Experimental and Computational Methods
This chapter includes the methods of purification of compounds, measurements of their absorption and emission spectra and the description of the method used for theoretical calculation.

3.01 Purification of Compounds

Nitro- and Amino- Phenols: All the phenols were purified by recrystallization from ethanol. Nitro phenols were repeatedly crystallized from 25% ethanol. Melting points were compared with the literature values to check the purity of the compounds. Amino phenols were treated with activated charcoal and the filtrate was concentrated. The process was repeated several times and the compound was crystallized in dark from ethanol-water mixture until the absorption spectra were constant and melting point agreed with value in literature. The crystalline preparations were stored under nitrogen in a desiccator protected from light and all solutions were prepared on the day those were to be used. Nitrogen was passed through the solution to remove oxygen.

Benzoic Acids: Benzoic acids were dissolved in hot ethanol and boiled for a few minutes. The solution was
then treated with activated charcoal and filtered. The 
filterate was cooled under ice or tap water. When the 
benzoic acid or Substituted benzoic acid crystals separate. 
The crystals were washed with cold ethanol and dried under 
vacuum.

Preparation of Fluoro Benzoic Acids : Fluoro benzoic acids 
were prepared from fluoro benzaldehydes (pure) by oxidation 
with Jones oxidising Agent. To a vigorously stirred 
solution of fluoro benzaldehyde (1.0 g ) in acetone (30 cc ) 
at 278 K was added Jones reagent (3.0 cc ) (a mixture of 
chromium trioxide (6.0 g) and sulphuric acid (7.0 cc) ) 
the total volume of the mixture was made 100.0 cc by 
addition of water. The mixture was stirred for one hour 
at 278 K. After one hour the mixture was removed from 
the ice bath and stirred as such for 30 minutes at room 
temperature. Reaction mixture was diluted with ether and 
water and the organic layer was separated. The organic 
layer contained both unreacted benzaldehyde and benzoic acid. 
This layer was washed with sodium bicarbonate saturated 
solution and the aqueous layer was collected. This layer 
contained the sodium salt of the acid and it was acidified 
with 10% HCl at 273 K and again shaken with ether. The 
etheral layer was collected which contained acid and it 
was dried with anhydrous sodium sulfate. On evaporation of 
ether the solid crystals were collected and dried. The 
melting points agreed with corresponding pure acids.
<table>
<thead>
<tr>
<th>Name of Chemical</th>
<th>Source</th>
<th>M.P/B.P (K) Literature value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>Bengal Chemicals and Pharmaceutical Works Ltd., Calcutta, India</td>
<td>- 352.0 351.0</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>B.D.H. LR, India</td>
<td>- 352.6 353</td>
</tr>
<tr>
<td>Isopentane</td>
<td>B.D.H. LR, India</td>
<td>- 309 310</td>
</tr>
<tr>
<td>Ether</td>
<td>Alembic Chemical Works Co. Ltd., Baroda, India</td>
<td>- - -</td>
</tr>
<tr>
<td>o-Nitrophenol</td>
<td>Thomas Baker Co. London, LR., UK.</td>
<td>317 - 318</td>
</tr>
<tr>
<td>m-Nitrophenol</td>
<td>B.D.H. LR., India</td>
<td>368 - 369</td>
</tr>
<tr>
<td>p-Nitrophenol</td>
<td>Thomas Baker Co. London LR, UK.</td>
<td>387 - 387</td>
</tr>
<tr>
<td>o-Amino phenol</td>
<td>Ward Blenkinsop and Co. Ltd., U.K.</td>
<td>446 - 447</td>
</tr>
<tr>
<td>m-Amino phenol</td>
<td>Riedel De Hahn. AG., Germany</td>
<td>394 - 395</td>
</tr>
<tr>
<td>p-Amino phenol</td>
<td>Ward Blenkinsop and Co. Ltd., U.K.</td>
<td>455\textsuperscript{d} - 457\textsuperscript{d}</td>
</tr>
<tr>
<td>o-Amino Benzoic acid</td>
<td>I.D.P.L. LR Hyderabad, India</td>
<td>417 - 418</td>
</tr>
<tr>
<td>m-Amino Benzoic acid</td>
<td>Nipa Fine Chemicals and Organic Intermediate, U.K.</td>
<td>446 - 447</td>
</tr>
<tr>
<td>p-Amino Benzoic acid</td>
<td>E. Merck AG. Dramstadt, Germany</td>
<td>460 - 460</td>
</tr>
<tr>
<td>o-Hydroxy Benzoic acid</td>
<td>Made in France</td>
<td>431 - 432</td>
</tr>
<tr>
<td>m-Hydroxy Benzoic acid</td>
<td>Fluka AG Buchs SG Pure, Switzerland.</td>
<td>474 - 474</td>
</tr>
</tbody>
</table>

