CHAPTER 7

STUDY OF INTERACTION POTENTIAL AND MOLECULAR SHAPE DETERMINATION USING HE - NE LASER

7.1 INTRODUCTION

The study of the Physical Association and chemical bonding can be understood through the study of effective potential or the interaction potential between the molecules in condensed phase. Such a study in addition to the molecular parameters like dipole moment, ionization potential, the polarizability and other bulk properties also require the knowledge of distribution function, the reaction field, the shape of the molecular cavity, a dimensionless parameter and the nature of the interactions between molecules. In this chapter, in section 7.2 we have made efforts to calculate effective potentials using the Classius-Massotti, the Onsager and Kirkwood reaction field with the Lennard-Jones and the Kihara potentials in non-polar liquids assuming spherical shape of the cavity as the simplest case for the calculation of interaction potential.

The theoretical approach used above for spherical molecular cavity in section 7.3 and for arbitrary shape of molecular cavity consists a pairwise potential¹. Hirschfelder¹ has described
intermolecular forces in liquids and has described reaction field techniques\(^1\). It is convenient to work with pairwise potential to deal with the statistical mechanics of liquids and solutions.

In section 7.3 of this chapter, interaction potential using an arbitrary shape of molecular cavity is formulated and applied to solid and liquid carbon di-oxide for \(\nu_3\) and \(\nu_2\) infrared fundamental vibrational modes.

Important information about intermolecular forces can be obtained for molecular systems through a knowledge of a oscillator strength and their relation to the absorption of the incident radiations. It is difficult to calculate oscillator strength by abinitio calculations. The abinitio calculation give sometimes results which differ from experimental values by factors of two to four for large molecules the quantum mechanical calculation are predicted only in semi-empirical way. Therefore, in the section 7.4 of this chapter, a theoretical model for determining oscillator strength using a non-spherical molecular cavity and measurement of He-Ne laser light absorption coefficients. Aqueous solution of sodium chloride for various concentration at room temperature are co-related with the model proposed in this work and the shape factor has been estimated. The ion solvent interaction are analyzed and an internal field correction was applied though analysis of the non-resonant scattered laser light.
7.2 DETERMINATION OF EFFECTIVE POTENTIAL FOR NON-POLAR LIQUIDS

USING THE CONTINUUM DIELECTRIC MODEL

Theoretical Formulation

The non-polar molecules chosen are nitrogen, Argon, Krypton, Zenon, Methane, Benzene, Carbon-Tetrachloride, Cyclo-hexane since they have spherical molecular cavity.

For non-polar interactions and almost spherical molecular cavities, the main part of the effective potential in liquids is given approximately by the following equation:

\[ V^{\text{eff}}(R,d) \approx V(R) + \Delta n_{\text{int}} \left[ C/(R-l) \right] DL, \]  

(7.1)

where \( R \) is the separation between two molecules of the liquid of density \( d \). The quantities \( \Delta \) and \( L \) are given by Hirschfelder\(^1\), \( n \) is the index of refraction of the medium, and \( D \) is defined later, the term \( C \) is the dispersion coefficient of the Kihara (K) potential given by:

\[ V^K(\rho) = C \left[ \alpha^6/\rho^{12} - 1/\rho^6 \right], \]  

(7.2)

where \( \alpha \) is a potential parameter and \( \rho \) is measure of the range over which the interaction holds. The \( k \)-potential given in eqn. (7.2) takes into consideration the size and shape of the molecule under consideration by assuming a core parameter of size \( l \). The shortest distance of separation between two molecules of the liquid is given by \( \rho^0 \) for a fixed orientation and a separation distance of \( R \) between molecular centers. The quantities \( \rho^0 \), \( C \) and \( \alpha \) are related by the equations,
\[ \rho^0 = (2)^{1/6} \sigma \]  
\[ c = 4 \varepsilon \sigma^6 = (3/4) I \alpha^2 \]

where \( I \) is the ionization potential, \( \alpha \) the polarizability and \( \varepsilon \) is the depth of the potential minimum. Two conditions for \( \lambda \) hold. For the Lennard-Jones potential, \( \lambda = 0 \), whereas, for the Kihara potential \( \lambda \neq 0 \) since there is an interaction between the peripheral atoms even when the center-to-center \( R^6 \) effect is weak.

