(x)dx \int B(r)\psi_{e'n'}(r)\psi_{e''n''}(r)\, dr$$

The integration involving the electron coordinates will be constant so that,

$$I = C_1\int \psi_{e'n'}(r)\psi_{e''n''}(r)\, dr + C_2\int B(r)\psi_{e'n'}(r)\psi_{e''n''}(r)\, dr$$

In case of symmetrical diatomic molecules, nuclear electric moment is always zero, i.e. the second term drops, so that:

$$I = C_1\int \psi_{e'n'}(r)\psi_{e''n''}(r)\, dr \qquad \ldots (4.6)$$

The aim of Hutchisson's method is to evaluate this integral.

With the harmonic oscillation approximation, the agreement of their method with number of cases was only fair.

Hutchisson developed his method by taking into account anharmonicity to a certain approximation. He applied this method to H_2 absorption and observed that the agreement is improved. For higher vibrational quantum numbers, the method produces some complications. But as the method is historically the first, it creates interest among the astrophysicists.

4.2.2 Bates Method:[3,4]

D.R. Bates has given a general set of tables from which it is possible to obtain relative transition probabilities in a band system of diatomic molecules, if the spectroscopic constants r_e, ω_e and x_e are known. Two methods for obtaining transition probabilities are described. One is appliicable if the electronic transition causes a small or moderate change in the equilibrium internuclear separation and the other is applicable if the change is moderate or large.

The electronic part of a molecular transition matrix element depends on r, the internuclear separation. But as the dependence is not too marked, it can be ignored and the spontaneous transition probability can be written as:

$$V(v'v'')^3 \; P(v',v'')^2 \qquad \ldots \quad (4.7)$$

where, $V(v',v'')$ is the frequency of radiation emitted, and

$P(v',v'')$ is the nuclear overlap integral.

$$\int P(r/v',A)\; P(r/v'',B)\; dr \qquad \ldots \quad (4.8)$$

$P(r/v',A)$ and $P(r/v'',B)$ are the normalized vibrational wave functions. $P(v'v'')^2$ is the important dimensionless quantity and because of its connection with Franck Condon Principle, it is referred as Franck-Condon factor of the particular band system.

In detailed calculations, the wave functions P are best represented by Morse approximation, but it is observed that such representation is not convenient in a more general investigation. The researches of Gaydon and Pearse,[17] Pillow[9,10] and Nicholls[18] show that the simple harmonic approximation of Hutchisson is satisfactory if it is allowed for distortion.

Method (1):

Change of equilibrium internuclear separation is small or moderate:

The constants required for the calculation of Franck-Condon factors are the reduced mass (μ), the equilibrium internuclear separations (r_e), the vibration constants (ω_e) and the anharmonic constants (x_e). For convenience, both the parameters and vibrational quantum numbers of the electronic states concerned in transition are distinguished by fixing the subscript 'S' to all quantities associated with the state, having the small ω_e value and the subscript 'L' to all quantities assocciated with the state having larger ω_e values. Therefore, r_{es}, ω_{es}, X_{es}, V_s are the parameters and vibrational quantum numbers of one state, i.e. state having smaller ω_e and r_e, ω_{eL}, X_{eL} and v_L are those of other state, i.e. state having larger ω_e. Then by definition, $\omega_{es}<\omega_{eL}$.

The nuclear overlap integrals will always be written as $P(v_s, v_L)$, i.e. the vibrational quantum number of S state will be placed before that of L state.

The molecule in both electronic states is regarded as simple harmonic oscillator, i.e. $X_{es}=X_{eL}=0$.

Hutchisson[1,2] has given formulae for the overlap integrals, $q(v_s, v_L)$ corresponding to this model. From these formulas, it is possible to express $q(v_s,v_L)$ for any chosen v_s and v_L values as a function of ω_{eL}/ω_{es} and a quantity Δ defined by:

$$\Delta = 2\Pi(\mu\omega_{eL}/h)^{\frac{1}{2}}[r_{es}-r_{eL}] \quad \ldots (4.9)$$

where, h = Planck's constant

The above equation can be written as $\Delta = 0.172 (\mu\omega_{eL})^{\frac{1}{2}}[r_{es}-r_{eL}]$.

$q(v',v'')$ is either a symmetrical or an antisymmetrical function of according to whether $(v'+v'')$ is even or odd. Therefore, it is sufficient to consider positive Δ only. There are cases of negative Δ, but they are rare because according to Birge-Mecke empirical rule the product of $r_e^2\omega_e$ has about the same value for all electronic states of any one molecules.

Bate's double entry table gives $q(v_s,v_L)$ as a function of ω_{eL}/ω_{es} and for all combinations of v_s and v_L, such that,

$$v_s + v_L = 4$$

For, $v_s = 0, \quad v_L = 5,6$

$v_L = 0, \quad v_s = 5,6$

They cover the ranges, $\omega_{eL}/\omega_{es} = 1.0(0.1)1.6$

$$\Delta = 0.0(0.1)5.0$$

In order to have a better approximation to $P(v_s,v_L)$, it is necessary that the potential of electronic state of a molecule should differ from the potential of simple harmonic oscillator. This matter has been investigated by Hutchisson, but his treatment is complicated.

In the region of minimum, the difference between potentials may be taken as,

$$-hc/4\ [8\Pi^2 c\mu/h]^{3/2}\omega_e^{5/2}\ x_e^{1/2}(r-r_e)^3 \qquad \ldots\ (4.10)$$

As this small, the first order perturbation theory is used to expand the true wave functions, P(r/v), in terms of the corresponding simple harmonic wave functions Q(r/v), as

$$\begin{aligned} P(r/v) = {} & Q(r/v) + x_e^{\frac{1}{2}}\ \{[v(v-1)(v-2)]^{\frac{1}{2}}Q(r/v-3)+[(3v)^{3/2}/4] \\ & Q(r/v-1)\ -3(v+1)^{3/2}/4\ Q(r/v+1)\ -\ [(v+1)(v+2)(\underline{v}+3)]^{\frac{1}{2}}/12 \\ & Q(r/v+3)\} \qquad \ldots\ (4.11) \end{aligned}$$

This is not the first order change in the energy levels. Substituting equation (4.11) in equation (4.8) and neglecting the terms involving the product $x_{es}^{\frac{1}{2}}x_{eL}^{\frac{1}{2}}$,

$$P(v_s,v_L) = q(v_s,v_L) + x_{es}^{\frac{1}{2}}S(v_s,v_L) + x_{eL}^{\frac{1}{2}}L(v_s,v_L)\ldots \qquad (4.12)$$

where,

$$\begin{aligned} S(v_s,v_L) = {} & \{[v_s(v_s-1)(v_s-2)]^{\frac{1}{2}}/12\quad q(v_s-3,v_L) + 3v_s^{3/2}/4 \\ & q(v_s-1,v_L) - 3(v_s+1)^{3/2}/4\ q(v_s+1,v_L) - \\ & [(v_s+1)(v_s+2)(v_s+3)]^{\frac{1}{2}}/12\quad q(v_s+3,\ v_L)\} \quad \ldots \quad (4.13) \end{aligned}$$

and

$$\begin{aligned} I(v_s,v_L) = {} & \{[v_L(v_L-1)(v_L-2)]^{\frac{1}{2}}\ q(v_s,v_L-3) + 3v_L^{3/2}/4\ q(v_s,v_L-1) \\ & -3(v_L+1)^{3/2}/4\quad q(v_s,v_L+1)\quad - \\ & [(v_L+1)(v_L+2)(v_L+3)]^{1/2}/12\quad q(v_s,v_L+3)\} \quad \ldots\ (4.14) \end{aligned}$$

In Bates double entry table, values of $s(v_s,v_L)$ and $I(v_s,v_L)$ are given, where $v_s + v_L < 3$.
the range of ω_{eL}/ω_{es} is from 1.10 to 1.6 and that of Δ is from 0.0 to 2.2.

Method (2):

Change of equilibrium internuclear separation is moderate or large:

When the equilibrium internuclear separation is sufficiently great, the cancellation effects in the overlap integral are less important. In this case, Franck-Condon factors can be obtained by using comparatively crude wave function. The simple harmonic approximation can be readily applied with the aid of $q(v_s,v_L)$ tables, which cover a wider range of than do the $S(v_s,v_L)$ and $I(v_s,v_L)$ tables. In this case, increased accuracy can be obtained with some additional labour.

The major contribution to each overlap integral arises from the region between the equilibrium internuclear separations of the two electronic states. In the simple harmonic approximation, an effective vibrational constant ω_e' is introduced to each wave function to make partial allowance for the symmetry of the molecular potential. ω_e' is greater or less than actual vibrational constant. ω_e according to whether the electronic state concerned has a smaller or larger equilibrium internuclear separation. Attempts are made to determine the value of this new constant. Here the simple harmonic potential is adjusted so that at the point mid-way between the equilibrium internuclear separations they become equal to the corresponding Morse potentials.

$$a = [(2\Pi^2 c\mu\omega_e x_e) / h]^{\frac{1}{2}} \cdot d \qquad \ldots (4.15)$$

where, d = the modulus of the difference between the equilibrium separations.

It is seen that this is equivalent in taking,

$$\omega_e' = \omega_e[1-\exp(\pm a)/+a]$$

$$= \omega_e[1\pm\tfrac{1}{2}a] \qquad \ldots \quad (4.16)$$

The upper sign refers to the state with larger r_e value and lower signs to the state with the smaller r_e. Above equation can be written in a more convenient form, as:

$$\omega_e' = \omega_e[1\pm 0.06d\ (\omega_e x_e \mu)^{\frac{1}{2}}]$$

In order to get further improvement, the central turning points or zeros of the simple harmonic functions are made to coincide with those of the corresponding function. This requires the introduction of an effective equilibrium internuclear separation r_e', such that

$$r_e' = r_e + \delta \qquad \ldots \quad (4.17)$$

where, $\delta = [hx_e/8\Pi^2\mu c\omega_e]^{\frac{1}{2}}\cdot(v+1) = 4.11[x_e/\mu\omega_e]^{\frac{1}{2}}\cdot(v+1)$ angstroms

Then the method of finding Franck-Condon factors consists of labelling the electronic states S and L, so that,

$$\omega_{es}' < \omega_{eL}'$$

Then, as before $q(v_s, v_L)$ values are taken from the Table with the use of the variables $\omega'_{eL}/\omega'_{es}$ and Δ given by,

$$\Delta'(v_s, v_L) = 0.172(\mu\omega'_{eL}) \quad \{(r_{es} + \delta_L) - (r_{eL} + \delta_L)\} \quad (4.18)$$

Generally, $\omega'_{eL}/\omega'_{es} < \omega_{eL}/\omega_{es}$ which has the effect of bringing additional band systems within the tabulated range.

The first method is not significantly less accurate than the second, although the second method itself does not yield results of such high precisions. It is useful for many purposes, since the method is applicable in the range $v_s + v_L < 4$, it is somewhat restricted.

4.2.3 Manneback's Method:[5]

In order to get Franck-Condon factors, Manneback[5] developed the method of evaluating Condon's overlap integral. He supposed the oscillator to be harmonic. He gave two fundamental formulae for Condon's overlap integral which are useful to obtain Franck-Condon factors.

The probability amplitudes or transition moments for an electronic vibrational transition is given by Condon's overlap integral,

$$((n', n'') = \int_0^\infty \psi_{n'}(R)\psi_{n''}(R) \cdot dr$$

where, R = the internuclear distance,

n'' = the vibrational quantum number in the lower ground state,

n' = the vibrational quantum number in the upper electronic (excited) state.

ψ's represent the corresponding normalized vibrational eigenfunctions.

The observed relative intensities in the vibrational spectrum are proportional to the square of c's (transition probabilities) and also to the fourth power of the line frequency and to the number of molecules present in the initial state (electronic and vibrational). All line intensities are moreover proportional to a common factor, the purely electronic transition probability between upper and lower state. This factor is considered to be independent of internuclear distance, at least in the first approximation. If its dependence on R is considered, it would lead to an additional computation of an integral over $R \cdot \psi_{n'}(R)\psi_{n''}(R)$, which can be obtained as straightforwardly as Condon's integral.