(contd...)
<table>
<thead>
<tr>
<th>Name of Chemical</th>
<th>Source</th>
<th>M.P.</th>
<th>B.P.</th>
<th>Literature value</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Hydroxy Benzoic acid</td>
<td>SISCO Research Laboratories Pvt. Ltd., Bombay, Pure, India</td>
<td>485</td>
<td>-</td>
<td>486</td>
</tr>
<tr>
<td>o-Fluoro Benzoic acid</td>
<td>Prepared in the Laboratory</td>
<td>394</td>
<td>-</td>
<td>395</td>
</tr>
<tr>
<td>m-Fluoro Benzoic acid</td>
<td>Prepared in the Laboratory</td>
<td>396</td>
<td>-</td>
<td>397</td>
</tr>
<tr>
<td>p-Fluoro Benzoic acid</td>
<td>Prepared in the Laboratory</td>
<td>455</td>
<td>-</td>
<td>455</td>
</tr>
</tbody>
</table>
3.03 **Purification of solvents**: Absolute ethanol was twice distilled over sodium metal and stored over molecular sieves. Water was triply distilled over potassium dichromate and potassium permanganate solutions. Cyclohexane was stirred with sulfuric acid washed with water and dried over fused calcium chloride and distilled twice over sodium (Boiling temperature 352.6 K). Isopentane was also washed with sulfuric acid and fractionally distilled (Boiling temperature 309 K).

3.04 **Cleaning of Glasswares**: All volumetric glasswares were detergent cleaned, washed three times with distilled water and oven dried. Pipettes were cleaned by overnight soaking in detergent solution washing with distilled water and again overnight soaking in dichromate solution, washed with distilled water and oven dried. Absorption and Emission cuvettes were kept in nitric acid for one night, washed with water, rinsed three times with Acetone and dried.

3.05 **Spectroscopic Measurements**

**Absorption Spectra**: The absorption studies have been carried out on a CARL-ZEISS UV-vis spectrophotometer.

The instrument was switched on at least for half an hour, before actual measurements were started. In the meantime, a $10^{-2}$ M solution of the desired compound in water was prepared. This was diluted to $10^{-3}$M, $10^{-4}$M, $5\times10^{-5}$M, $10^{-5}$M and the spectral bands of different
Fig. 3.1. ABSORPTION SPECTRA OF ORTHO HYDROXY BENZOIC ACID IN ACIDIC MEDIA AT DIFFERENT CONCENTRATIONS (1.) $10^{-4}$ M, (2.) $5 \times 10^{-5}$ M & (3.) $10^{-5}$ M
intensities were recorded. The same procedure was repeated for the preparation and recording of spectra of the compounds in ethanol. In a few cases solutions up to 0.1 M were also used. A typical absorption spectrum at several concentration is shown in fig. 3.1. Due to poor solubility of most of the compounds in cyclohexane, the concentration of the compounds in cyclohexane were very dilute and sometimes unknown. In a few cases a band of very low extinction coefficient was recorded in the excitation spectra. All measurements were made at room temperature (298K - 303K).

The zero reference was taken with pure solvents in both cuvettes. One of the cuvette was used as reference and the solution of appropriate concentration was taken in the other. For the sake of completeness and for understanding Acid-Base behaviour in the excited state the protonated and deprotonated species corresponding to the parent molecule were also studied. This was achieved by adding known amounts of alkali (NaOH) and acid (HCl).

