CHAPTER X.

r-Centroids and their evaluation.

Introduction

The concept of the r-centroid was introduced by Nicholls and Jarmin as a means of studying the variation of molecular parameters with internuclear separation. It is defined as the r-coordinate of the centroid of the area represented by the overlap integral and takes a unique value for each band of a system. It is represented by the expression:

\[
\overline{r}_{\nu,v''} = \frac{\int \varphi_{\nu'} \varphi_{v''} \, dy}{\int \varphi_{\nu'} \varphi_{v''} \, dy}
\]  

(1)

Fraser has shown that the equation (1) and the following equation (2) and (3) given below

\[
\int \varphi_{\nu'} \gamma \varphi_{v''} \, dy = (\gamma_{\nu,v''}) \int \varphi_{\nu'} \varphi_{v''} \, dy \]  

(2)

\[
\int \varphi_{\nu'} \frac{\partial}{\partial \gamma} \varphi_{v''} \, dy = \frac{\partial}{\partial \gamma} \int \varphi_{\nu'} \varphi_{v''} \, dy \]  

(3)

are valid under certain definite criteria. These criteria are:

1. \(\mu_A \omega_c \sim 10^4\) for the molecule under consideration where \(\mu_A\) is the reduced mass of the molecule in atomic
weight units, and \( \omega_c \) is the vibrational frequency in cm\(^{-1}\) units.

\((11)\) \(0.01 A^0 < |r_{el}-r_{e2}| < 0.25 A^0\) where \(r_{el}\) and \(r_{e2}\) are the two equilibrium internuclear separations concerned in the transition.

\((111)\) \(v'\) and \(v''\) do not exceed about 10.

\((iv)\) if \(f(r)\) is a polynomial in \(r\), the highest power of \(r\) should not exceed about 10.

Equation (1) shows that the \(r\)-centroid is a weighted mean of internuclear separations encountered by the molecule in the two vibrational levels concerned with respect to the weight function. The \(r\)-centroids vary slowly from band to band in a system and the variation is systematic with respect to band wavelength \(\lambda\). It is found that for band systems in which \(r_{e'} > r_{e''}\), \(\bar{r}_{v'v''}\) increases with \(\lambda v'v''\) and for band systems in which \(r_{e'} < r_{e''}\) decreases with \(\lambda v'v''\).

2.

The methods of evaluation

Nicholls and Jarmain have given three methods of evaluating the \(r\)-centroids. These are

(a) The direct method.

(b) The mean value method.
The broad steps in the methods are summarised in the following sections. These methods are employed to evaluate the r-centroids for the bands of BaO \( \sum_1 \sum \) system, as this system has been found to satisfy the required criteria, viz.,

(i) \( \mu' \omega' = 7150 \text{ gm.cm}^{-1}, \mu'' \omega'' = 9557 \text{ gm.cm}^{-1} \) both being of the order of \( \sim 10^5 \) as required by the first criterion.

(ii) \( \epsilon_{11} - \epsilon_{22} = 0.194 \text{ A}^0 \) for the system, which is greater than 0.01 \text{ A}^0 but less than 0.25 \text{ A}^0 as required by the second criterion, and

(iii) \( v', v'' \) are taken not to exceed 10 for the bands to satisfy the third criterion.

(a) **The direct method:** In this method the r-centroids are obtained directly from the relation (1) namely

\[
\gamma_{v',v''} = \frac{\int \gamma_{v'} (\gamma) \psi_{v',\gamma} \psi_{v'',\gamma} d\gamma}{\int \psi_{v',\gamma} \psi_{v'',\gamma} d\gamma}
\]

The overlap integrals \( \int \gamma_{v'} (\gamma) \psi_{v',\gamma} \psi_{v'',\gamma} d\gamma \) and \( \int \psi_{v',\gamma} \psi_{v'',\gamma} d\gamma \) are evaluated by numerical integration after Bate's method. Knowing the value of these integrals, r-centroids can be computed by relation (1)

(b) **The mean value method:** The reduced one dimensional Schrodinger equations which describe the molecule in
levels \( v' \) and \( v'' \) respectively, give the relation

\[
\left( E_{v'} - E_{v''} \right) \int \psi_{v'}(\gamma) \psi_{v''}(\gamma) d\gamma = \int \psi_{v'}(\sqrt{v'_1 - v'_2}) \psi_{v''}(\sqrt{v''_1 - v''_2}) d\gamma
\]  

(4)

where \( v'_1(\gamma) \) and \( v''_2(\gamma) \) are the potentials of the upper and lower states respectively and \( E_{v'} \), \( E_{v''} \) are the vibrational energies concerned.