An important property of the c's is that they build a real orthogonal matrix and this property is independent of any particular hypothesis made on the oscillator, such as harmonicity. In this procedure, $\sqrt{n'n''}$ and $\Gamma(n'n'')$ are defined as:

$$\Gamma(n',n'') = C(n',n'') \, / \, C(0,0)$$

$$\sqrt{n',n''} = (2^{n'+n''}/n'!n''!)^{\frac{1}{2}}\Gamma(n'n'')$$

$$\therefore \; C(n',n'') = \int_{-\infty}^{\infty} \psi_{n'}\psi_{n''} \; dr$$

$$= \sqrt{n',n''} \quad C_{(00)} \left\{\frac{n'!n''!}{2^{n'+n''}}\right\}$$

$$\text{where, } C_{(00)} = \exp(-\tfrac{1}{2}M^2) \, (\text{Sin}2\theta)^{\frac{1}{2}}$$

$$= \exp(-\tfrac{1}{2}M^2)(k^+)^{\frac{1}{2}} \qquad \ldots \quad (4.23)$$

$$M = 0.172205\ \mu^{\frac{1}{2}}(r'_e - r''_e)\ [\nu'\nu''/(\nu'+\nu'')]^{\frac{1}{4}} \qquad \ldots \quad (4.24)$$

and

$$\surd n',n'' = \sum_{n=0}^{n' \text{ or } n''} [(2k^+)^q \surd(0,n''-q)\ \surd(n'-q,0)\ \ /q \qquad \ldots \quad (4.25)$$

are the coefficients of $\frac{s^{n'}t^{n''}}{n'!n''!}$ in the expansion of

$$\exp[(t^2-s^2)K + 2tsk^+ + b2^{\frac{1}{2}}t - a2^{\frac{1}{2}}s]$$

where, $K = \mathrm{Cos}2\theta = (\nu''-\nu')/(\nu'+\nu'')$

$K^+ = \mathrm{Sin}2\theta = (2\nu'\nu'')^{\frac{1}{2}}/(\nu'+\nu'')$

$a = 2^{\frac{1}{2}}\mathrm{Cos}\theta = M[(2\nu''/(\nu'+\nu'')]^{\frac{1}{2}}$

$b = 2^{\frac{1}{2}}\mathrm{Sin}\theta = M[2\nu'/(\nu'+\nu'')]^{\frac{1}{2}}$

Manneback has given two fundamental formulae for C(n',n") as,

$$\begin{aligned} C(n'+1,n'') &= -[n'/(n'+1)]^{\frac{1}{2}}\ KC(n'-1,n'') + \\ &\quad +[n''/(n'+1)]^{\frac{1}{2}}\ k^+C(n',n''-1) - \\ &\quad -(n'+1)^{-\frac{1}{2}}\ ac(n',n'') \end{aligned}$$

$$\begin{aligned} C(n',n''+1) &= +[n''/(n''+1)]^{\frac{1}{2}}\ KC(n',n''-1) + \\ &\quad +[n'/(n''+1)]^{\frac{1}{2}}\ k^+C(n^1-1,n'') + \\ &\quad +(n''+1)^{-\frac{1}{2}}\ bc(n',n'') \end{aligned} \qquad \ldots \quad (4.26)$$

These formulas are valid and simplify for progressions n'=0 or n"=0. Thus, the sides of the C-matrix array are obtained. One can then proceed computing successively lines parallel or perpendicular to the initial one chosen using either of the two recurrence formulas. At each stp, there is already mentioned check of orthogonality.

Formula (1) can be used to compute a progression in n" or in n'. The latter case requires only the data of the preceding progression, whereas the former requires the data of two preceding progressions. If an automatic computer is used, the requirements of memory will be less if a progression in n' is calculated by formula (1) and progression in n" by formula (11).

4.2.4 Extension of Manneback Method:[6]

In Manneback's Method, it is considered that both the electronic states under consideration provide a perfectly harmonic potential for nuclear vibration. Manneback and Rehman[6] have extended this method, taking into account te effect of electrical anharmonicity while conserving the mechanical harmonicity of the two electronic potentials. They have found out the vibrational transition probabilities of OH $A^2\Sigma^+ \rightarrow X^2\Pi$ system. They have examined the relative merits and demerits of their method and Hutchisson method. It is observed that the method is extremely simple and very handy for computation.

Manneback and Rehman have obtained the recurrence relations by a close parallel treatment as that of Manneback. In the Manneback's method, the recurrence relations are given for

$$C(n'n'') = {}_0\int^{\infty} \psi_{n'}(R)\psi_{n''}(R)\ dr.$$

In this method, the recurrence relations are obtained for,

$$D(n',n'') = {}_0\int^{\infty} \psi_{n'}(R).R.\psi_{n''}(R).dR \qquad \ldots (4.27)$$

ψ_n are given by,

$$\psi_{n'}(R) = N'e^{-\eta^2/2}H_{n'}(\eta) \qquad \ldots (4.28)$$

where, $N' = (e'2^{n'}\eta'!\sqrt{\Pi})^{-\frac{1}{2}}$

$e' = (h/4\Pi^2\mu\nu')^{\frac{1}{2}}$

$\eta = (R-R')/e'$

ν' = vibration frequency of particular electronic state,

R' = the equilibrium distance

μ = the reduced mass

$Hn(\eta)$ = the Hermite polynomials.

Exactly, as for $C(n',n'')$, it is easy to show that $D(n'n'')$ is the coefficietn of $(S^{n'}/n'!)(t^{n''}/n''!)$ in the expansion of

$$N'N''\int_{\infty}^{\infty} e^{-\frac{1}{2}|\xi^2+\eta^2|+2\xi t+2\eta s-t^2-s^2} RdR$$

$$= N'N'e^{\omega}\int_{-\infty}^{\infty} e^{-\frac{1}{2}[rB-R/r]^2} RdR$$

$$= N'N''e^{\omega}r^3\sqrt{2\Pi}B \qquad \ldots (4.29)$$

where r is the unit length given by,

$$r^{-2} = (\rho')^{-2} + (\rho'')^{-2} = 4\Pi^2\mu(\nu'+\nu'')/n \qquad \ldots (4.30)$$

$$\omega = (t^2-s^2)\mathrm{Cos}2\theta + 2t\mathrm{Sin}\theta + 2m\ (t\mathrm{Sin}\theta-s\mathrm{Cos}\theta)-\tfrac{1}{2}M^2 \quad .. (4.31)$$

The new quantity B is defined as,

$$r^2B = (R'\mathrm{Sin}^2\theta+R''\mathrm{Cos}^2\theta) + 2s(\rho'\mathrm{Sin}^2\theta) + 2t(e''\mathrm{Cos}^2\theta). \qquad (4.32)$$

with $\tan\theta = \sqrt{\nu'/\nu''} = e''/e'$ and $r = e''\mathrm{Cos}\theta = e'\mathrm{Sin}\theta$ ... (4.33)

For simplicity, we shall write,

$$r^2B = X + Ys + Zt \qquad \ldots \quad (4.34)$$

As given in the Manneback method $C(n'n'')$ is the coefficient of $(S^{n'}/n'!)(t^{n''}/n''!)$ in the expansion of $N'N''e^{\omega}r\sqrt{2\Pi}$, it can be seen that,

$$\begin{aligned}\sum D(n',n'')(S^{n'}/n'!) &= r^2B\sum C(n',n'')(S^{n'}/n'!)(t^{n''}/n''!)\\ &= (X+Ys+Zt)\sum C(n',n'')(S^{n'}/n'!)(t^{n''}/n''!)\end{aligned} \qquad \ldots \quad (4.35)$$

Therefore, $D(n',n'')$ is given by,

$$D(n',n'') = XC(n',n'') + Yn'C(n'-1,n'') + Zn''C(n',n''-1) \qquad \ldots \quad (4.36)$$

where,

$$\left.\begin{aligned} X &= (R'\mu' + R''\nu'')/(\nu'+\nu'')\\ Y &= 2r\mathrm{Sin}\theta\\ Z &= 2r\mathrm{Cos}\theta\end{aligned}\right] \qquad \ldots \quad (4.37)$$

Therefore, once the matrix $C(n',n'')$ has been tabulated according to the rule given by Manneback, the tabulation of the matrix, $D(n',n'')$ is quite straightforward.

The electric dipole moment between the two electronic states as is taken as,

$$M_{e',e''}(R) = C(1+eR) \qquad \ldots \quad (4.38)$$

Its matrix element calculated between vibrational states n',n'' is

$$M_{n',n''} = C[n',n'') + eD(n',n'')] \qquad \ldots \quad (4.39)$$

The coefficient ρ in the above expression may be estimated by taking the ratios of integrated intensities.

Manneback and Rehman have calculated the values of $|M_{nm}|^2$ under different conditions. They found out that with a negative e, the intensities tend to increase for $n' > n''$ and tend to decrease for $n' < n''$.

4.2.5 Fraser and Jarmain Method:[7,8]

Fraser and Jarmain method[7] consists of evaluating the so-called overlap integral using wave functions in Morse type. The overlap integral is given by,

$$(v',v'') = \int_0^\infty \psi_1(v')\psi_2(v'')\, dr \qquad \ldots \quad (4.40)$$

when a Morse function,[19]

$$U_{i(r)} = D_i\{1-\exp[-\alpha_i(r-r_{ei})]\}^2 \qquad \ldots \quad (4.41)$$

represents the potential of nuclear vibration in the electronic state i, the vibrational wavefunction for level v is given by, ignoring phase factor,

$$\psi_i(v) = [\alpha_i(k_i-2v-1)/v!\Gamma(k_i-v)]^{\frac{1}{2}}\,[\exp(-z_i/2)]\; Z_i^{(k_i-2v-1)/2}\,(-1)^v \times$$

$$\sum_{k=v}^{v} (-1)^k \binom{v}{k} \times [\Gamma(k_i-v)/\Gamma(k_i-v-k)]\; Z_i^{v-k} \qquad \ldots \quad (4.42)$$

$$= N_i^{(v)}[\exp(-Z_i/2)]Z_i^{(k_i-2v-1)/2}\; L_{k_i-v-1}^{k_i-2v-1}(Z_i) \qquad \ldots \quad (4.43)$$

Here, $L_{k_i-v-1}^{k_i-2v-1}(Z_i)$ = the associated laguerre Polynomial of degree v in Z_i,

$$Z_i = K_i\exp[-\alpha_i(r-r_{ei})] = \lambda_i\exp(-\alpha_i r) \qquad \ldots \quad (4.44)$$

k_i and D are related to the constants in the vibrational energy expression, $E_i(v) = (\omega_e)_i(v+\frac{1}{2}) - (\omega_e x_e)_i(v+\frac{1}{2})^2$ ... (4.45)

$$k_i = (\omega_e)_i/(\omega_e x_e)_i, \quad D_i = (\omega_e)_i^2/4(\omega_e x_e)_i, \quad (\omega_e x_e)_i = (h/4\Pi C\mu_i)\alpha_i^2 \qquad \ldots \quad (4.46)$$

μ_i is the reduced mass of the molecule in the state i.

Integrating the integral in equation (4.40) from - to ,

$$(v',v'') = \int_{-\infty}^{\infty}\psi_1(v')\psi_2(v'')\,dr$$

$$= (-1)^{(v'+v'')} N_1^{(v')} N_2^{(v'')} \lambda_1^{(k_1-1)/2} \lambda_2^{(k_2-1)/2}$$

$$(-1)^{k+l} \genfrac{}{}{0pt}{}{v'}{k} \genfrac{}{}{0pt}{}{v''}{k} \;\mathbf{X}\; [1/\lambda_1\lambda_2]$$

$$[\Gamma(k_1-v')\Gamma(K_2-v'')/\Gamma(k_1-v'-k)\Gamma(K_2-v''-l)] \; J(kl) \qquad \ldots \; (4.47)$$

$$\text{where, } J(kl) = \int_{-\infty}^{\infty} dr \, \exp\{-\tfrac{1}{2}[\lambda_1 \exp(-\alpha_1 r) + \lambda_2 \exp(-\alpha_2 r)]\} \;\mathbf{X}$$

$$\exp\{-([\tfrac{1}{2}(K_1-1)-k]\alpha_1 r + [\tfrac{1}{2}(K_2-1)-l]\alpha_2 r)\} \qquad \ldots \quad (4.48)$$

The J(kl) cannot be evaluated exactly as $\alpha_1 \neq \alpha_2$. Hence $U_1(r)$ and $U_2(r)$ are replaced by new potentials, $U_1'(r)$ and $U_2(r)$. The new potentials have their α-value equal to some mean of the original α_1 and α_2. It is easiest to take the arithmetic mean $\alpha = \frac{1}{2}(\alpha_1+\alpha_2)$. Then, the adjusted molecular constants are as follows:

$$\left.\begin{array}{llll} K_1' = K(\alpha_1/\alpha)^2, & & K_2' = K_2(\alpha_2/\alpha)^2 \\ \lambda_1' = K_1' \exp\alpha r_{e1} & & \lambda_2' = K_2' \exp\alpha r_{e2} \\ \alpha_1 = \alpha + \delta r, & & {}_2 = \alpha - \delta r \end{array}\right| \quad \ldots \; (4.49)$$

Hence, it is seen that the errors introduced will be proportional to $|\delta\alpha/\alpha|$ and the error will be less, the smaller the overlapping of two potentials. Small values of $|\delta\alpha/\alpha|$, i.e. 5%, imply slight change in the description of the states and the wave functions in the new potentials are seen to be suitable for the evaluation of overlap integral.