The Lennard-Jones potential can be expressed as:

\[ R^0 \text{(LJ)} = \rho^0 + L \quad (7.5) \]

Hirschfelder has given values of \( \Delta \) and \( L \) as

\[ \Delta = [I_s (I_b + I_{b'} + I_a)]/(I_a + I_b)(I_{b'} + I_a) \quad (7.6) \]

and

\[ L = \langle \Sigma_a [(R_{bb'} - l_{bb'})^3 R_a^3 (1 + 3 \cos (\Theta_b) \cos (\Theta_{b'}) \cos (\Theta_a))] \rangle \langle (R_{ba} - l_{ba})^3 (R_{b'a} - l_{b'a})^3 \rangle > a, \quad (7.7) \]

where \( I_a \) is the ionization potential of the solvent molecule \( a \), \( I_b \) and \( I_{b'} \), that for the solute molecules \( b \) and \( b' \), respectively. The angle \( \Theta_i \) is the angle whose vertex is on molecule \( i \), in the continuum dielectric model, we have assumed the product between \( L \) and \( \Delta \) to be 1.5, i.e.,

\[ L \Delta = 1.5 \quad (7.8) \]

This approximation, eqn. (7.8), avoid computational difficulty and eliminates the requirement that \( L \) be calculated. We have assumed the validity of eqn. (7.8) for solute-solute interaction or for pure liquids where \( b = b' = a \) holds. It is
also assumed that $R \geq 3r_o$, where $r_o$ is the radius of the molecule. An exact solution of eqn. (7.7) for $L$ can be obtained by a computer simulation technique.

**Derivation of the Expression for $D$**

The dependence of the polarization $P$ on the electric field strength $E$ is given by the following expression

$$P = (\varepsilon - 1) E/4\pi$$

(7.9)

where $\varepsilon$ is called the dielectric constant. The induced polarization $P_\alpha$ is then given by;

$$P_\alpha = \sum_k N_k \alpha_k (E_1)_k$$

(7.10)

where $N$ is the number of particles per cm$^3$, $\alpha$ is the scalar polarizability of any particle and $E_1$ is the average field strength acting upon that particle. The calculation of $E_1$ is a central problem in the theory of electric polarization. We have adopted a continuum approach in which the given molecule interacts with its environment producing a field of strength $E_1$. If the system is composed of non-polar species, Equations (7.9) and (7.10) become equal and

$$(\varepsilon - 1)E/4\pi = \sum_k N_k \alpha_k (E_1)_k$$

(7.11)

The Lorentz equation for the internal field and Maxwell field for a spherical molecular cavity is

$$E_1 = \left[ (\varepsilon + 2)/3 \right] E$$

(7.12)
Thus, from eqns. (7.11) and (7.12) we get

$$\frac{(\varepsilon - 1)}{(\varepsilon + 2)} = \left(\frac{4\pi}{3}\right) \sum K N_k \alpha_k$$

(7.13)

This is the "Classius-Mossoti" relation with $n$ (the index of refraction) $\equiv \varepsilon^2$

$$D = \frac{(n^2 - 1)}{(n^2 + 2)} = \left(\frac{4\pi}{3}\right) N \alpha$$

(7.14)

In this derivation the Lorentz field, eqn. (7.12) was used for both the internal and the external directing field. Onsager showed, however, that this is not permissible because of the manner in which the lorentz field arises. For non-polar liquids the internal field can be considered as the sum of two parts; one the cavity field and the other the reaction field of the dipole induced in the molecule.

In order to calculate the directing field $E_d$, the polarizability of the molecular must be considered. The field $E_d$ produces a dipole $\alpha E_d$ and a reaction field $\frac{3}{2} f \alpha E_d^2$. Thus, $E_d$ is given by

$$E_d = 3n^2 E \left[1/(1-f\alpha)\right]/(2n^2+1)$$

(7.15)

with

$$f = 2(n^2 - 1)/a^3(2n^2+1).$$

(7.16)

Therefore

$$D = 1-f\alpha = 1 - 2(n^2-1)/(2n^2+1)$$

(7.17)

with $\alpha \equiv a^3$ and it is assumed that the particles are spherical with no specific interaction between particles.
Kirkwood\textsuperscript{5} generalised Onsager's treatment for the case of specific molecular interactions. The method consists of taking a region with \(N\) molecules which are treated explicitly and \(N-N\) molecules assumed to comprise the continuum. The approximation can be adjusted by changing the value of \(N\). Kirkwood introduced a factor "\(g\)"—the Kirkwood factor which when set equal to 1 gives the result of Onsager. Kirkwood neglected translational fluctuations as had been done in the derivation of the Classius-Mossotti equation.\textsuperscript{3} Buckingham\textsuperscript{6} derived an expression for \(D\) from Kirkwood's concept of the reaction field as given below

\[
D = \frac{9n^2}{(2n^2+1)(n^2+2)} \tag{7.18}
\]

which differs from Onsager's expression for \(D\) by a factor of \(3n^2/(n^2+1)\) and which arises when short-range forces are included.