Fraser has shown that if \( V_1(\gamma) - V_2(\gamma) \) is a slowly and smoothly varying function of \( \gamma \) over the significant range of integration, the relation

\[
\int \psi_{v'}(\gamma) f(\gamma) \psi_{v''}(\gamma) d\gamma = \int (\sqrt{v'_1 - v'_2}) \int \psi_{v'}(\gamma) \psi_{v''}(\gamma) d\gamma
\]  

(5)

holds. Hence from equation (4) we have

\[
E_{v'} - E_{v''} = \psi_{v'}(\sqrt{v'_1 - v'_2}) - \psi_{v''}(\sqrt{v''_1 - v''_2})
\]  

(6)

If \( v_1 \) and \( v_2 \) are represented by Morse functions,

\[
\begin{align*}
  v_1 &= D_1 \left[ -e^{\kappa_1 (\sqrt{v'_1 - v'_2})} \right]^2 \\
  v_2 &= D_2 \left[ -e^{\kappa_2 (\sqrt{v''_1 - v''_2})} \right]^2
\end{align*}
\]

where \( D = \frac{\epsilon^2}{2 \omega^2 e} \), \( \kappa = 0.2454 \sqrt{\frac{1}{2 \omega^2 e}} \) and \( r_e \) are the internuclear distances corresponding to the states concerned, viz., the upper and lower states 1 and 2 respectively then the equation (6) becomes

\[
E_{v'} - E_{v''} = D \left[ -e^{\kappa_1 (\sqrt{v'_1 - v'_2})} \right]^2 - D_2 \left[ -e^{\kappa_2 (\sqrt{v''_1 - v''_2})} \right]^2
\]  

(7)
where \( E_v = \omega_e (v + \frac{1}{2}) - \omega_x e (v + \frac{1}{2})^2 \)

Equation (7) may be solved for \( r_{v'v''} \) by two procedures, viz.,

(i) The graphical procedure

(ii) The quadratic equation procedure

(i) The graphical procedure: In this procedure values of the right hand side of equation (7) may be calculated for different values of \( 'r' \) over the significant range of \( r \). These computed values are plotted against the corresponding values of \( 'r' \). The difference between \( E_v \) and \( E_{v''} \) is evaluated for each band and the values of \( r_{v'v''} \) corresponding to these energy differences are then read from the graph.

(ii) Quadratic equation procedure: Equation (7) may be considered as a quadratic equation in \( x = \exp(-\kappa_{v',v''}) \) by replacing \( \kappa \) and \( \kappa_2 \) by the arithmetic mean value of \( \kappa \). Equation (7) then can be written as

\[
E_{v'} - E_{v''} = D_1 \left[ \exp(-\kappa (\gamma_{v',v''}) - \gamma_e) \right] - D_2 \left[ \exp(-\kappa (\gamma_{v',v''} - \gamma_e)) \right].
\] (8)

where \( E_{v'}, E_{v''}, D_1, D_2 \) are the adjusted quantities with respect to \( \kappa \) the mean of \( \kappa \), and \( \kappa_e \). This equation (8) can be expressed as

\[
x^2 - 2\alpha x + R_{v'v''} = 0 \] (9)
where
\[ F = F_1^{2D_1} - F_2^{2D_2} \]
\[ Q = F_1^{D_1} - F_2^{D_2} \]
\[ R_{v', v''} = D_1 - D_2 - (b_{v'} - b'_{v''}) \]

and in these latter,
\[ F_1 = \exp (\infty \gamma_{e_1}) \]
\[ F_2 = \exp (\infty \gamma_{e_2}) \]

Equation (9) as quadratic in 'x' has two roots of which often one, \( x_1 \) is positive and the other \( x_2 \) is negative. The array of r-centroids may be determined by solving equation (9) as a quadratic and interpreting each positive root according to equation
\[ \bar{y}_{v', v''} = -\frac{1}{\infty} \ln x_1 \ldots \ldots \ldots \] (10)

In cases where both roots are positive, the physically meaningful \( r_{v', v''} \) is that which lies within the range \( r_{e1} \) to \( r_{e2} \) or in the neighbourhood of it. When both roots are negative or complex, the quadratic equation method is not applicable.

(c) The difference method.