(v',v") takes the same form as in equation (4.47). But J(kl) now is given by,

$$J(k,l) = \int_{-\infty}^{\infty} dr \, \exp\{-[\lambda \exp(-\alpha r)]\} \, \exp\{-[(K-1)-(k+l)]\alpha r\}$$

$$= J(k+1) \qquad \ldots \qquad (4.50)$$

where, $K = \frac{1}{2}(K_1+K_2)$, $\lambda = \frac{1}{2}(\lambda_1+\lambda_2)$

J(k+l) can now be integrated exactly,

$$J(k+l) = \frac{1}{\alpha}\left(\frac{1}{\lambda}\right)^{(k-1)-(k+l)} \Gamma[(k-1-(k+l)] \qquad \ldots \qquad (4.51)$$

Hence, the overlap integral given by equation (4.40) can be evaluated and the Franck-Condon factors are given by,

$$P(v',v") = (v',v")^2 \qquad \ldots \qquad (4.52)$$

In the above discussion, the Morse constant α is replaced by averaging α_1 and α_2. This method is also known as α-averaging method.[10]

Fraser and Jarmain[8] have modified this method for $|\delta\alpha/\alpha| > 5\%$. In this method, the new potentials are replaced into the original one by changing the equilibrium internuclear distance r_e for the electronic state with $|\delta\alpha/\alpha| < 5\%$. This is called the method of r_e-shift.

Using Pekeris[20] vibration-rotation wave function, the effect of vibration-rotation interaction on these integrals can be calculated with α-average method. But as the method involves the distortion of potential curves, the errors will increase as $(\alpha_1-\alpha_2)$ and (v_1+v_2) increases.

4.3 r-Centroids:

4.3.1 Concept of r-centroid:

The characteristic internuclear separation associated with v'-v" band of a diatomic molecular band system is called the r-centroid. The concept of r-centroids was first introduced by Nicholls and Jarmain.[21] Fraser[22] suggested an approximation for calculating matrix elements of function of r. This approximation is used to determine r-centroids. The matrix elemetnts of $R_e(r)$ between different vibrational wave functions is given by,

$$\langle v'/R_e(r)/v''\rangle \simeq R_e(\bar{r}_{v',v''}) \quad \langle v'/v''\rangle \qquad \ldots \quad (4.53)$$

$\bar{r}_{v',v''}$ are r-centroids given by

$$\bar{r}_{v'v''} = \langle v'|r|v''\rangle / \langle v'|v''\rangle \qquad \ldots \quad (4.54)$$

The correctness of equation (4.53) depends upon the validity of the equation,

$$\langle v'|r^n|v''\rangle \cong (\bar{r}_{v'v''})^n \langle v'|v''\rangle \qquad \ldots \quad (4.55)$$

This equation follows from the approximate equality of the following quantities,

$$\frac{\langle v'|r^n|v''\rangle}{\langle v'|r^{n-1}|v''\rangle} = \frac{\langle v'|r^{n-1}|v''\rangle}{\langle v'|r^{n-2}|v''\rangle} = \qquad = \frac{\langle v'|r^n|v''\rangle}{\langle v'|v''\rangle} \ldots \quad (4.56)$$

If the equation (4.56) is true for all n, then the equation (4.55) would be correct. Nicholls and Jarmain have found that the equations are valid provided that,

1) $\mu_A \omega_e \simeq 10^4$ for molecule under consideration,
2) $0.01A^\circ < |r_{e1} - r_{e2}| < 0.25A^\circ$, r_{e1} and r_{e2} are the two equilibrium internuclear separations considered in transition,
3) v' and v" do not exceed 10,
4) The highest power of r should not exceed 10.

r-centroids may be considered as some sort of average r, involved in particular (v'v") band. It is also regarded as the r-coordinate of the centroid of the area represented by the overlap integral from which its suggested name is derived.

4.3.2 Determination of r-centroids:

Nicholls and Jarmain[23,24] have suggested three methods for the evaluation of r-centroids. These are:

1. Direct Method
2. Difference Method,
3. Mean Value Method, with two submethods,
    a) Quadratic Equation Method, and
    b) Graphical Method.

The direct method consists of evaluation of the integrals of the type $\int \psi_{v'} r \psi_{v''} dr$ and $\int \psi_{v'} \psi_{v''}$ by analytical or numerical procedures. Both the methods are laborious, tedious and cumbersome. Hence, the other methods are considered as easier methods.

The Difference Method depends on its application on the constant value v. It was observed that there is a constant difference in the value of r-centroid along the sequence. With the knowledge of this difference and with the value of r-centroid of a leading member of a sequence, it is possible to build up a complete set of $\bar{r}_{v',v''}$ values.

Out of the two submethods of the Mean Value Method, the Quadratic Equation method has restrictions. But graphical method is easier and can be applied to all diatomic molecules.

Let us consider two identical oscillators whose Hamiltonians differ by having different potential energies $v_1(r)$ and $v_2(r)$. Let $\psi_{v''}$ be the wavefunction corresponding to H_1 and $\psi_{v'}$ be the wave function corresponding to H_2. Then,

$$(H_1 + \Delta V_{2,1}) = H_2 \qquad \ldots \qquad (4.57)$$

where, $\Delta V_{2,1} = V_2(r) - V_1(r)$

Nicholls-Jarmain used Morse function to find v(r). Therefore,

$$\begin{aligned}\int \psi_{v'}(H_1+\Delta V_{2,1})\psi_{v''}dr &= E_{v'} \langle v'/v'' \rangle \\ &= E_{v''}\langle v'/v'' \rangle + \int \psi_{v'}(\Delta V_{2,1})\psi_{v''}dr \qquad \ldots (4.58)\end{aligned}$$

$$\text{or} \qquad (E_{v'}-E_{v''}) \langle v'/v'' \rangle = \langle v'/\Delta V_{2,1}/v'' \rangle \qquad \ldots \qquad (4.59)$$

Using the r-centroid approach,

$$\langle v'/\Delta v_{2,1}(r)/v'' \rangle = \Delta V_{2,1}(\bar{r}_{v',v''}) \langle v'/v'' \rangle \ldots \qquad (4.60)$$

Hence, $(E_{v'}-E_{v''}) = \Delta V_{2,1}(\bar{r}_{v'v''}) \qquad \ldots (4.61)$

The equation (4.61) provides a very convenient graphical method for obtaining r-centroids. It is not necessary to evaluate the integrals v'/r/v" from the plot of $V_{2,1}(r)$, one simply finds the internuclear distance where this difference in potential energy $V_{2,1}$ is equal to the difference of vibrational energies of the two levels. This value for r is the r-centroid.This method gives very accurate values of r-centroid because $V_{2,1}$ is fairly smooth function of internuclear distance and does not devite too much from linearity.

Graphical procedure is used for a number of diatomic molecules to obtain r-centroids. Nicholls and Jarmain[23] have shown that r-centroids would vary directly or inversely with wavelengths according to $(r_e' - r_e'')$ is positive or negative. This fact is confirmed thereafter by a number of workers.

Fraser's method for the determination of r-centroid has been improved by Halevi.[25] James[26] suggested a method for r-centroids which relies on overlap integral to find out constants involved in the comparison of experimental and theoretical intensities. Smith[27] has provided semiclassical grounds for the validity of James r-centroids approximation.

4.3.3 r-centroids using functional relation:

The functional relation is given by,[28]

$$U(r) = \gamma r^2 + \rho r + C \qquad \dots (4.62)$$

Using this equation the graph of $U_1(r)-U_2(r)$ vs. r is plotted over the significant range of r. From these graphs, the r-centroids for different transitions v'-v". For the characteristic energy difference $E_{v'}-E_{v''}$ are determined.

4.4 Results and Discussion:

The values of molecular constants required to compute f.c. factors and r-centroids for different band systems of various molecules are listed in Table (4.1)

4.4.1 Franck-Condon Factors for Different Band Systems of CuF, CuO, CuSe, CuTe, PN, NH, ND, AlSe and XeF and InBr.

Applying three different methods, i.e. Bates Tabular Method, Manneback Method and Fraser & Jarmain Method, Franck-Condon factors are computed for the band systems, $A'\Pi-X'\Sigma^+$ and $B'\Sigma^+-X'\Sigma^+$ of CuF, $E^2\Delta_{5/2}-X_2^2\Pi_{1/2}$ of CuO, $A^2\Sigma^+-X^2\Pi_i$ of CuSe, A-X CuTe, $A^2\Sigma^+-X^2\Sigma^+$ of AlSe, $d'\Sigma^+-c'\Pi$ and $d'\Sigma^+-b'\Sigma^+$of NH, $d'\Sigma^+-c'\Pi$ of ND, $A'\Pi-X'\Sigma^+$ of PN, B-X of Xef, $A^2\Pi_0^+-X'\Sigma^+$ and $B^3\Pi_1-X'\Sigma^+$ of InBr molecules. The Franck-Condon factors are reported in the Tables (4.2) to (4.14). From these tables, it is observed that the values obtained are comparable to those obtained with the help of Fraser and Jarmain Method.

4.4.2 r-Centroids for Different Band Systems of CuF, CuSe, CuTe, AlSe, XeF and InBr.

By using graphical method as suggested by Nicholls and Jarmain, r-centroids are calculated for the band systems of

$A^1\Pi-X^1\Sigma^+$ and $B^1\Sigma^+-X^1\Sigma^+$ of CuF, $A^2\Sigma^+-X^2\Pi_i$ of CuSe, A-X of CuTe, $A^2\Sigma^+-X^2\Sigma^+$ of AlSe, B-X of XeF, $A^2\Pi_0^+-X^1\Sigma^+$ and $B^3\Pi_1-X^1\Sigma^+$ of InBr.

Similarly, using functional relation, r-centroids are obtained for the systems of B-X of XeF and $A^2\Pi_0^+-X^1\Sigma^+$ and $B^3\Pi_1-X^1\Sigma^+$ of InBr.

The values of $\bar{r}_{v'v''}$ are reported in Tables (4.15) to (4.21), with available wavelengths. It is observed that the values of $\bar{r}_{v'v''}$ vary directly or inversely with the wavelength $(\bar{\lambda}_{v'v''})$ depending upon $(r'_e-r''_e)$ is positive or negative, which is in agreement with the conclusions drawn by Nicholls and Jarmain. It is also observed that $\bar{r}_{v'v''}$ computed using functional relation differ from those obtained by using Morse potential. This difference is attributed to the deviations from the Morse potential function for the electronic states of XeF and InBr molecules.