Eq. (7.1) can now be used to calculate the interaction potential \(V = V_{\text{eff}}(R,d) - V(R)\) for the solute-solute interaction \((n_{\text{int}} = 1)\). i.e.

\[
V = \frac{9}{8} \alpha^2 D/\rho^0 \tag{7.19}
\]

In eq. (7.19), the reaction field term is defined as \(1/D^2\) for a spherical cavity with a shape factor of 1/3 when SI units are employed.

RESULTS AND DISCUSSION

The interaction potential, eqn. (7.19), was derived from eq. (7.1) with the approximation given in eqn. (7.8) for the continuum dielectric model and an assumed spherical cavity geometry. It was also assumed that a multiple of the ionization
potential \( (I) \) in accordance with the approximation made by London\(^7\). This result can be obtained when the proportionality constant \( (\mu) \) is set equal to \( 1 \) in the eqn. \( \Delta = \mu I \). The constant of proportionality varies between \( 1 \) and \( 2 \), as pointed out by Pitzer\(^8\). The polarizability was taken from elsewhere. The parameter \( \rho^0 \) in eqn. (7.5) is the Kihara potential parameter\(^9,10\).

The value of \( D \) for the Classius-Mossotti\(^3\), the Onsager\(^4\) and the Kirkwood\(^5\) reaction field was derived from eqn. (7.14), (7.17) and (7.18), respectively.

The main part of the effective potential, the interaction potential, obtained from eqn. (7.19) for nitrogen, argon, krypton, xenon, methane, benzene, carbontetra-chloride, carbon-disulfide, n-hexane and cyclohexane, along with the value of \( D \), are given in Table 7.1. The various molecular parameters used in the calculations are given in Table 7.2.

The principal advantage in using eqn. (7.19) is that we do not need to consider exact calculations for the dimensionless parameters \( L \) in eqns. (7.1) and (7.19) and \( \Delta \) in eqn. (7.1) to obtain satisfactory results.

All of the systems considered are non-polar or weakly polar. Both carbon disulfide and n-hexane have been reported by Mopsik\(^11\) to be slightly polar. (Dipole moments are slightly less than 0.3D). Thus, the approximation in eqn. (7.8) is reasonable for the spherical molecular cavity model for non-polar molecules.

An examination of the results in Table 7.1 shows that interaction potentials can be ranked in the following order.
and the LJ-potential gives smaller values of the interaction potential than does the Kihara potential. This difference arises due to a neglect of the core potential \( l \) in the LJ-potential. Use of the LJ-potential in the treatment of nitrogen, argon, Krypton, Xenon and methane gives 10 to 15\% less interaction potential than that found when the K-potential is employed in the calculations. When the same procedure is employed for benzene, carbon-tetrachloride, carbon disulfide, n-hexane and cyclohexane, the difference between the two approaches gives much larger differences.

The effect of considering a slightly polar or a non-spherical molecular cavity in the systems considered in this work should not alter the results more than a few percent. The approximations made should lead to results that are good to better than 10\%.

It is worth noting that a reaction field introduced when the Classius-Mossotti equation is employed requires that higher order terms in the energy of interaction be included in the calculations. Also, the model does not take into consideration either long-range solute-solute interactions, which are effective in even in the dilute solution limit, or the short range (complex) solute-solute interactions. Onsagers reaction field concept accounts for the local field correction and includes the long range solute-solute interactions in the liquid environment. The solute-solvent and the short range solute-solute interactions, however, were not considered. The approach of Kirkwood takes
Table 7.1 Interaction Potentials in non-polar liquid with a Comparison of Leonard-Jones and Kihara potentials.