The oscillator strengths for the various absorption bands were calculated from the approximate equation.

\[ f = 4.319 \times 10^{-9} \times \frac{\varepsilon_U}{\lambda} \]

where \( \varepsilon_U \) is molar Extinction coefficient at the maximum of the band (\( \lambda \)) and \( \Delta \lambda \) is half width of the maxima in the absorption band.
Emission Studies

The emission spectra have been taken on PERKIN ELEMER - MPF 44B Fluorescence spectrophotometer. These spectra have been taken in Ethanol, water and cyclohexane. For those compounds for which fluorescence is not observed at room temperature, studies have been made at liquid nitrogen temperature (77 K) in Ethanol and EPA (a 5:5:2 mixture of ethyl ether; iso-pentane and Ethanol) glasses.

The wave length callibration of the scale was done by ovalene, compound 610 and Rhodamine B (fluorescence standards provided with the instrument). Allignment of the light source Xenon Lamp was done by adjusting the screws until the image (see Figure 3.2) appeared correctly on white paper placed above the turntable, parallel to the excitation lens in the sample compartment.

![Correct Image](image)

![Incorrect Adjustments](image)

**Fig. 3.2: Excitation Beam Images indicating Correct and Incorrect Xenon Lamp Adjustment.**
Fig. 3.3 Fluorescence spectra of ortho hydroxy benzoic acid in water at different excitation wavelengths (1 x 10^{-4} M)
The instrument was put on for half an hour till it sets at -750 at HV in energy mode. In the meantime a solution of the compound in water was prepared and diluted to $10^{-3}$M, $10^{-4}$M and $10^{-5}$M. Their fluorescence spectra were recorded by choosing the Excitation wave length as the longest wave length at which absorption takes place. The slit width was kept at 3 nm, both in excitation and emission monochromators. It was same for all the compounds. The gain of the signal was adjusted accordingly, so that pen of the recorder is within range. The same procedure of measurement of fluorescence was repeated in ethanol and cyclohexane solvents. In order to avoid scattering errors appropriate filters were used while recording fluorescence spectra. Fluorescence of undissociated compounds (such as phenol, benzoic acids and benzaldehydes) were obtained in 1M hydrochloric acid and those for anions were recorded in 0.10 M potassium hydroxide. To see the existence of zwitter ions of amino benzoic Acids the fluorescence measurements were repeated in suitable pH range. The fluorescence spectra of the pure solvents were taken to see if these give Raman peaks in the range of fluorescence species. Fluorescence studies were also conducted by varying excitation $\lambda$ in order to ensure that the peaks are only due to compounds and not due to scattering. For some of the compounds (nitro phenols, nitro benzoic acids, fluoro benzaldehydes and p-hydroxy benzaldehyde) fluorescence
studies were done at liquid nitrogen temperature as these compounds did not show fluorescence at room temperature. A typical fluorescence spectrum is shown in fig. 3.03.

PHOSPHORESCENCE

For phosphorescence studies the accessory with amplifier which control the speed of chopper was assembled. A $10^{-2}$M solution of the compounds in ethanol were prepared and diluted to $10^{-4}$M. Phosphorescence was observed by using $10^{-4}$M solution. The excitation wave lengths used were again the longest wave length absorption peak. The slit width of 20 nm was used and gain was adjusted accordingly using appropriate filter to observe the peaks on the Amplifier, while the exact position of the phosphorescence peak was observed on oscilloscope and also confirmed by its decay on opening and closing the sample shutter. The phosphorescence studies were made in EPA which gives a good glass matrix at low temperature. Phosphorescence studies of pure solvents ethanol and EPA were also made separately to find out if there is any impurity in these which may give phosphorescence. Phosphorescence spectra of the compounds were repeated in ethanolic sodium hydroxide and ethanolic hydrochloric acid glasses at 77 K to observe the phosphorescence of various species resulting from acid-base equilibrium.
3.06 METHOD OF COMPUTATION

We have used CNDO/S method as developed by Del Bene and Jaffe for the calculations of theoretical electronic spectra.