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* * *

TABLE 4.1

Constants used in the calculation of F.C.Factors and r-centroids

Molecule	State	ω_e cm^{-1}	$\omega_e x_e$ cm^{-1}	r_e A°	References
CuF	$A'\Pi$	649.20	4.00	1.7730	M.V.Ramanainth &
	$B'\Sigma^+$	657.00	3.92	1.7630	S.V.Lakshman [29]
	$X'\Sigma^+$	622.65	3.95	1.7449	
CuO	$E^2\Delta_{5/2}$	733.00	5.50	1.7244	-do-
	$X^2\Pi_{1/2}$	636.18	4.36	1.7251	
CuSe	$A^2\Sigma^+$	253.00	2.74	2.1699	-do-
	$X^2\Pi_i$	302.37	0.99	2.1081	
CuTe	A	200.58	2.009	2.4310	-do-
	X	252.67	0.701	2.3490	
PN	$A'\Pi$	1103.00	7.25	1.547	Saraswathy P and
	$X'\Sigma^+$	1337.0	6.88	1.491	Krishnamurthy G. [30]
AlSe	$A^2\Sigma^+$	391.72	1.56	2.307	H.Lavendy and
	$X^2\Sigma^+$	472.60	2.81	2.158	B.Pinchemel [31]
NH	$d'\Sigma^+$	2672.6	71.2	1.1163	W.R.M.Graham and
	$c'\Pi$	2551.2	214.3	1.1106	H.Lew [32]
	$b'\Sigma^+$	3352.43	74.2	1.0360	
ND	$d'\Sigma^+$	1953.7	38.2	1.1156	-do-
	$c'\Pi$	1756.5	50.95	1.1055	
XeF	B	308.23	1.4266	2.80	Allan L.Smith and
	X	225.06	1.0568	2.45	Peter C.Kobrinsky [33]
InBr	$A^3\Pi_0$	227.4	1.58	2.97	Singh V.B. et al. [34]
	$B^3\Pi_1$	218.0	1.60	2.78	Singh, V.B. et al. [35]
	$X'\Sigma$	221.0	0.65	2.57	Singh V.B. et al. [36]

NB: Figures in brackets indicate ref.numbers

TABLE 4.2

Franck-Condon Factors of the $A'\Pi$-$X'\Sigma^{+}$ System of CuF

V'	V"	0	1	2	3	4	5
0	a)	0.9213	0.0785	0.001			
	b)	0.8982	0.0988	0.0077			
	c)	0.9561	0.1779	0.0231			
1	a)	0.0688	0.7822	0.1485	0.003	0.002	
	b)	0.0968	0.7130	0.1728	0.0209	0.0018	
	c)	0.1778	1.0062	0.4185			
2	a)	0.0085	0.1133	0.6664	0.2109	0.0004	0.0004
	b)	0.0034	0.1768	0.5572	0.0205	0.0378	0.0011
	c)	0.0232	0.3969				
3	a)	0.0011	0.0213	0.1394	0.5701		
	b)	0.0003	0.0098	0.2417	0.5137		
	c)	0.0058					
4	a)	0.0002	0.0038	0.0355	0.1521	0.4900	0.3163
	b)	0.0000	0.0001	0.0188	0.0591	0.4824	0.0176
	c)	-	-	--	-	-	-
5	a)	-	0.0007	0.0078	0.0492	1.1551	0.4236
	b)	-	-	0.0003	0.0165	0.1035	0.4552
	c)	-	-	-	-	-	-

a] Fraser & Jarmain Method.
b] Manneback's Method.
c] Bates Method.

TABLE 4.3

Franck-Condon Factors of $B'\Sigma^{+}-X'\Sigma^{+}$ Transition of CuF.

V'	V''	0	1	2	3	4	5
	a)	0.9555	0.0443	0.0001			
0	b)	0.9552	0.0446	0.0026			
	c)	0.9820	0.0275	0.0045			
	a)	0.0393	0.8753	0.0848	0.0004	0.0001	
1	b)	0.0422	0.8697	0.0828	0.0073	0.0005	
	c)	0.1017	1.0051	0.1216			
	a)	0.0046	0.0664	0.8061	0.1217	0.0010	0.0002
2	b)	0.0014	0.0829	0.7895	0.1151	0.0141	0.0011
	c)	0.0039	0.3472				
	a)	0.0005	0.0118	0.0839	0.7465	0.1550	0.0016
3	b)	0.3282	0.0011	0.1193	0.7142	0.1420	0.0222
	c)	0.0008					
	a)	0.0001	0.0018	0.0203	0.0938	0.6952	0.1850
4	b)	0.0036	0.0801	0.0015	0.1567	0.6493	0.1638
	c)	-	-	-	-	-	-
	a)	-	0.0003	0.0038	0.0292	0.0980	0.6513
5	b)	-	0.0028	0.0304	0.0022	0.1922	0.5784
	c)	-	-	-	-	-	-

a] Fraser and Jarmain Method

b] Manneback's Method

c] Bates Method

TABLE 4.4

Franck-Condon Factors of the A-X System of CuTe

V'	V"	0	1	2	3	4	5
	a)	0.3798	0.3762	0.1781	0.0530	0.0110	0.0017
0	b)	0.3861	0.4071	0.2640	0.1328	0.568	0.0216
	c)	0.4726	0.3518	0.1947			
	a)	0.3520	0.0002	0.2058	0.2601	0.1325	0.0399
1	b)	0.2861	0.0046	0.2062	0.3252	0.2694	0.1623
	c)	0.4728	0.0623	0.2635			
	a)	0.1779	0.1685	0.0890	0.0388	0.2195	0.1955
2	b)	0.0756	0.2199	0.0628	0.0390	0.2171	0.3115
	c)	0.2500	0.5807				
	a)	0.0650	0.2261	0.0206	0.1603	0.0019	0.1220
3	b)	0.0075	0.1478	0.0891	0.1519	0.0062	0.0797
	c)	-	-	-	-	-	-
	a)	0.0192	0.1411	0.1546	0.0085	0.1308	0.0493
4	b)	0.0013	0.0262	0.1793	0.0113	0.1598	0.0699
	c)	-	-	-	-	-	-
	a)	0.0048	0.0603	0.1739	0.0580	0.0640	0.0582
5	b)	0.0002	0.0046	0.0547	0.1655	0.0045	0.1052
	c)	-	-	-	-	-	-

a] Fraser and Jarmain Method

b] Manneback's Method

c] Bates Method

TABLE 4.5

Franck-Condon Factors of the $A^2\Sigma^+$-$X^2\Pi_i$ System of CuSe

V'	V"	0	1	2	3	4	5
0	a)	0.6028	0.3108	0.0746	0.0108	0.0010	0.0001
	b)	0.5751	0.3440	0.1356	0.0428	0.0117	0.0029
	c)	0.6876	0.3299	0.1358			
1	a)	0.2960	0.1423	0.3568	0.1642	0.0359	0.0047
	b)	0.2878	0.1159	0.3200	0.2268	0.1125	0.0412
	c)	0.1529	0.4439				
2	a)	0.0816	0.3167	0.0050	0.2765	0.2330	0.0734
	b)	0.2394	0.3421	0.0011	0.1931	0.2447	0.1793
	c)	0.1529	0.4439				
3	a)	0.0167	0.1653	0.2220	0.0227	0.1619	0.2645
	b)	0.3143	0.2456	0.2531	0.0609	0.0779	0.2033
	c)	0.0468					
4	a)	0.0028	0.0508	0.2115	0.1104	0.0845	0.0661
	b)	0.0259	0.1678	0.2804	0.0904	0.1965	0.0141
	c)	-	-	-	-	-	-
5	a)	0.0004	0.0116	0.0939	0.2108	0.0317	0.1399
	b)	0.0004	0.0264	0.1488	0.2738	0.0224	0.2650
	c)	-	-	-	-	-	-

a] Fraser & Jarmain Method

b] Manneback's Method

c] Bates Method

TABLE 4.6

Franck-Condon Factors of E-X System of CuO

V'	V"	0	1	2	3	4	5
0	a)	0.9977	0.0001	0.0021	0.0001	0.0000	0.0000
	b)	0.9975	0.0001	0.0025	0.0000	0.0000	0.0000
	c)	0.9874	0.0002	0.0040			
1	a)	0.0001	0.9924	0.0012	0.0058	0.0005	0.0000
	b)	0.0001	0.9926	0.0001	0.0075	0.0000	0.0000
	c)	0.0197	0.9599	0.0027			
2	a)	0.0022	0.0010	0.9808	0.0041	0.0105	0.0015
	b)	0.0024	0.0001	0.9826	0.0002	0.0148	0.0001
	c)	0.0001	0.0902				
3	a)	0.0001	0.0063	0.0031	0.9619	0.0099	0.0154
	b)	0.0000	0.0073	0.0001	0.9678	0.0002	0.0244
	c)	0.0001					
4	a)	0.0000	0.0002	0.0123	0.0070	0.9347	0.0197
	b)	0.0000	0.0000	0.0147	0.0000	0.9483	0.0003
	c)	-	-	-	-	-	-
5	a)	0.0000	0.0001	0.0003	0.0203	0.0129	0.8987
	b)	0.0000	0.0001	0.0000	0.0243	0.0000	0.9244
	c)	-	-	-	-	-	-

a] Fraser & Jarmain Method

b] Manneback's Method

c] Bates Method.

TABLE 4.7

Franck-Condon Factors of A'Π-X'Σ^+ System of PN.

V'	V"	0	1	2	3	4	5
0	a)	0.6433	0.3047	0.1044			
	b)	0.6808	0.3277	0.1362			
1	a)	0.2510-	-	0.3308	0.2022		
	b)	0.6068	-	0.3241			
2	a)	0.0280	0.3489	-	0.2408	0.2259	
	b)	0.1410	0.4300	-			
3	a)	-	0.0750	0.3240	-	0.1326	0.1595
	b)	-	-	-	-	-	-
4	a)	-	-	0.1268	0.2699	0.0366	
	b)	-	-	-	-	-	-

a] Manneback's Method

b] Bate's Method

TABLE 4.8

Franck-Condon Factors of $d^1\Sigma^+ - C^1\Pi$ Transition of ND

V' \ V"		0	1	2	3
0	a)	0.9966	0.0028	-	-
	b)	0.9859	0.0006	-	-
1	a)	0.0025	0.9886	0.0052	-
	b)	0.0418	0.9501	0.0244	-
2	a)	-	-	0.9778	0.0073
	b)	-	-	-	-
3	a)	-	-	-	0.9643
	b)	-	-	-	-

a] Manneback's Method

b] Bates Method

TABLE 4.9

Franck-Condon Factors of the $d'\Sigma^+$-$C'\Pi$ Transitions of NH

V'	V"	0	1	2
0	a)	0.9973	0.0012	-
	b)	0.9759	0.0016	-
1	a)	0.0012	0.9944	-
	b)	0.0897	0.9021	-
2	a)	-	0.0024	0.9910
	b)	-	0.5517	-

a] Mannback Method

b] Bates Method

TABLE 4.10

Franck-Condon Factors of $d'\Sigma_+ - b'\Sigma^+$ system of NH molecule

V'	V"	0	1	2	3	4	5	6	7	8	9
0	a)	0.7296	0.2501	0.0046	-	-	-	-	-	-	-
	b)	0.9759	0.2809	0.1099	-	-	-	-	-	-	-
1	a)	-	-	0.4462	0.0066	-	-	-	-	-	--
	b)	-	-	0.3546	-	-	-	-	-	-	-
2	a)	-	-	-	0.6043	0.0044	0.0300	-	-	-	-
	b)	-	-	-	-	-	-	-	-	-	-
3	a)	-	-	-	-	0.7405	0.0008	0.0471	-	-	-
	b)	-	-	-	-	-	-	-	-	-	-
5	a)	-	-	-	-	-	-	1.0000	0.0119	0.0799	-
	b)	-	-	-	-	-	-	-	-	-	-
6	a)	-	-	-	-	-	-	-	-	0.0393	0.0931
	b)	-	-	-	-	-	-	-	-	-	-

a) Manneback's method,
b) Bate's method.

TABLE 4.11

Franck-Condon factors of $A^2\Sigma^+-X^2\Sigma^+$ System of AlSe

V'	V"	0	1	2	3	4
0	a)	0.060	0.195	0.286	0.248	0.140
	b)	0.059	0.125	0.195	0.200	0.115
	c)	0.062	0.180	0.205	-	-
1	a)	0.149	0.196	0.041	0.025	0.172
	b)	0.110	0.125	0.039	0.020	0.155
	c)	0.139	0.040	-	-	-
2	a)	0.203	0.062	0.031	0.133	0.030
	b)	0.196	0.052	0.029	0.125	0.021
	c)	0.200	0.059	-	-	-
3	a)	0.200	0.000	0.111	0.023	0.052
	b)	0.200	0.000	0.100	0.021	0.049
	c)	0.201	-	-	-	-
4	a)	0.158	0.037	0.074	0.019	0.086
	b)	0.140	0.031	0.065	0.011	0.075
	c)	-	-	-	-	-
5	a)	0.106	0.100	0.009	0.079	0.008
	b)	0.101	0.095	0.008	0.070	0.007
	c)	-	-	-	-	-
6	a)	0.063	0.123	0.009	0.079	0.008
	b)	0.059	0.120	0.009	0.069	0.007
	c)	-	-	-	-	-
7	a)	0.033	0.112	0.056	0.010	0.065
	b)	0.030	0.109	0.051	0.009	0.060
	c)	-	-	-	-	-
8	a)	0.016	0.082	0.095	0.005	0.047
	b)	0.011	0.080	0.093	0.003	0.041
	c)	-	-	-	-	-
9	a)	0.007	0.049	0.102	0.044	0.006
	b)	0.006	0.043	0.103	0.041	0.005
	c)	-	-	-	-	-
10	a)	0.003	0.026	0.083	0.084	0.004
	b)	0.002	0.021	0.079	0.081	0.008
	c)	-	-	-	-	-

a) Fraser and Jarmain method,
b) Manneback's method,
c) Bate's method.