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>CLASSIUS-MOSSOTTI REACTION FIELD</th>
<th>ONSAGER REACTION FIELD</th>
<th>KIRKWOOD REACTION FIELD</th>
<th>( v^{K}(\rho^0) )</th>
<th>( v^{LJ}(\rho^0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( (\text{erg-cm}^5) ) ( (10^{52}) )</td>
<td>( (\text{erg-cm}^4) ) ( (10^{52}) )</td>
<td>( (\text{erg-cm}^5) ) ( (10^{52}) )</td>
<td>( \times 100 )</td>
<td></td>
</tr>
<tr>
<td>NITROGEN</td>
<td>0.131</td>
<td>3.07</td>
<td>0.676</td>
<td>15.872</td>
<td>0.933 21.909</td>
</tr>
<tr>
<td>ARGON</td>
<td>0.148</td>
<td>3.159</td>
<td>0.741</td>
<td>15.814</td>
<td>0.962 20.530</td>
</tr>
<tr>
<td>KRYPTON</td>
<td>0.180</td>
<td>7.030</td>
<td>0.695</td>
<td>27.147</td>
<td>0.692 36.912</td>
</tr>
<tr>
<td>XENON</td>
<td>0.227</td>
<td>19.488</td>
<td>0.630</td>
<td>54.085</td>
<td>0.917 78.723</td>
</tr>
<tr>
<td>METHANE</td>
<td>0.181</td>
<td>7.377</td>
<td>0.692</td>
<td>28.205</td>
<td>0.945 38.517</td>
</tr>
<tr>
<td>BENZENE</td>
<td>0.292</td>
<td>145.789</td>
<td>0.548</td>
<td>273.604</td>
<td>0.867 432.871</td>
</tr>
<tr>
<td>CARBON TETRA-CHLORIDE</td>
<td>0.273</td>
<td>183.015</td>
<td>0.572</td>
<td>369.911</td>
<td>0.884 571.698</td>
</tr>
<tr>
<td>CARBON DIOXIDE</td>
<td>0.354</td>
<td>122.992</td>
<td>0.477</td>
<td>165.927</td>
<td>0.814 282.811</td>
</tr>
<tr>
<td>n-HEXANE</td>
<td>0.234</td>
<td>171.370</td>
<td>0.621</td>
<td>454.791</td>
<td>0.913 668.638</td>
</tr>
<tr>
<td>CYCLO-HEXANE</td>
<td>0.256</td>
<td>146.868</td>
<td>0.593</td>
<td>340.207</td>
<td>0.913 523.793</td>
</tr>
</tbody>
</table>
Table 7.2  Refractive index $n$, ionization potential $I$, Polarizability $\alpha$, the Kihara gas phase potential minimum $\rho^0$ and the quasi-spherical Kihara core diameter $l$.

<table>
<thead>
<tr>
<th>SYSTEM (TEMP. K)</th>
<th>$n$</th>
<th>$I$ (eV)</th>
<th>$\alpha$ ($\text{Å}^3$)</th>
<th>$\rho^0$ ($\text{Å}$)</th>
<th>$l$ ($\text{Å}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (67)</td>
<td>1.31050</td>
<td>15.70</td>
<td>1.703</td>
<td>3.49</td>
<td>0.604</td>
</tr>
<tr>
<td>Argon (81)</td>
<td>1.23300</td>
<td>15.75</td>
<td>1.653</td>
<td>3.63</td>
<td>0.273</td>
</tr>
<tr>
<td>Krypton (112)</td>
<td>1.28800</td>
<td>13.99</td>
<td>2.450</td>
<td>3.87</td>
<td>0.292</td>
</tr>
<tr>
<td>Xenon (155)</td>
<td>1.37100</td>
<td>12.16</td>
<td>4.010</td>
<td>4.10</td>
<td>0.347</td>
</tr>
<tr>
<td>Methane (102)</td>
<td>1.129200</td>
<td>12.99</td>
<td>2.567</td>
<td>3.78</td>
<td>0.416</td>
</tr>
<tr>
<td>Benzene (300)</td>
<td>1.49635</td>
<td>9.25</td>
<td>10.390</td>
<td>3.60</td>
<td>2.103</td>
</tr>
<tr>
<td>Carbon Tetra Chloride (297)</td>
<td>1.47759</td>
<td>11.46</td>
<td>10.490</td>
<td>3.51</td>
<td>2.370</td>
</tr>
<tr>
<td>Carbon Disulfide (291)</td>
<td>1.62704</td>
<td>10.08</td>
<td>8.440</td>
<td>3.72</td>
<td>1.294</td>
</tr>
<tr>
<td>n-Hexane (271)</td>
<td>1.38460</td>
<td>10.40</td>
<td>11.810</td>
<td>3.57</td>
<td>2.860</td>
</tr>
<tr>
<td>Cyclo Hexane (296)</td>
<td>1.42470</td>
<td>9.50</td>
<td>10.990</td>
<td>3.60</td>
<td>2.489</td>
</tr>
</tbody>
</table>
into consideration both long and short range interactions. Thus, the variations of the interaction potential given in eqn. (7.13) follows more closely the trend predicted by Kirkwood's approach. His reaction field approach is convenient and seems to better predict interaction among molecules in the liquid environment, which may arise due to associative behaviour or chemical bonding or both depending upon the nature of the molecules.