During the development of the above methods, it was observed that nearly linear trends existed in \( r_{v', v''} \) along sequences. The constant difference in r-centroids
along a sequence suggested that a further method of obtaining arrays of $r_{v+1}^{v'}$ would be to compute the value for the leading member of each sequence by, say, a quadratic equation method, then successively to apply the appropriate constant difference to build up the rest of the sequence.

Let $r_1 = r_{v+1}^{v'}$, $\alpha = \frac{1}{2}(\omega_{v'} + \omega_v)$ and let all $\omega$-dependent quantities be adjusted suitably. Using the standard expression for the vibrational energies of the $v' , v''$ and $v' + 1$, $v'' + 1$ levels it could be easily shown that

$$ (E_{v'+1} - E_{v'+1}) - (E_{v'} - E_{v''}) = \omega_v - \omega_{v''} - 2 \Delta \omega \omega \chi \chi $$

Now in Morse potential

$$ E_{v'+1} - E_{v'+1} = D_1 \left[ -F_x \exp(-\alpha \gamma) \right]^p - D_2 \left[ -F_x \exp(-\alpha \gamma) \right]^q \quad (12) $$

$$ E_{v'} - E_{v''} = D_1 \left[ -F_x \exp(-\alpha \gamma) \right]^p - D_2 \left[ -F_x \exp(-\alpha \gamma) \right]^q \quad (13) $$

where $r_1 = r_{v+1}^{v'}$, $v' + 1$ and $W$ is clearly the difference between right hand members of (12) and (13).

For most systems $(r_1 - r) \sim 0.01 \text{A}^0$. This difference depends basically upon the width of the potential curves, as the change $(r_1 - r)$ in the $r$-centroid is determined by how much the wave functions are spread as quantum numbers are increased. The difference $(r_1 - r)$ would exceed 0.01 $\text{A}^0$ only if the potentials are very wide. For
cases where \((\bar{r}_1 - \bar{r})\) is not much greater than 0.01 a good approximation is:

\[
W = D_1 \int 2F_1 x^2 \alpha (\bar{r}_1 - \bar{r}) - 2F_1 x^2 \alpha (\bar{r}_1 - \bar{r}) J - D_2 \int 2F_2 x^2 \alpha (\bar{r}_1 - \bar{r}) - 2F_2 x^2 \alpha (\bar{r} - \bar{r}) J \quad \ldots \quad (14)
\]

This represents first order approximation in

\[
\exp\left\{-\alpha(C, \bar{r})\right\} \quad \text{and} \quad \exp\left\{-2\alpha(C, \bar{r})\right\}
\]

Thus

\[
(\bar{r}_1 - \bar{r}) = \Delta \bar{r} = \frac{W}{2\cos(x(Q - P))} \quad \ldots \ldots \quad (15)
\]

\(P, Q\) and \(X\) are defined in equation (9).

Equation (15) enables a constant difference in \(r\)-centroids to be obtained for each sequence. Data for the complete sequence can then be built up once \(r_{v', v''}\) for one member usually the leading member is known.

3

Calculations and Results

Of these methods, the method (a) requires the calculation of overlap integrals which is done usually by numerical integration. But this latter involves laborious, protracted and thus often times tedious calculations and is therefore usually not adopted for evaluating \(r\)-centroids.

In the present case, however, such overlap integrals are available to us from the study of BaO \((\overline{1} \overline{1} \overline{1} - \overline{1} \overline{1} \overline{1})\) system...
made by application of anharmonic (Morse) oscillator wave function to derive the transition probabilities. Those values are therefore straightway used here to calculate the r-centroids without any extra labour by using the direct method (a). The values of overlap integrals used are repeated here in Table VIII from chapter VIII for ready reference. The calculations for $r_{V'V''}$ are shown in Table XI at (a) along the rows.

**Table VIII**

<table>
<thead>
<tr>
<th>Band $V'V''$</th>
<th>$\int \psi_{V'} \psi_{V''} d\gamma$</th>
<th>$\int \psi_{V'} \psi_{V''} r d\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,0</td>
<td>0.74845112</td>
<td>1.52108341</td>
</tr>
<tr>
<td>0,1</td>
<td>0.16939429</td>
<td>0.34832777</td>
</tr>
<tr>
<td>0,2</td>
<td>0.26519680</td>
<td>0.55176068</td>
</tr>
<tr>
<td>1,0</td>
<td>0.15194417</td>
<td>0.30607552</td>
</tr>
<tr>
<td>1,1</td>
<td>0.27000977</td>
<td>0.55084737</td>
</tr>
<tr>
<td>1,2</td>
<td>0.30679928</td>
<td>0.62726896</td>
</tr>
<tr>
<td>2,0</td>
<td>0.22916723</td>
<td>0.45759925</td>
</tr>
<tr>
<td>2,1</td>
<td>0.30115118</td>
<td>0.60799559</td>
</tr>
<tr>
<td>2,2</td>
<td>0.19212548</td>
<td>0.39259141</td>
</tr>
<tr>
<td>3,0</td>
<td>0.26890947</td>
<td>0.53222332</td>
</tr>
<tr>
<td>3,1</td>
<td>0.23127501</td>
<td>0.46288920</td>
</tr>
<tr>
<td>3,3</td>
<td>0.19126087</td>
<td>0.39343711</td>
</tr>
</tbody>
</table>