TABLE 4.12

Franck-Condon Factors of B-X system of XeF Molecule

V' \ V"	0	1	2	3	4	5
a)	0.068	0.200	0.281	0.410	0.550	0.630
b)	0.059	0.190	0.275	-	-	-
a)	0.051	0.240	0.037	0.110	0.181	0.210
b)	0.049	0.235	0.032	-	-	-
a)	0.094	0.068	0.047	0.330	0.250	0.235
b)	0.090	0.062	-	-	-	-
a)	0.137	0.110	0.090	0.075	0.060	0.065
b)	0.135	-	-	-	-	-
a)	0.179	0.152	0.132	0.097	0.009	0.025
b)	-	-	-	-	-	-
a)	0.142	0.100	0.007	0.050	0.008	0.006
b)	-	-	-	-	-	-
a)	0.063	0.123	0.009	0.071	0.006	0.039
b)	-	-	-	-	-	-
a)	0.043	0.101	0.046	0.009	0.055	0.035
b)	-	-	-	-	-	-
a)	0.025	0.075	0.082	0.069	0.004	0.037
b)	-	-	-	-	-	-
a)	0.008	0.036	0.104	0.032	0.003	0.002
b)	-	-	-	-	-	-
a)	0.006	0.026	0.071	0.078	0.004	0.003
b)	-	-	-	-	-	-
a)	0.004	0.019	0.092	0.046	0.039	0.001
b)	-	-	-	-	-	-
a)	0.002	0.017	0.065	0.037	0.026	0.001
b)	-	-	-	-	-	-

a) Manneback's Method
b) Bate's Method.

TABLE 4.13

Franck-Condon Factors of $A'\Pi_0-X'\Sigma^+$ System of InBr Molecule

V'	V"	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	a)	0.6030	0.2841	0.0861	0.0211	0.0046	0.0009	0.0002	-	-	-	-	-	-	-
	b)	0.5950	0.2030	0.0800	0.0190	0.0039	0.000	0.0002	-	-	-	-	-	-	-
	c)	0.6140	0.2551	0.0810	-	-	-	-	-	-	-	-	-	-	-
1	a)	0.3273	0.1538	0.2863	0.1562	0.0555	0.0158	0.0040	0.0009	0.0002	-	-	-	-	-
	b)	0.3020	0.1059	0.2559	0.1560	0.0549	0.0105	0.0042	0.0009	0.0002	-	-	-	-	-
	c)	0.3190	0.1450	0.2601	-	-	-	-	-	-	-	-	-	-	-
2	a)	0.0644	0.4010	0.0135	0.2000	0.1846	0.0904	0.0326	0.0099	0.0027	0.0007	0.0002	-	-	-
	b)	0.0604	0.4015	0.0102	0.1950	0.0989	0.0900	0.0310	0.0090	0.0020	0.0006	0.0001	-	-	--
	c)	0.0599	0.4001	-	-	-	-	-	-	-	-	-	-	-	-
3	a)	0.0052	0.1442	0.3628	0.0058	0.1096	0.1768	0.1164	0.0521	0.0188	0.0059	0.0017	0.0005	0.0001	-
	b)	0.0050	0.1005	0.3220	0.0053	0.1050	0.1560	0.1010	0.0490	0.0170	0.0060	0.0015	0.0004	0.0001	-
	c)	0.0049	-	-	-	-	-	-	-	-	-	-	-	-	-
4	a)	0.0001	0.0165	0.21756	0.2864	0.0421	0.0450	0.1466	0.1293	0.0707	0.0298	0.0108	0.0035	0.0011	0.0003
	b)	0.0001	0.0170	0.2070	0.2550	0.0410	0.0395	0.1050	0.1200	0.0695	0.0195	0.0105	0.0029	0.0010	0.0002
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	a)	-	0.0005	0.0329	0.2762	0.2075	0.0820	0.0103	0.1076	0.1289	0.0855	0.0419	0.0172	0.0063	0.0022
	b)	-	0.0004	0.0301	0.2150	0.1985	0.0798	0.0100	0.1062	0.0989	0.0795	0.0399	0.0169	0.0059	0.0025
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	a)	-	-	0.0010	0.0526	0.3193	0.1405	0.1098	0.0000	0.0697	0.1178	0.0947	0.0536	0.0248	0.0010
	b)	-	-	0.0009	0.0500	0.2993	0.1030	0.0998	0.0000	0.0599	0.1018	0.0897	0.0436	0.0201	0.0010
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	a)	-	-	-	0.0016	0.0742	0.3491	0.0895	0.1222	0.0058	0.0387	0.0994	0.0975	0.0636	0.0332
	b)	-	-	-	0.0012	0.0692	0.3080	0.0798	0.1200	0.0049	0.0378	0.0960	0.0900	0.0596	0.0292
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table cond. on next page.

Table 4.13 (contd.)

V'' V'		0	1	2	3	4	5	6	7	8	9	10	11	12	13
	a)	-	-	-	-	0.0023	0.0964	0.3685	0.0537	0.1212	0.0201	0.0169	0.0777	0.0943	0.0708
8	b)	-	-	-	-	0.0019	0.0860	0.3575	0.0498	0.1010	0.0191	0.0098	0.0697	0.0900	0.6900
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	a)	-	-	-	-	0.0002	0.0027	0.1182	0.3812	0.0303	0.1105	0.0372	0.0045	0.0558	0.0859
9	b)	-	-	-	-	0.0001	0.0019	0.1120	0.3510	0.0293	0.1005	0.0292	0.0050	0.0566	0.0909
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	a)	-	-	-	-	-	0.0004	0.0028	0.1386	0.3896	0.0161	0.0940	0.0534	0.0000	0.0363
10	b)	-	-	-	-	-	0.0003	0.0021	0.0989	0.2090	0.0100	0.0839	0.0435	0.0000	0.0360
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	a)	-	-	-	-	-	-	0.0008	0.0025	0.1569	0.3962	0.0081	0.0745	0.0666	0.0017
11	b)	-	-	-	-	-	-	0.0006	0.0019	0.1430	0.4062	0.0090	0.0750	0.0596	0.0020
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	a)	-	-	-	-	-	-	0.0002	0.0017	0.0018	0.1722	0.4030	0.0041	0.0558	0.0758
12	b)	-	-	-	-	-	-	0.0001	0.0015	0.0020	0.1022	0.3930	0.0039	0.0560	0.0698
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	a)	-	-	-	-	-	-	-	0.0002	0.0031	0.0009	0.1835	0.4115	0.0024	0.0386
13	b)	-	-	-	-	-	-	-	0.0001	0.0029	0.0009	0.2350	0.4200	0.0019	0.0276
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-

a) Fraser and Jarmain Method,

b) Manneback Method,

c) Bate's Method.

TABLE 4.14

Franck-Condon factors of $B^2\Pi_1$-$X^1\Sigma$ System of InBr Molecule

V'	V"	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	a)	0.5929	0.2851	0.0911	0.0238	0.0056	0.0012	0.0003	-	-	-	-	-	-	-
	b)	0.6029	0.2049	0.0899	0.0198	0.0060	0.0011	0.0003	-	-	-	-	-	-	-
	c)	0.5410	0.2010	0.0900	-	-	-	-	-	-	-	-	-	-	-
1	a)	0.3371	0.1443	0.2753	0.1585	0.0600	0.0183	0.0049	0.0015	0.0003	-	-	-	-	-
	b)	0.3060	0.1441	0.2154	0.1685	0.0599	0.0170	0.0050	0.0020	0.0003	-	-	-	-	-
	c)	0.3115	0.1390	0.2500	-	-	-	-	-	-	-	-	-	-	-
2	a)	0.0654	0.4110	0.0118	0.1849	0.1805	0.0939	0.0362	0.0117	0.0034	0.0009	0.0002	-	-	-
	b)	0.0539	0.3990	0.0098	0.0989	0.2050	0.0930	0.0252	0.0110	0.0029	0.0009	0.0002	-	-	-
	c)	0.0601	0.4001	-	-	-	-	-	-	-	-	-	-	-	-
3	a)	0.0046	0.1454	0.3757	0.0057	0.0978	0.1674	0.1167	0.0555	0.0212	0.0071	0.0022	0.0006	0.0002	-
	b)	0.0030	0.1040	0.3010	0.0060	0.0898	0.0974	0.1070	0.0350	0.0200	0.0069	0.0019	0.0006	0.0001	-
	c)	0.0040	-	-	-	-	-	-	-	-	-	-	-	-	-
4	a)	0.0001	0.0140	0.2189	0.3056	0.0380	0.0387	0.1353	0.1256	0.0727	0.0325	0.0124	0.0043	0.0014	0.0005
	b)	0.0001	0.0095	0.2200	0.2986	0.0370	0.0300	0.0956	0.0957	0.0720	0.0225	0.0094	0.0039	0.0010	0.0005
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	a)	-	0.0002	0.0269	0.2793	0.2341	0.0716	0.0085	0.0976	0.1221	0.0853	0.0441	0.0191	0.0074	0.0027
	b)	-	0.0001	0.0196	0.3090	0.2050	0.0720	0.0090	0.0896	0.0923	0.1500	0.0390	0.0200	0.0069	0.0030
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	a)	-	-	0.0002	0.0417	0.3266	0.1738	0.9937	0.0000	0.0628	0.1093	0.0920	0.0547	0.0266	0.0114
	b)	-	-	0.0001	0.0397	0.2966	0.2080	0.9830	0.0000	0.0598	0.0993	0.0895	0.0497	0.0259	0.0100
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	a)	-	-	0.0001	0.0024	0.0566	0.3633	0.1276	0.1023	0.0052	0.0352	0.0909	0.0927	0.0631	0.0344
	b)	-	-	0.0002	0.0019	0.0496	0.3033	0.0975	0.1001	0.0049	0.0229	0.1090	0.1250	0.1300	0.0299
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table contd. on next page.

Table 4.14 (contd.)

V'	V"	0	1	2	3	4	5	6	7	8	9	10	11	12	13
8	a)	-	-	-	0.0003	0.0001	0.0705	0.3923	0.0945	0.0996	0.1760	0.0161	0.0705	0.0881	0.0686
	b)	-	-	-	0.0002	0.0001	0.0692	0.2910	0.0895	0.0895	0.1650	0.0096	0.0671	0.0780	0.0501
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9	a)	-	-	-	-	0.0006	0.0000	0.0822	0.4163	0.0720	0.0890	0.0326	0.0050	0.0506	0.0793
	b)	-	-	-	-	0.0004	0.0000	0.0791	0.3990	0.0650	0.0801	0.0295	0.0047	0.0501	0.0699
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
10	a)	-	-	-	-	-	0.0012	0.0001	0.0905	0.4371	0.0577	0.0736	0.0475	0.0004	0.0331
	b)	-	-	-	-	-	0.0009	0.0001	0.0900	0.4010	0.0493	0.0691	0.0397	0.0003	0.0300
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
11	a)	-	-	-	-	-	-	0.0023	0.0009	0.0944	0.4561	0.0499	0.0565	0.0610	0.0001
	b)	-	-	-	-	-	-	0.0019	0.0007	0.0894	0.3950	0.0381	0.0398	0.0601	0.0001
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12	a)	-	-	-	-	-	-	-	0.0039	0.0033	0.0926	0.4734	0.0473	0.0387	0.0728
	b)	-	-	-	-	-	-	-	0.0040	0.0029	0.0810	0.5340	0.0393	0.0297	0.0691
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
13	a)	-	-	-	-	-	-	-	-	0.0058	0.0084	0.0842	0.4883	0.0493	0.0793
	b)	-	-	-	-	-	-	-	-	0.0060	0.0079	0.0762	0.5331	0.0390	0.0801
	c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-

a) Fraser and Jarmain Method,
b) Manneback's Method,
c) Bate's Method.