7.3 INTERACTION POTENTIAL USING AN ARBITRARY SHAPE OF MOLECULAR CAVITY AND ITS APPLICATIONS

Theoretical Formulation

In a solution with $N_1$ solvent molecules (a), and $N_2$ solute molecules (b) there is pairing like solvent-solvent (aa), solvent-solute (ab) and solute-solute (bb) interactions. The effective pair potential can be defined as the effective potential of the pair immersed in a medium of given bulk composition $(x_a + x_b = 1)$; $x_a = \frac{N_1}{N_1 + N_2}$. In a dilute solution of b in a, the situation is relatively much simpler. The environment of bb pair is essentially all a. The same is true for an ab on an aa pair. The effective potential in solution can be written as

$$v^{KL}_{\text{eff (solution)}} = v^{KL} + \frac{v^{KL}}{n_{\text{inf}}} \left( \frac{1}{n_{\text{inf}}} \right) \sum_{i,j,K,L} \left( \sum_{r} v^{KL}_{S} \right)$$

(7.21)

where $n_{\text{int}} = 3$, $K = L = M = a$, $r = ijk$, $s = ij$ for aa pair; $n_{\text{int}} = 2$, $K = M = a$, $L = b$, $r = imj$ and $s = im$ for ab pair; and $n_{\text{int}} = 1$, $K = L = b$, $M = a$, $r = ml$ and $s = ml$ for bb pair. $i,j,K,L,m$ indicate various sites of the molecules. The summation and average is carried out for these three cases over $K$, $j$ and $i$.
respectively. All the terms which are put to see the effect of medium depend upon the solvent density \(d_2\). The values of \(n_{int}\) depend whether potential is considered for solvent or solute molecules. For dilute solutions one can approximately write

\[
\mathbf{v}_{ij; \text{eff}}(\text{solution}) \approx \mathbf{v}_{ij}(\text{pure liquid})
\]  

(7.22)

where \(i\) and \(j\) are near \(ab\) molecule and it is assumed that \(ab\) molecule first create a cavity in the pure solvent and \(b\) molecule is placed in it to interact with its environment, the discrepancy between L.H.S. and R.H.S. of eqn. (7.22) around \(b\) appears in the microscopic surface tension term.

Eqn. (7.21) for non-polar interactions and quasi spherical molecules, the main part of the effective potential in a pure liquid or dilute solution is approximately given \(^1\) by the following equation

\[
\mathbf{v}_{bb'}(R_{bb'}, \Delta a) \approx \mathbf{v}_{bb}(R_{bb}) + \frac{\Delta}{n_{int}} \left( \frac{C_{bb'}}{R_{bb'} - \frac{1}{2} bb'} \right) D_{bb'}L_{bb'}
\]  

(7.23)

where \(bb'\) molecules of solute are near to the solvent molecule \(a\).

The eqn. (7.23) discusses third order three body forces. \(R_b\) and \(R_{bb'}\) are radius of solute molecule separated by \(R_{bb'}\). \(C_{bb'}\) is the dispersion coefficient of Kihara (or LJ) potential. From Kihara potential \(^8\) is given following relation

\[
V_K(\rho) = C \left[ \left( \frac{\sigma_6}{\rho^{12}} \right) - \frac{1}{\rho^6} \right]
\]  

(7.24)

The \(K\)-potential in eqn. (7.24) considers the sizes as well as the shape of a molecule through a core parameter \(l_{bb'}\). \(\rho\) is the shortest distance between \(b\) and \(b'\) in fixed orientations with
centres R-apart. In terms of minimum point parameters or lowest potential for Kihara potential we can express the parameters in eqn. (7.24) as

\[ \rho_0^0 = 2^{1/6} \sigma \]  
(7.25)

\[ C = 4 \varepsilon \sigma^6 \]  
(7.26)