In the mean value method (b) the graphical procedure is simplest one for evaluating the r-centroids and,
therefore is commonly used. This procedure does not involve any approximation and so the results obtained by this method are comparatively more accurate than the results obtained by direct method. The results of r-centroids are obtained here also by the use of this procedure.

In this procedure the values of $V_1$ and $V_2$ are computed by using Morse function for different values of 'r' over the range 1.45 to 2.70 of $r$ for the molecule. Then $V_1 - V_2$ are plotted as a function of $r$. Then the vibrational energies $E_v$ and $E_v''$ are calculated and the different $E_v - E_v''$ evaluated from them. Corresponding to these values $E_v - E_v''$ the appropriate $r_{v',v''}$ values are read from the graph. The data needed for the construction of the graph and hence to evaluate the r-centroids are given in Table IX and X.
Table X.

| V  | $E_v, \text{cm}^{-1}$ | $E_v, \text{cm}^{-1}$ | $V_1V_2$ | $E_{v_1} - E_{v_2}$ |
|----|------------------|------------------|---------|----------------|---|
| 0  | 249.0            | 334.4            | 0.0     | -35.4          |   |
| 1  | 747.6            | 1000.1           | 0.1     | -252.3         |   |
| 2  | 1237.6           | 1661.7           | 0.2     | -1412.7        |   |
| 3  | 1727.4           | 2319.2           | 1.0     | 413.4          |   |
| 4  | 2214.2           | 2972.6           | 1.1     | -252.3         |   |
| 5  | 2698.0           | 3621.9           | 1.2     | -423.9         |   |
| 6  | 3178.8           | 4267.1           | 2.0     | 903.2          |   |
|    |                  |                  | 2.1     | 237.5          |   |
|    |                  |                  | 2.2     | -424.1         |   |
|    |                  |                  | 3.0     | 1393.0         |   |
|    |                  |                  | 3.1     | 727.3          |   |
|    |                  |                  | 3.2     | 65.8           |   |
|    |                  |                  | 3.3     | -591.7         |   |
|    |                  |                  | 3.4     | -1245.2        |   |

The relation of $V_1-V_2$ against $r$ is represented graphically in Fig. 5. The results of $r$-centroids are entered as rows (b) in Table XI.

In the quadratic equation procedure an approximation is made that $\infty_1$ and $\infty_2$ are replaced by the arithmetic mean value of $\infty$ and moreover when both roots
are negative or complex, the conditions under which the equation (3) holds do not obtain and then the quadratic equation method does not become applicable. In the case of the present BaO system both the roots are negative and therefore this method is not applicable.

The difference method depends on the quadratic equation procedure and is only an approximate method. For that reason and results being available by more accurate methods viz., (a) the direct method and (b) the mean value method (graphical procedure), the difference method has not been used for calculating the r-centroids.

<table>
<thead>
<tr>
<th>v</th>
<th>v''</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
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<td>(a)</td>
<td>2.032</td>
<td>2.037</td>
<td>2.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>2.032</td>
<td>2.037</td>
<td>2.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>(a)</td>
<td>2.014</td>
<td>2.038</td>
<td>2.043</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>2.014</td>
<td>2.037</td>
<td>2.043</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(a)</td>
<td>1.996</td>
<td>2.018</td>
<td>2.043</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>1.996</td>
<td>2.020</td>
<td>2.043</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(a)</td>
<td>1.979</td>
<td>2.002</td>
<td>-</td>
<td>2.052</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>1.979</td>
<td>2.002</td>
<td>-</td>
<td>2.05</td>
<td>2.06</td>
</tr>
</tbody>
</table>
The r-centroids computed by the direct method (a) will be used for the study of variation of electronic transition moment with r being preferable to the graphical ones in point of accuracy. This study will be taken up in the next chapter.
REFERENCES.