In this method Roothan's equations are used as a basis for calculation of molecular orbitals of molecules. Molecular orbitals are formed by linear combination of atomic orbitals of the valence electrons considering is electron as a part of the unpolarizable core.

$$\psi_i = \sum_\nu \phi_{\nu}^i c_{\nu i} \quad \ldots \quad 3.01$$

where $\psi_i$ is the i th molecular orbital, $\phi_{\nu}$ are valence atomic orbitals and $c_{\nu i}$ are the coefficients. For molecules with closed shell configuration, variational treatment of atomic orbital co-efficient $c_{\nu i}$ leads to

$$\sum_\nu F_{\mu \nu} c_{\nu i} = \sum_\nu S_{\mu \nu} c_{\nu i} \epsilon_i \quad \ldots \quad 3.02$$

where

$$F_{\mu \nu} = H_{\mu \nu} + G_{\mu \nu} \quad \ldots \quad 3.03$$

$$H_{\mu \nu} = \int \phi_{\mu}^i \left[ -\frac{1}{2} \nabla^2 - \sum_A V_A \right] \phi_{\nu} \ d\tau \quad \ldots \quad 3.04$$

$$G_{\mu \nu} = \sum_{\lambda \sigma} P_{\lambda \sigma} \left[ \mu_{\nu}(\lambda \sigma) - \frac{1}{2}(\mu \sigma / \nu \lambda) \right] \quad \ldots \quad 3.05$$

$$\left( \mu_{\nu} \lambda \sigma \right) = \int \phi_{\mu}^i(1) \phi_{\nu}^j(1) \chi_{ij}^{l} \phi_{\lambda}^i(2) \phi_{\sigma}^i(2) d\tau_1 d\tau_2 \quad \ldots \quad 3.06$$

$$S_{\mu \nu} = \int \phi_{\mu}^i \phi_{\nu}^i d\tau \quad \ldots \quad 3.07$$

$$P_{\lambda \sigma} = 2 \sum_{i=1}^{O_{\text{Occ}}} C_{i \lambda} C_{i \sigma} \quad \ldots \quad 3.08$$

In these equations $\epsilon_i$ represents orbital energy corresponding to molecular orbital $\psi_i$. $H_{\mu \nu}$ gives the matrix element of one electron Hamiltonian including KE and PE whereas $G_{\mu \nu}$ is the matrix element of the potential due to
other valence electrons and depends on the MO's via population matrix \( P_{\lambda \sigma} \). Applying the CNDO approximations including the use of ZDO approximation of Pople et al.\(^{237-240}\) in which the two electrons integrals are approximated as

\[
(\mu \nu / \lambda \lambda) = (\mu \mu / \lambda \lambda) \delta_{\mu \nu} \delta_{\lambda \sigma} \quad \ldots \quad 3.09
\]

and core integral

\[
\int \phi_{\mu} (1) \text{H core} \phi_{\nu} (1) \, dT \quad \ldots \quad 3.10
\]

are treated in semi-empirical manner. It is assumed that:

\[
(\mu \mu / \lambda \lambda) = \gamma_{AB} \quad \ldots \quad 3.11
\]

\( \gamma_{AB} \) gives the average electrostatic repulsion between any electron on nucleus A and any electron on nucleus B.

The expressions for matrix elements \( F_{\mu \nu} \), \( F_{\mu \mu} \), \( H_{\mu \nu} \) and \( H_{\mu \mu} \) simplify to:

\[
F_{\mu \nu} = H_{\mu \nu} - \frac{1}{2} \rho_{\mu \nu} \gamma_{AB} \quad (\mu \neq \nu) \quad \ldots \quad 3.12
\]

\[
F_{\mu \mu} = H_{\mu \mu} - \frac{1}{2} \rho_{\mu \mu} \gamma_{AA} + \rho_{AA} \gamma_{AA} \quad \ldots \quad 3.13
\]

\[
+ \rho_{BB} \gamma_{AB} \quad , \quad B \neq A
\]

\( \mu \) belongs to atom A and \( \rho_{BB} \) is total valence electron density on Atom B.