For Lennard Jones potential \( l_{bb'} = 0 \) but for Kihara potential \( l_{bb'} \neq 0 \) because two molecules have interaction between the peripheral atoms before centre to centre \( R_{bb}^6 \), effect

\[ R_{bb'}^{(0)}(LJ) = \rho_0^0 + l \]  
(7.27)

For two component system we can approximately write following relations

\[ \alpha_{bb'} \approx \frac{\alpha_b + \alpha_{b'}}{2} \]  
(7.28)

\[ l_{bb'} = \frac{l_b + l_{b'}}{2} \]  
(7.29)

and

\[ C_{bb'} = \frac{3}{2} \left( \frac{\varepsilon_b \varepsilon_{b'}}{\varepsilon_b + \varepsilon_{b'}} \right) \alpha_b \alpha_{b'} \]  
(7.30)

According to London\(^6\) the proportionality constant between \( \alpha_i \) (i = b, b') and ionization potential \( I_i \) is unity, therefore

\[ C_{bb'} = \frac{3}{2} \left( \frac{I_b I_{b'}}{I_b + I_{b'}} \right) \alpha_{bb'} \]  
(7.31)

In eqn. (7.23) \( \Delta \) and \( L_{bb'} \) for three body forces are given\(^1\) by

\[ \Delta = \frac{I_a (I_b + I_{b'}, + I_a)}{(I_b + I_a)(I_{b'} + I_a)} \]  
(7.32)

and
\[ L_{bb'} = \sum_a \frac{(R_{bb'} - l_{bb'}) \cos \theta_a}{(R_{ba} - l_{ba})^3 (R_{b'a} - l_{b'a})^3} \quad (7.33) \]

\( L_{bb'} \) is a dimensionless factor which is dependent on the relative sizes of the fixed molecules \( b \) and \( b' \) with radii \( R_b \) and \( R_{b'} \), solvent molecule \( a \) and on \( R_{bb'} \). The angle \( \theta_i \) is subtended with vertex at molecule \( i \) (\( i = b, b', a \)). The radius \( R_a \) of solvent molecule can be obtained from the relation \( R_a = \left( \frac{3}{4 \pi d_a} \right)^{1/2} \), where it is assumed that sphere of radius \( R_a \) contains on an average one solvent molecule \( a \).

For an ellipsoidal solute surrounded by a continuum such that continuum touches the active molecule, Buckingham has given the following relation for \( D_{bb'} \)

\[ D_{bb'} = \frac{3n_{bb'}^2}{(n_{bb'}^2 + 2) \left( n_{bb'}^2 (n_{bb'}^2 - 1) S_p \right)} \quad (7.34) \]

where \( S_p \) is the shape factor for the principal axis \( P \) and is written as

\[ S_p = \frac{abc}{2} \int_0^\infty \frac{ds}{\sqrt{(s+a^2)(s+b^2)(s+c^2)}} \quad (7.35) \]

where \( a, b, c \) are semi axes of ellipsoid. The integral eqn. (7.35) cannot be solved in closed form. However Osborn and Stoner have tabulated the values of \( S_p \) corresponding to the ratios of semi axes \( a, b, \) and \( c \).

The calculation of effective potential in eqn. (7.23) require \( n_{int}, C_{bb'}, \) and \( (R_{bb'} - l_{bb'}) \) which can be substituted for specific interaction \( (n_{int} = 1, 2, 3) \) and Kihara potential parameters from
eqn. (7.25), (7.26) and (7.31). $D_{bb'}$ can be calculated either by known value of $Sp$ from this tables 5, 6 or by using a relation (7.26) fitting with the measured data of the intensity. The problem now lies in the calculation of $\Delta$ in (7.32) and $L_{bb'}$ in eqn. (7.33) which need exact geometry and the distribution function in addition to some reasonable approximations for the short or the large distance $R$, a function of radii of molecules $a$, $b$ and $b'$.