TABLE 4.15

r-centroids of the $A^2\Sigma^+ - X^2\Pi_i$ System of CuSe

V'	V"	0	1	2	3	4	5
	a)	2.1386	2.1019	2.2651	-	-	-
0	b)	2.128	2.134	2.140	-	-	-
	c)	5694.3	-	-			
	a)	2.0849	2.1491	2.2176	2.2753	2.1334	-
1	b)	2.1228	2.1288	2.1348	2.1408	2.1448	-
	c)	-	5685.7	-	-	-	-
	a)	2.0293	2.0965	2.1595	2.2213	2.2835	2.3473
2	b)	2.1176	2.124	2.130	2.1356	2.1416	2.1476
	c)	-	-	5677.2	-	-	-
	a)	1.9679	2.0424	2.1079	2.1700	2.2311	2.2928
3	b)	2.1128	2.1188	2.12252	2.1312	2.136	2.1428
	c)	-	-	-	5668.2	-	-
	a)	1.8871	1.9841	2.0553	-	-	--
4	b)	2.102	2.1142	2.1208	-	-	-
	c)	-	-	-	-	5660.4	-
	a)	-	1.9130	1.9925	-	-	-
5	b)	-	2.0988	2.0896	-	-	-
	c)	-	-	-	-	-	5652.2

a] Quadratic Equation method

b] Graphical method

c] Wavelength.

TABLE 4.16

r-centroids of the A-X System of CuTe

V'	V"	0	1	2	3	4	5
0	a)	2.3981	2.4393	2.4868	2.5348	-	2.6341
	b)	2.3703	2.3708	2.383	-	-	-
	c)	6263.5	6464.0	6466.9	6571.9	-	-
1	a)	2.3542	2.4022	2.4495	2.4968	2.5447	2.5936
	b)	2.369	2.374	2.380	2.384	2.389	2.395
	c)	6187.2	6285.2	6387.6	6487.9	6592.7	6701.0
2	a)	2.3166	2.3655	2.4130	-	2.5073	-
	b)	2.364	2.370	2.375	-	2.385	-
	c)	6113.0	6208.7	6307.0	-	6508.6	6613.7
3	a)	-	2.3290	-	-	-	-
	b)	-	2.366	-	-	-	-
	c)	-	6134.4	6230.0	6330.2	6335.0	6640.0
4	a)	-	2.3418	-	-	-	-
	b)	-	2.361	-	-	-	-
	c)	-	-	6155.16	-	-	-

a] Quadratic Equation method

b] Graphical Method

c] Wavelength.

TABLE 4.17

r-centroids of the $A'\Pi$-$X'\Sigma^+$ System of CuF Molecule

V'	V"	0	1	2	3	4	5
	a)	1.7550	-	-	-	-	-
0	b)	1.7558	-	-	-	-	-
	c)	5061.2	-	-	-	-	-
	a)	1.660	1.749	-	-	-	-
1	b)	1.7525	1.759	-	-	-	-
	c)	4901.4	5052.3	-	-	-	-
	a)	1.601	1.656	1.743--	-	-	-
2	b)	1.744	1.753	1.759	-	-	-
	c)	-	4895.2	5043.5	-	-	-
	a)	1.559	1.600	1.654	1.738	-	-
3	b)	1.715	1.7445	1.7449	1.7528	-	-
	c)	-	-	4888.5	5034.8	-	-
	a)	1.526	1.539	1.599	1.652	1.732	-
4	b)	1.705	1.7558	1.7435	1.7520	1.7575	
	c)	-	-	-	4882.0	5026.2	-
	a)	1.498	1.526	1.559	1.598	1.650	1.727
5	b)	1.705	-	-	1.7425	1.7515	1.7580
	c)	-	-	-	-	-	-

a] Quadratic Equation Method

b] Graphical Method

c] Wavelegnth.

TABLE 4.18

r-centrods of $A^2\Sigma^+ - X^2\Sigma^+$ System of AlSe molecule

V'	V"	0	1	2	3	4
0	a)	2.239	2.269	2.300	2.333	2.369
	b)	2.225	2.240	2.298	2.305	2.345
1	a)	2.215	2.242	2.266	2.316	2.342
	b)	2.191	2.235	2.255	2.295	2.337
2	a)	2.192	2.216	2.254	2.277	2.296
	b)	2.180	2.215	2.240	2.271	2.285
3	a)	2.170	2.097	2.225	2.243	2.288
	b)	2.195	2.105	2.214	2.235	2.275
4	a)	2.149	2.177	2.200	2.237	2.255
	b)	2.155	2.200	2.225	2.235	2.249
5	a)	2.218	2.154	2.177	2.208	2.218
	b)	2.210	2.155	2.165	2.210	2.211
6	a)	2.215	2.154	2.174	2.208	2.218
	b)	2.200	2.225	2.227	2.230	2.235
7	a)	2.088	2.113	2.137	2.168	2.193
	b)	2.075	2.110	2.125	2.155	2.185
8	a)	2.067	2.093	2.117	2.134	2.173
	b)	2.070	2.095	2.115	2.138	2.169
9	a)	2.045	2.072	2.097	2.119	2.164
	b)	2.055	2.079	2.095	2.120	2.125
10	a)	2.021	2.050	2.077	2.100	2.110
	b)	2.052	2.059	2.079	2.110	2.118

a) Quadratic equation method,
b) Graphical method.

TABLE 4.19

r-Centroids of $A^1\Pi_0 - X^1\Sigma^+$ System of InBr Molecule

V'	V''	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	a)	2.5185	2.4622	2.4164	2.3759	2.3396	2.3068	2.2774	-	-	-	-	-	-	-
	b)	2.5105	2.4550	2.4104	2.3650	2.3295	2.3055	2.2950	-	-	-	-	-	-	-
	c)	2.5115	2.4650	2.4114	2.3750	2.3390	2.3045	2.3910	-	-	-	-	-	-	-
1	a)	2.5757	2.5312	2.4658	2.4189	2.3781	2.3417	2.3089	2.2794	2.2536	-	-	-	-	-
	b)	2.5500	2.5250	2.4595	2.4095	2.3695	2.3410	2.3410	2.3079	2.2789	-	-	-	-	-
	c)	2.5510	2.5240	2.4575	2.4085	2.3680	2.3400	2.3065	2.2750	2.2495	-	-	-	-	-
2	a)	2.6413	2.5815	2.5835	2.4701	2.4214	2.3802	2.3437	2.3110	2.2817	2.2559	2.2342	-	-	-
	b)	2.5995	2.5785	2.5750	2.4651	2.4210	2.3780	2.3440	2.3101	2.2750	2.2560	2.2305	-	-	-
	c)	2.5975	2.5765	2.5730	2.4631	2.4110	2.3760	2.3420	2.3100	2.2770	2.2570	2.2315	-	-	-
3	a)	2.7455	2.6514	2.5884	2.4050	2.4759	2.4240	2.3822	2.3456	2.3129	2.2838	2.2583	2.2365	2.2188	-
	b)	2.7505	2.6450	2.5780	2.4150	2.4800	2.4200	2.3750	2.3460	2.3130	2.2675	2.2495	2.2290	2.1988	-
	c)	2.7515	2.6460	2.5790	2.4140	2.4810	2.4210	2.3751	2.3470	2.3150	2.2695	2.2505	2.2280	2.1978	-
4	a)	2.9520	2.7522	2.6566	2.5971	2.4747	2.4856	2.4269	2.3841	2.3474	2.3147	2.2857	2.2604	2.2387	2.2209
	b)	2.9330	2.6921	2.5980	2.4801	2.3941	2.3912	2.3010	2.3562	2.3210	2.2992	2.2710	2.2450	2.2260	2.2150
	c)	2.9340	2.6932	2.5995	2.4811	2.3953	2.3917	2.3020	2.3573	2.3225	2.2996	2.2725	2.2465	2.2272	2.2162
5	a)	-	2.9754	2.7590	2.6620	2.6086	2.4870	2.5112	2.4305	2.3860	2.3490	2.3164	2.2876	2.2623	2.2407
	b)-	-	2.8955	2.6595	2.6505	2.6058	2.4575	2.4561	2.4350	2.3750	2.3502	2.3054	2.2795	2.2590	2.2395
	c)	-	2.8755	2.6585	2.6515	2.6068	2.4565	2.4571	2.4360	2.3760	2.3512	2.3064	2.2775	2.2570	2.2385
6	a)	-	-	3.0042	2.7660	2.6678	2.6249	2.4911	3.4059	2.4352	2.3879	2.3506	2.3180	2.2892	2.2641
	b)	-	-	3.0050	2.7510	2.5950	2.5840	2.5010	2.4190	2.4201	2.3779	2.3495	2.3095	2.2752	2.2550
	c)	-	-	3.0042	2.7500	2.5940	2.5850	2.5020	3.4180	2.4211	2.3789	2.3485	2.3075	2.2742	2.2540
7	a)	-	-	-	3.0380	2.7730	2.6740	2.6489	2.4917	2.4017	2.4427	2.3899	2.3521	2.3194	2.2908
	b)	-	-	-	3.0250	2.7650	2.6700	2.6395	2.5005	2.4005	2.4000	2.3850	2.3475	2.3092	2.3008
	c)	-	-	-	3.0240	2.7630	2.6710	2.6375	2.5015	2.4015	2.4010	2.3860	2.3485	2.3082	2.3018

Table contd.on next page.

Table 4.19 (contd.)

V'	V"	0	1	2	3	4	5	6	7	8	9	10	11	12	13
	a)	-	-	-	-	3.0800	2.7803	2.6807	2.6860	2.4899	2.4372	2.4572	2.3922	2.3536	2.3207
8	b)	-	-	-	-	3.0750	2.6750	2.6720	2.6650	2.5950	2.4450	2.4501	2.4002	2.3505	2.3205
	c)	-	-	-	-	3.0760	2.6760	2.6730	2.6660	2.5960	2.4470	2.4510	2.4022	2.3525	2.3235
	a)	-	-	-	-	2.5572	3.1344	2.7877	2.6878	2.7463	2.4851	2.4478	2.4984	2.3950	2.3551
9	b)	-	-	-	-	2.3475	2.9540	2.7570	2.6750	2.7550	2.5500	2.4480	2.4350	2.33800	2.3450
	c)	-	-	-	-	2.3465	2.9550	2.7550	2.6760	2.7550	2.5520	2.4470	2.4830	2.3810	2.3470
	a)	-	-	-	-	-	2.4509	3.2094	2.7953	2.6956	2.8475	2.4767	2.4543	3.0522	2.3989
10	b)	-	-	-	-	-	2.4495	3.2085	2.8500	2.7565	2.8450	2.4850	2.4505	3.1250	2.4050
	c)	-	-	-	-	-	2.4475	3.2095	2.8520	2.7575	2.8460	2.4860	2.4515	3.1260	2.4070
	a)	-	-	-	-	-	-	2.5225	3.3242	2.8032	2.7040	3.0204	2.4639	2.4597	2.2667
11	b)	-	-	-	-	-	-	2.4950	3.3195	2.9500	2.6550	3.0105	2.5500	2.4650	2.3650
	c)	-	-	-	-	-	-	2.4960	3.3175	2.9520	2.6570	3.0125	2.5530	2.4670	2.3670
	a)	-	-	-	-	-	-	2.9356	2.5801	2.5280	2.8116	2.7130	3.3056	2.4406	2.4655
12	b)	-	-	-	-	-	-	2.9400	2.6000	2.5350	2.7850	2.7100	3.3150	2.4400	2.4750
	c)	-	-	-	-	-	-	2.9410	2.6010	2.5370	2.7880	2.7110	2.3160	2.4420	2.4760
	a)	-	-	-	-	-	-	-	2.9924	2.6289	2.0189	2.8207	2.7225	3.7016	2.4039
13	b)	-	-	-	-	-	-	-	2.9850	2.6355	2.0250	2.8200	2.7350	2.6950	2.5950
	c)	-	-	-	-	-	-	-	2.9840	2.6365	2.0260	2.8220	2.7340	2.6960	2.5930

a) Quadratic equation method,
b) Graphical method,
c) Graphical method using functional relation.