\[
\rho_{BB} = \sum_{\nu} \rho_{\nu, \nu} \quad \ldots \quad 3.14
\]

and \( H_{\mu \nu} \) and \( H_{\mu \mu} \) are given

\[
H_{\mu \nu} = U_{\mu \nu} - \sum_{B \neq A} (\mu / V_{B} / \nu) \quad \ldots \quad 3.15
\]
Integrals \((\mu/V_B/V)\) in which \(\phi_{\mu}\) and \(\phi_{\mu}\) belongs to Atom A are put equal to zero if \(\mu \neq \nu\)

\[
H_{\mu\mu} = \left(\mu - \frac{1}{2} \nabla^2 - V_A/\mu\right) - \sum_{B \neq A} \left(\mu/V_B/\mu\right) \quad \ldots \quad 3.16
\]

\[
= U_{\mu\mu} - \sum_{B \neq A} \left(\mu/V_B/\mu\right) \quad \ldots \quad 3.17
\]

\[
\left(\mu/V_B/\mu\right) = \nu_{AB} \quad \ldots \quad 3.18
\]

As all atomic orbitals are on Atom A,

In consequence we may write

\[
H_{\mu\mu} = U_{\mu\mu} - \sum_{B \neq A} \nu_{AB} \quad \ldots \quad 3.19
\]

\[
H_{\mu\nu} = 0 \quad (\mu \neq \nu) \quad \ldots \quad 3.20
\]

as both on the same atom off, diagonal core matrix elements between Atomic orbitals on different atoms are estimated as

\[
H_{\mu\nu} = \beta_{\mu\nu} = \beta_{AB}^{\sigma} \quad \ldots \quad 3.21
\]

\(S_{\mu\nu}\) is the overlap integral and \(\beta_{AB}\) is Pople Bonding parameter and depend only on the nature of atoms A and B.

In this framework of CNDO method \(E_{\mu\nu}\) and \(E_{\mu\mu}\) matrix element now reduce to the form

\[
E_{\mu\mu} = U_{\mu\mu} + \left(P_{AA} - \frac{1}{2} P_{\mu\mu}\right) \gamma_{AA} + \sum_{B \neq A} \left(P_{BB} \gamma_{AB} - \nu_{AB}\right) \quad \ldots \quad 3.22
\]

which by putting the value of \(U_{\mu\mu}\) from the relation

\[-\frac{1}{2} \left(I_{\mu} + A_{\mu}\right) = U_{\mu\mu} + (Z_A - \frac{1}{2}) \gamma_{AA} \quad \ldots \quad 3.23\]

In which \(I_{\mu}\) and \(A_{\mu}\) are valence state ionization potential and electron affinity respectively, These substitutions give
\[ F_{\mu\mu} = -\frac{1}{2} \left( I_\mu + A_\mu \right) + (P_{AA} - Z_A) - \frac{1}{2} (P_{\mu\mu} - 1) \]

\[ \gamma_{AA} + \sum(P_{BB} - Z_B) \ \gamma_{AB} \]

\[ \text{and } P_{AA} \text{ and } P_{\mu\mu} \text{ are atomic and orbital charge densities respectively. } Z_A \text{ is core charge on atom A.} \]

\[ F_{\mu\nu} = \frac{1}{2} \left( J_A^0 + J_B^0 \right) S_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \ \gamma_{AB} \]

\[ \text{P}_{\mu\nu} \text{ is bond order and } \gamma_{AB} \text{ is electron repulsion integral.} \]

The closed shell spectroscopic CNDO/S. CI molecular programme of Del Bene and Jaffe used in carrying out the present semi-empirical MO has modified values for parameters \( \gamma_{AA} \) and \( \frac{1}{2} (J_A^0 + J_B^0) \) where \( \gamma_{AA} \) are evaluated as difference between ionization potential and electron affinity of valence orbital on Atom A. The Quantum chemistry programme exchange (174) used here employs Nishimoto Mataga approximations for the evaluations of two centre

\[ J_{AB(\text{ev})} = 14.38 \left( R_{AB} + \frac{28.76}{J_{AA} + J_{BB}} \right)^{-1} \]

where \( R_{AB} \) is the distance between centres and \( J_{AA} \) and \( J_{BB} \) are appropriate one centre terms. The term \( \frac{1}{2} (J_A^0 + J_B^0) \) is a measure of bonding energy between the orbitals \( \mu \& \nu \) on Atoms A & B. This is given different values depending upon whether \( \mu \) and \( \nu \) forms \( \sigma \) or \( \pi \) orbitals. From the spectroscopic studies of a series of compounds it has been found that values of \( \beta_{\mu\nu}, \sigma \) and \( \pi \) orbitals are related as

\[ \beta_{\mu\nu}^\sigma = \frac{1}{2} \left( \beta_A^0 + \beta_B^0 \right) = 1.71 \beta_{\mu\nu}^\pi \]

The CNDO method with these modified parameters reproduces the energies of electronic transition in fair agreement and has been used successfully for different variety of organic and inorganic molecules. Excited states of the
molecules under study are generated from the respective ground state occupied and virtual orbitals through a configuration interaction procedures between the 40 lowest energy singly excited one electron transitions. Various empirical parameters and Slater exponents used in the calculations are given in table- 3.02.

Table- 3.02 : Constants and Parameters used in CNDO- CI Calculations

<table>
<thead>
<tr>
<th>Atom Parameter</th>
<th>H</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic No.</td>
<td>1</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>Valence Electrons</td>
<td>1</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Slater Exponent</td>
<td>1.200</td>
<td>1.625</td>
<td>1.950</td>
<td>2.150</td>
<td>2.600</td>
</tr>
<tr>
<td>Resonance Integral</td>
<td>12.00</td>
<td>17.00</td>
<td>26.00</td>
<td>45.00</td>
<td>50.00</td>
</tr>
<tr>
<td>$\beta^*$ (ev)</td>
<td>12.85</td>
<td>11.11</td>
<td>12.01</td>
<td>13.00</td>
<td>17.36</td>
</tr>
<tr>
<td>One centre repulsion Integral</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\gamma$ (ev)</td>
<td>14.35</td>
<td>28.10</td>
<td>38.63</td>
<td>50.78</td>
<td>56.96</td>
</tr>
<tr>
<td>Core Integral S-orbital (ev)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Core Integral p-orbital (ev)</td>
<td>11.144</td>
<td>14.550</td>
<td>18.222</td>
<td>24.360</td>
<td></td>
</tr>
</tbody>
</table>
CALCULATION OF PROPERTIES

**Total Energy**: Total energy of the molecule in this frame work is given by

\[
E_{\text{total}} = \sum_A \left[ \sum_{\mu} R_{\mu} \rho_{\mu} \mu + \frac{1}{2} \sum_{\mu} \sum_{\nu} (\rho_{\mu} \rho_{\nu} - \frac{1}{2} \rho_{\mu}^2 \rho_{\nu}^2) \gamma_{\mu\nu} \right] \\
+ \sum_{A<B} \sum_{\mu} \sum_{\nu} (2 \rho_{\mu} \rho_{\nu} \rho_{\mu}^2 - \frac{1}{2} \rho_{\mu}^2 \rho_{\nu} \gamma_{\mu\nu}) \\
+ Z_{A}^{2} E_{R_{A B}}^{-1} - P_{A A} V_{A B} - P_{B B} V_{B A} + P_{A A} P_{A B} \gamma_{A B} \]

... 3.28

where \( \mu \) is the valence basis set of atom A and \( \nu \) is that of atom B. \( \rho_{\mu} \mu \) and \( \rho_{\nu} \nu \) are given by the expressions

\[
\rho_{\mu} \mu = (\mu / - 1/2 \nabla^2 - V_A / \mu) \\
\rho_{\nu} \nu = (\mu / V_B / \mu)
\]

... 3.29

... 3.30

**Excitation Energies**: Energy required to promote an electron from filled orbital \( i \) to unfilled orbital \( f' \) is given by the expressions

\[
\Delta E_{\text{singlet}} = \xi_f' - \xi_i - J_{if'} + 2 K_{if'} \]