TABLE 4.20

r-centroids of $B^3\Pi_1$-$X'\Sigma^+$ System of InBr Molecule

V'	V''	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	a)	2.5182	2.4619	2.4180	2.3796	2.3452	2.3138	2.2852	-	-	-	-	-	-	-
	b)	2.3995	2.3015	2.2010	2.1901	2.1565	2.1221	2.1050	-	-	-	-	-	-	-
	c)	2.3975	2.3025	2.2030	2.1921	2.1575	2.1241	2.1070	-	-	-	-	-	-	-
1	a)	2.5744	2.5329	2.4949	2.4200	2.3810	2.3470	2.3153	2.2869	2.2614	-	-	-	-	-
	b)	2.5001	2.4905	2.4858	2.4505	2.4000	2.3010	2.2902	2.2105	2.2005	-	-	-	-	-
	c)	2.5010	2.4925	2.4868	2.4525	2.4020	2.3030	2.2910	2.2085	2.2025	-	-	-	-	-
2	a)	2.6468	2.5805	2.6005	2.4684	2.4217	2.3823	2.3477	2.3166	2.2885	2.2632	2.2421	-	-	--
	b)	2.6110	2.6850	2.5902	2.4214	2.4191	2.3665	2.3350	2.3065	2.2050	2.2045	2.2005	-	-	-
	c)	2.6120	2.6070	2.5922	2.4224	2.4171	2.3645	2.3320	2.3045	2.2030	2.2065	2.2015	-	-	--
3	a)	2.7600	2.6521	2.5880	2.3729	2.4733	2.4340	2.3830	2.3490	2.3180	2.2900	2.2650	2.2430	2.2250	-
	b)	2.7552	2.6450	2.5675	2.4520	2.4358	2.4050	2.4001	2.3902	2.3525	2.2500	2.2475	2.2425	2.2195	-
	c)	2.7562	2.6430	2.5685	2.4530	2.4368	2.4060	2.4020	2.3912	2.3535	2.2520	2.2485	2.2435	2.2175	-
4	a)	3.1282	3.7685	2.6576	2.5977	2.4547	2.4818	2.4259	2.3845	2.3500	2.3188	2.2911	2.2664	2.2450	2.2270
	b)	3.1010	3.0990	2.7020	2.6000	2.4345	2.4210	2.4205	2.3700	2.3495	2.3101	2.2705	2.2600	2.2395	2.2025
	c)	3.1020	3.0970	2.7030	2.6020	2.4365	2.4220	2.4215	2.3720	2.3475	2.3121	2.2715	2.2570	2.2375	2.2015
5	a)	-	3.2159	2.7774	2.6634	2.6104	2.4671	2.5042	2.4288	2.3854	2.3506	2.3197	2.2922	2.2677	2.2485
	b)	-	3.2055	2.6775	2.6590	2.6005	2.4050	2.4010	2.3959	2.3750	2.3450	2.3005	2.2050	2.2040	2.2005
	c)	-	3.2065	2.6785	2.6570	2.6025	2.4070	2.4020	2.3979	2.3760	2.3460	2.3025	2.2070	2.2060	2.2025
6	a)	-	-	3.3515	2.7868	2.6700	2.6277	2.4685	2.0464	2.4333	2.3862	2.3513	2.3204	2.2931	2.2689
	b)	-	-	3.3450	2.7750	2.6650	2.6340	2.4670	2.0355	2.0350	0.0345	2.0341	2.0339	2.0337	2.0325
	c)	-	-	3.3461	2.7762	2.6670	2.6350	2.4680	2.0365	2.0351	2.0355	2.0353	2.0345	2.0342	2.0336
7	a)	-	-	2.5292	3.6000	2.7989	2.6764	2.6513	2.4644	2.4208	2.4411	2.3869	2.3520	2.3209	2.2938
	b)	-	-	2.4995	2.4875	2.4770	2.5500	2.4675	2.4600	2.4455	2.4401	2.3750	2.3600	2.3405	2.3005
	c)	-	-	2.4975	2.4865	2.4750	2.5520	2.4685	2.4610	2.4465	2.4421	2.3770	2.3610	2.3425	2.3025

Table contd. on next page.

Table 4.20 (contd.)

V'	V"	0	1	2	3	4	5	6	7	8	9	10	11	12	13
8	a)	-	-	-	2.5816	2.2173	2.8077	2.6834	2.6827	2.4551	2.4465	2.4576	2.3876	2.3526	2.3213
	b)	-	-	-	2.5510	2.5235	2.5250	2.5115	2.5100	2.4450	2.4440	2.4350	2.3750	2.3450	2.3250
	c)	-	-	-	2.5520	2.5245	2.5262	2.5136	2.5120	2.4470	2.4461	2.4360	2.3771	2.3462	2.3265
9	a)	-	-	-	-	2.6285	2.9532	2.8194	2.6909	2.7235	2.4394	2.4581	2.5031	2.3879	2.3534
	b)	-	-	-	-	2.6195	2.6095	2.7500	2.5750	2.5650	2.4250	2.4150	2.4005	2.3850	2.3650
	c)	-	-	-	-	2.6175	2.6070	2.6775	2.5765	2.5665	2.4261	2.4165	2.4025	2.3872	2.3670
10	a)	-	-	-	-	-	2.6687	2.2634	2.8323	2.6988	2.7732	2.4140	2.4679	2.7771	2.3878
	b)	-	-	-	-	-	2.6580	2.6050	2.7500	2.6750	2.6700	2.5450	2.4500	2.4000	2.3550
	c)	-	-	-	-	-	2.6590	2.6070	2.7521	2.6745	2.6718	2.5465	2.4562	2.4025	2.3565
11	a)	-	-	-	-	-	-	2.7040	1.7830	2.8472	2.7069	2.8292	2.3730	2.4787	1.9755
	b)	-	-	-	-	-	-	2.7000	2.0500	2.7700	2.6500	2.7500	2.4050	2.4550	2.0500
	c)	-	-	-	-	-	-	2.7020	2.0521	2.7721	2.6531	2.7530	2.4060	2.4562	2.0512
12	a)	-	-	-	-	-	-	-	2.7403	2.1870	2.8649	2.7152	2.8844	2.3040	2.4924
	b)	-	-	-	-	-	-	-	2.6750	2.0995	2.7505	2.7000	2.6515	2.2510	2.2350
	c)	-	-	-	-	-	-	-	2.6760	2.0985	2.7525	2.7020	2.6535	2.2520	2.2370
13	a)	-	-	-	-	-	-	-	-	2.7774	2.3781	2.8876	2.7233	2.9314	2.1791
	b)	-	-	-	-	-	-	-	-	2.7650	2.3775	2.7550	2.7200	2.8515	2.0195
	c)	-	-	-	-	-	-	-	-	2.7662	2.3785	2.7561	2.7221	2.8526	2.0200

a) Quadratic equation method,
b) Graphical method,
c) Graphical method using functional relation.

TABLE 4.21

r-centroids of B-X system of XeF Molecule

V'	V"	0	1	2	3	4	5
0	a)	2.136	2.245	2.300	2.306	2.375	2.450
	b)	2.137	2.249	2.305	2.309	2.385	2.470
1	a)	2.235	2.401	2.435	2.505	2.551	2.575
	b)	2.239	2.435	2.475	2.509	2.561	2.591
2	a)	2.336	2.445	2.575	2.711	2.775	2.785
	b)	2.372	2.455	2.585	2.725	2.786	2.792
3	a)	2.415	2.465	2.500	2.535	2.575	2.590
	b)	2.435	2.475	2.532	2.567	2.580	2.598
4	a)	2.497	2.515	2.585	2.920	2.934	2.937
	b)	2.499	2.517	2.567	2.905	2.945	2.965
5	a)	2.565	2.570	2.581	2.615	2.635	2.750
	b)	2.572	2.581	2.583	2.626	2.646	2.772
6	a)	2.600	2.645	2.679	2.731	2.845	2.900
	b)	2.610	2.655	2.675	2.742	2.865	2.913
7	a)	2.775	2.795	2.801	2.825	2.905	3.000
	b)	2.782	2.797	2.803	2.846	2.907	2.315
8	a)	2.821	2.836	2.855	2.925	2.975	3.150
	b)	2.823	2.839	2.877	2.936	2.976	3.161
9	a)	2.920	2.930	2.860	2.915	2.955	3.115
	b)	2.927	2.933	2.872	2.919	2.956	3.117
10	a)	2.935	2.942	2.954	2.955	3.120	3.135
	b)	2.942	2.945	2.956	2.959	3.125	3.137
11	a)	2.936	2.946	2.825	2.870	3.015	3.221
	b)	2.957	2.949	2.842	2.883	3.022	3.233
12	a)	3.001	3.016	2.905	3.007	3.050	2.910
	b)	3.011	3.023	2.912	3.012	3.062	2.920

a) Graphical method,

b) Graphical method using functional relation.

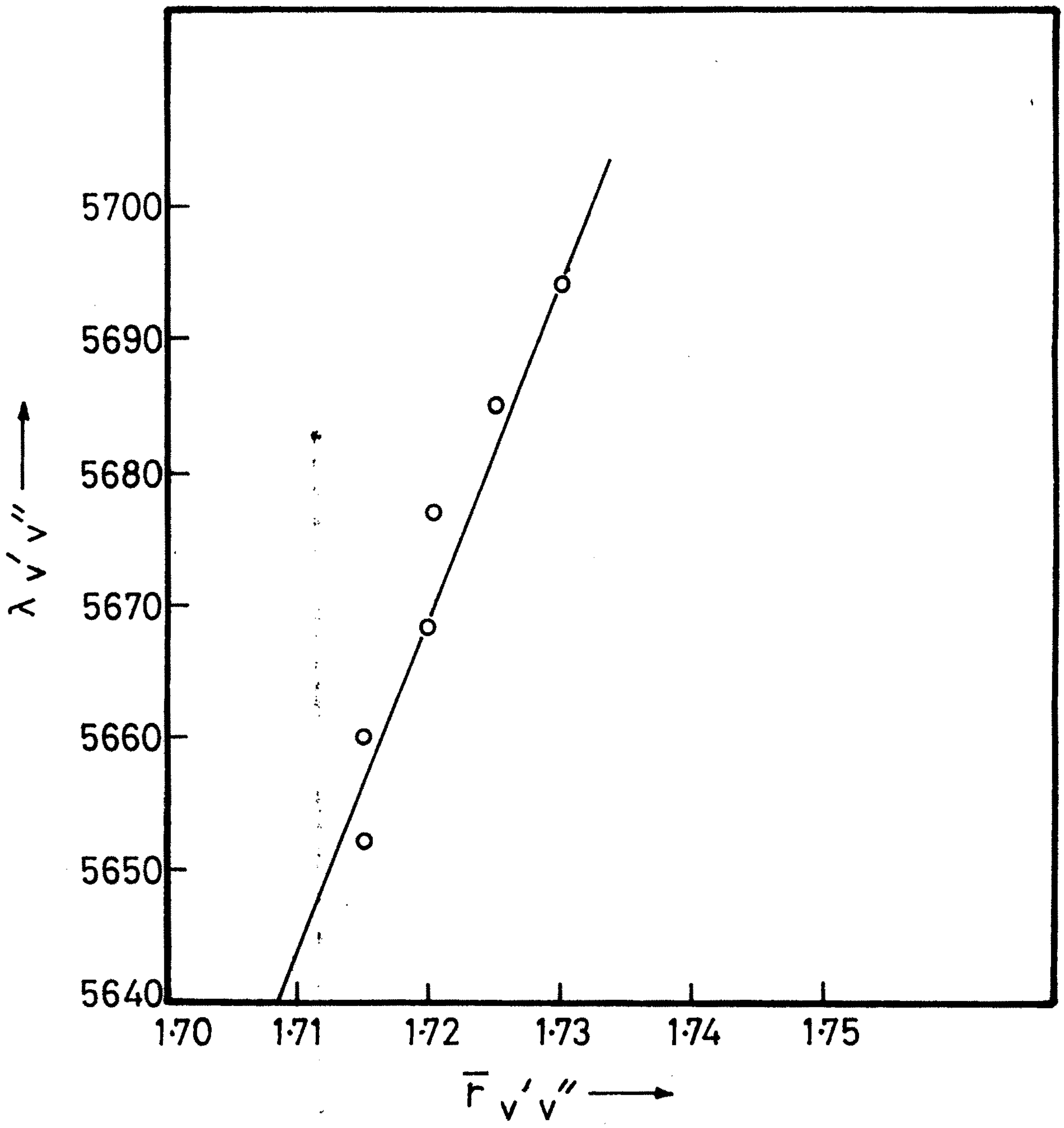

Fig. 4·1 – VARIATION OF $\bar{r}_{v'v''}$ WITH $\lambda_{v'v''}$ IN $A'\Pi - X'\Sigma$ SYSTEM OF CuF.

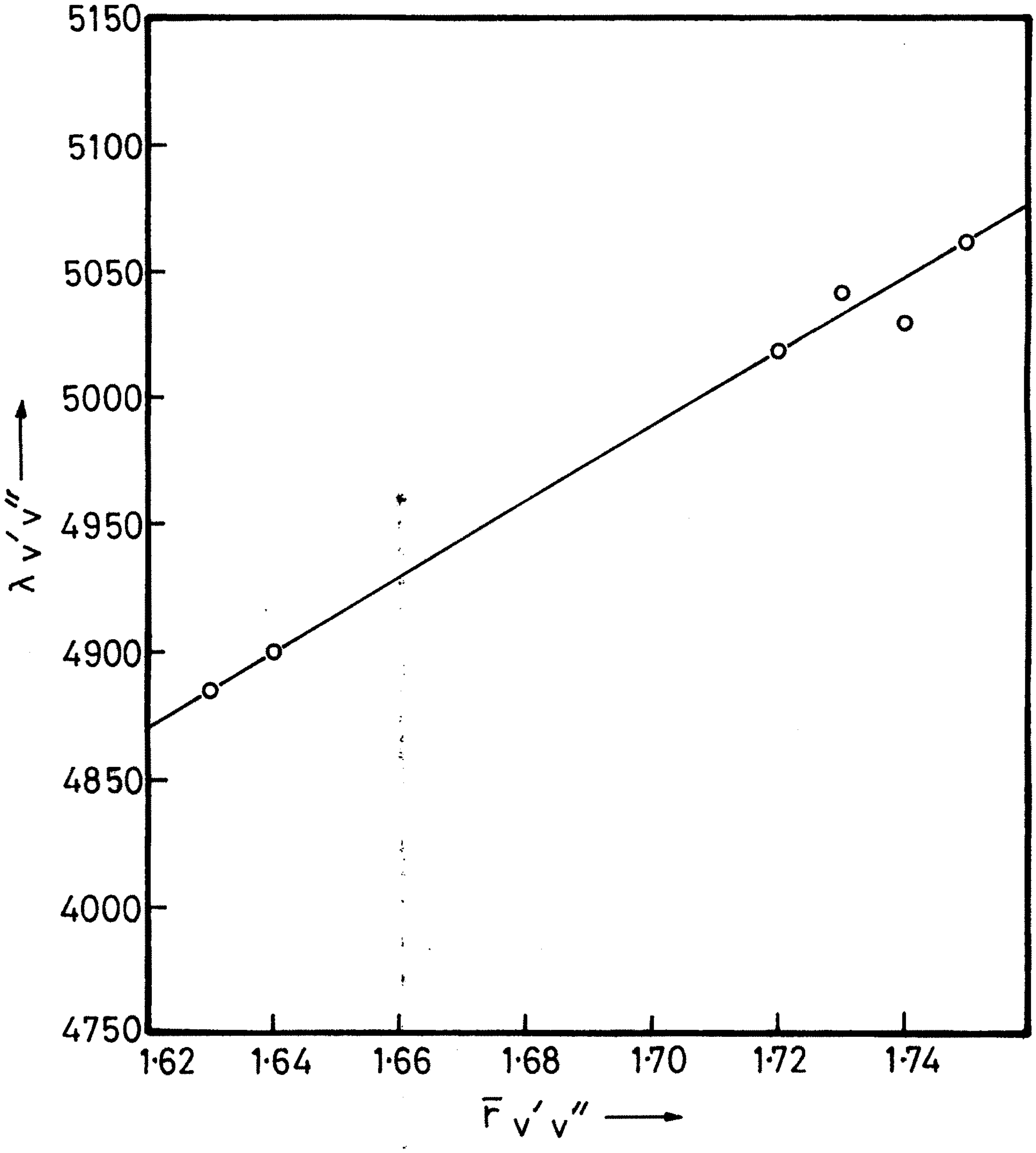

Fig.4·2- VARIATION OF $\bar{r}_{v'v''}$ WITH $\lambda_{v'v''}$ IN $B'\Sigma^{+}-X'\Sigma^{+}$ SYSTEM OF CuF.

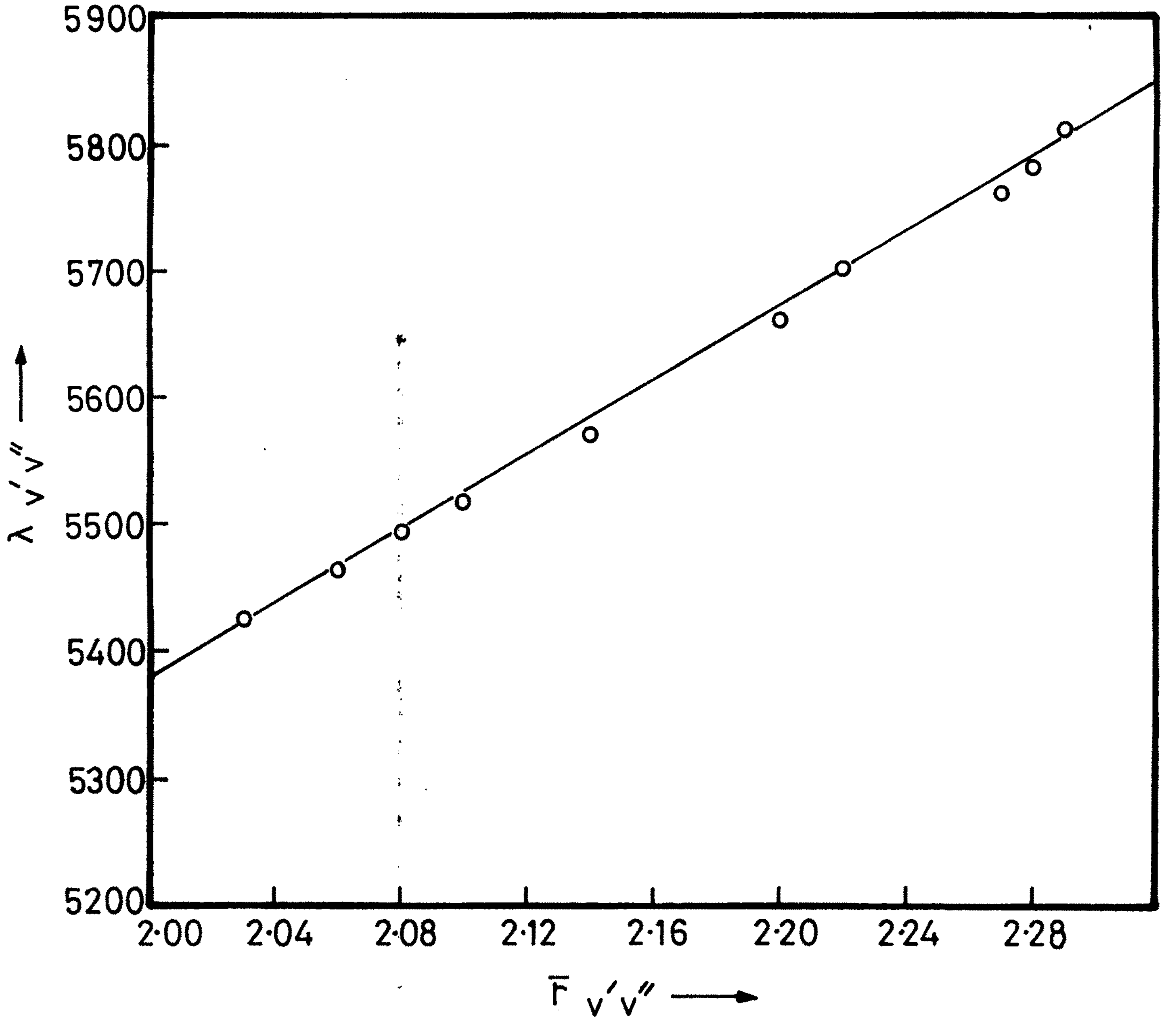

Fig. 4·3 - VARIATION OF $\bar{r}_{v'v''}$ WITH $\lambda_{v'v''}$ IN $A^2\Sigma^+ - X^2\Pi_i$ SYSTEM OF CuSe.

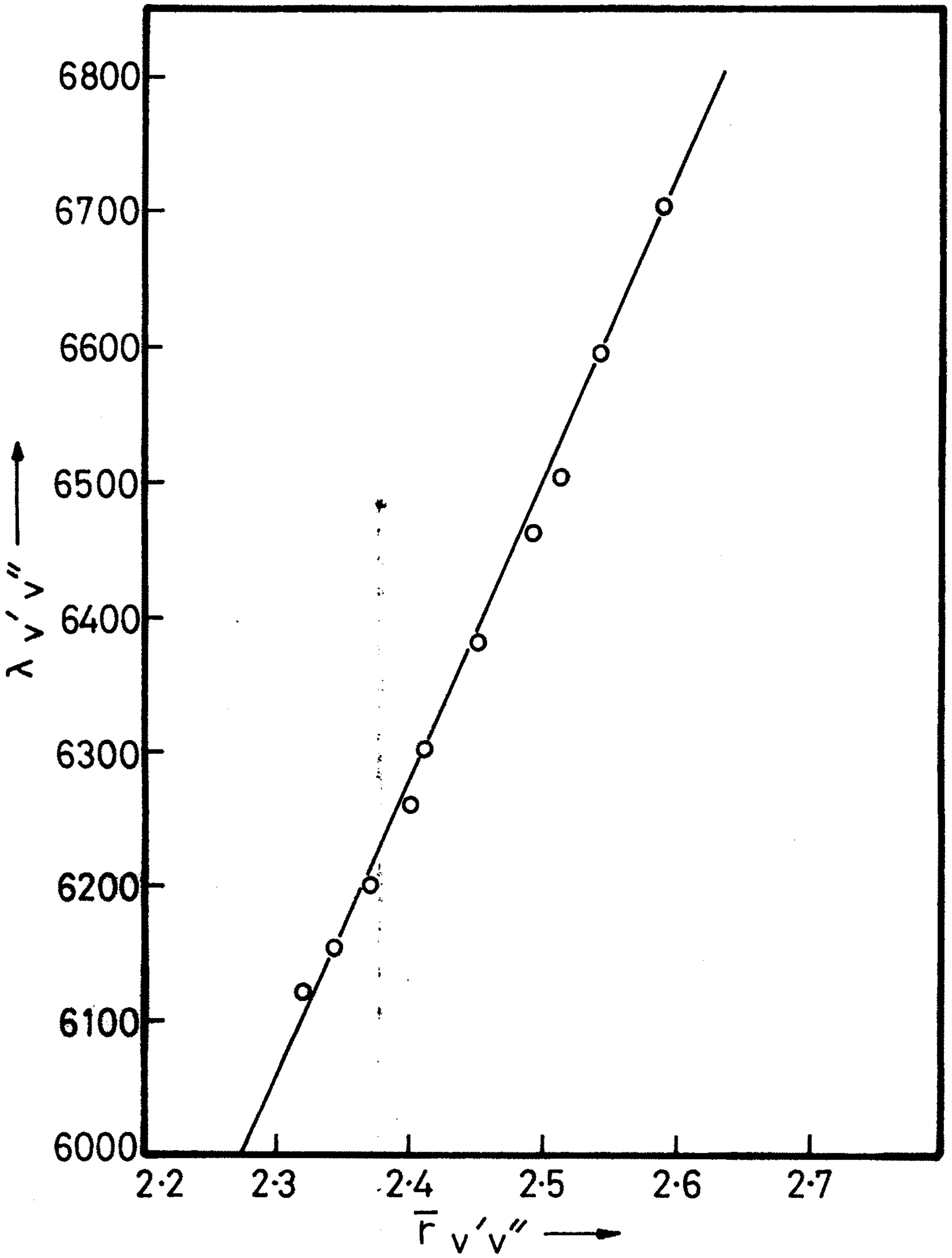

Fig. 4·4 – VARIATION OF $\bar{r}_{v'v''}$ WITH $\lambda_{v'v''}$ IN A–X SYSTEM OF CuTe.