... 3.31

\[
\Delta E_{\text{triplet}} = \xi_f' - \xi_i - J_{if'} \]

... 3.32

for singlet and triplet states respectively. \( \xi_i \) and \( \xi_f' \) are the energies of the initial and final molecular orbitals involved in excitation. \( J_{if'} \) and \( K_{if'} \) are the molecular coulomb and exchange integrals respectively. As can be seen from the expression for singlet and triplet energies, the
singlet triplet separation is directly related to the value of $K_{if}$ (the Exchange integral). In the CNDO framework this integral vanishes for $n-\pi^*$ transitions and therefore $1\pi^*$ and $3\pi^*$ states come out to be degenerate.

Oscillator Strength: The oscillator strength of a transition from $i$th orbital to unoccupied orbital $f'$ is given by

$$f_{i,f'} = 108.50 \times 10^{-7} \times \frac{\nu_s}{\mu} \left[ (a^{x}_{if'})^2 + (a^{y}_{if'})^2 + (a^{z}_{if'})^2 \right]$$

where

$$a^{x}_{if'} = \sum_{\mu} \sum_{\nu} C_{i\mu} C_{f'\nu} X_A$$

and similar expressions hold for $a^{y}_{if'}$ and $a^{z}_{if'}$. Here $X_A$ is the atomic position of atom $A$, $C_{i\mu}$ and $C_{f'\mu}$ are eigen vectors of orbital $\mu$ in $i$th and $f'$th molecular level respectively.

The oscillator strength, as we see from this expression depends upon the product $C_{i\mu} C_{f'\mu}$. In the case of excitation from a non-bonding orbital to antibonding orbital i.e., $n-\pi^*$ transitions, the orbital $i$ and $f'$ are respectively $\sigma$ and $\pi$. Therefore for all values of $\mu$ either $C_{i\mu}$ or $C_{f'\mu}$ (or both) is zero, and hence the calculated oscillator strength for such transition is zero.
Charge densities in Excited states: The electron density of an atom in an excited state can be obtained from

\[ \rho_{(AA)}^* = \rho_{(AA)}^0 + \sum_m \sum_{ij} \mu C^2 \left( C^2_{fi} \mu - C^2_{j\mu} \right) \]

where \( \rho_{(AA)}^0 \) is ground state charge density on Atom A, \( C_{jm} \) being the CI coefficient for the contributing jth state of the mth electronic configuration arising from the excitation of an electron from occupied orbital i to virtual orbital f'.

\( n_{CI} \) is the number of lowest energy electronically excited configurations considered which is 40 throughout the present work. \( C_{i\mu} \) and \( C_{f'\mu} \) are the expansion coefficients of ith and f'th molecular orbitals.

Dipole Moments in the ground and Excited states: The dipole moment of molecules in the ground or excited state is calculated on the basis of point charge model. The charge \( q_i \) for an atom i having coordinates \( x_i, y_i \) and \( z_i \) is calculated as described above (\( q = (\text{core charge} - \rho) \)).

The dipole moment \( \mu \) is given by the expression:

\[ \mu = \sqrt{(\mu_x)^2 + (\mu_y)^2 + (\mu_z)^2} \]

where

\[ \mu_x = \sum q_i x_i \quad \text{etc.} \]

N is number of atoms in the molecule.

The method cannot be applied to cations or anions because in these cases the dipole moment depends on the choice of the origin whereas it is independent of origin for a
Fig. 3.4 MOLECULAR AXES DESIGNATIONS. THE Y-AXIS IS OUT OF PLANE
a, b, c, d, e are different atoms of the substituted groups.
neutral molecule.

3.00 Procedure of Calculations: The calculations of the LCAO co-efficients, orbital energies, transition energies, oscillator strengths, energies of excited singlet and triplet states and wave functions of these excited states are carried out by QCPE Programme No. 174. For finding the electron densities in first three excited states a separate computer programme is written by the author. All these calculations have been done on DECS-2050 machine.

3.09 Geometry of the molecules: The choice of the x and z axis is shown in figure. The y axis is perpendicular to the plane of benzene ring. Standard bond distances and bond angles have been used for those molecules for which experimental values are not available.