We assume an arbitrary molecular cavity and moderate distance of interaction (i.e. a distance which is neither tending to infinity nor to zero). For such interactions we assume that the product of $L_{bb'}$, and $\Delta$ is approximately unity i.e.

$$L_{bb'} \Delta \approx 1$$  \hspace{1cm} (7.36)

Substituting eqn. (7.25), (7.31), (7.34) and (7.36) in eqn. (7.23) we get final expression for the effective potential as given below

$$v_{bb'}^{\text{eff}}(R_{bb'}, \text{da}) \approx v_{bb'}(R_{bb'}) + \frac{q}{2n_{\text{int}}} \left( \frac{I_b}{I_b + I_b'} \right) \frac{\alpha_b \alpha_{b'}}{R_{bb'} - l_{bb'}}$$

$$\times \frac{n_{bb'}^2}{(n_{bb'}^2 + 2)(n_{bb'}^2 - (n_{bb'}^2 - 1)Sp)}$$  \hspace{1cm} (7.37)

The equation (7.16) for spherical molecular cavity has already been derived by Johri and Roberts\textsuperscript{14}.
RESULTS AND DISCUSSION

Eqn. (7.37) has been derived in this work with an approximation in eqn. (7.36) and $D_{bb'}$, value in eqn. (7.34). The main part of the effective potential is the second term on R.H.S. of eqn. (7.37), which can be called as interaction potential $V$ which for solute-solute interaction ($n_{int} = 1$) or for pure liquid is (dropping suffix $bb'$)

$$V = \frac{9}{21} \frac{I a^2}{R-1} \frac{n^2}{(n^2+2)(n^2-(n^2-1)Sp)}$$

Eqn. (7.38)

Yamada and Person defined the ratio of intensity in any medium (in liquid or solid) to that in gas as (Ig) as given below

$$\frac{I_m}{I_g} = n^{-1} \left[ \frac{n^2}{n^2-(n^2-1)Sp} \right]^2 \frac{1}{(1-g_p \alpha ^2)}$$

Eqn. (7.39)

The data used and the calculated interaction potential for carbon disulfide for stretching mode $v_3$ and bending mode $v_2$ are given in the Table 7.3. The cavity factor is defined by

$$\text{Cavity factor} = \left[ \frac{n^2}{n^2-(n^2-1)Sp} \right]^2$$

Eqn. (7.40)

and the reaction field term $= (1 - \alpha_p g_p)^{-2}$

Eqn. (7.41)

where Scholte has given the value of $\alpha$ and $g$ for a uniformly polarized ellipsoid of semi axes $a,b,c$ in a continuum of dielectric constant $\varepsilon = n^2$.

The ratio $(a/b)$ in the CS$_2$ ellipsoid is estimated to be 1.83 from the C-S bond distance and Vanderwall's of radius of
Table 7.3 Interaction Potential for $\nu_3$ and $\nu_2$ infrared fundamental vibrational modes of carbon-di-sulfide using refractive index, cavity factor and measured ratio $(I_m/I_g)$ of intensity in any dense medium ($I_m$) to that in gas ($I_g$).

<table>
<thead>
<tr>
<th>Vibration mode</th>
<th>Refractive Index</th>
<th>Cavity factor</th>
<th>Measured $(S_p)$</th>
<th>Interaction Potential $(V) \times 10^5$ (erg cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_3$</td>
<td>1.8199</td>
<td>1.3285</td>
<td>1.4</td>
<td>0.19</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>1.8199</td>
<td>1.9473</td>
<td>1.5</td>
<td>0.41</td>
</tr>
</tbody>
</table>

**SOLID CS$_2$**

| $\nu_3$        | 1.8199          | 1.4687        | 1.3             | 0.25                                              | 510.136                                          |
| $\nu_2$        | 1.8199          | 2.0019        | 1.4             | 0.42                                              | 79.746                                           |

**LIQUID CS$_2$**

** = Ionization potential = 10.08 eV, Kihara Potential Parameter $(R-p) = 3.72 A^0$, $\alpha = 15.14 A^{0.3}$ for $\nu_3$, $\alpha = 5.54 A^{0.3}$ for $\nu_2$.**
sulfur. The molecular volume $abc$ is calculated from the density using the following relation:

$$\frac{4}{3} \pi abc = \frac{\text{Molecular weight}}{\text{density} \times A \text{Vogadro number}}$$

$$= 19.4 \text{ Å}^3 \text{ for CS}_2$$

Using refractive index $= 1.8199$, $g_\alpha = 1.93 \times 10^{22} \text{ cm}^{-3}$ and $g_b = 3.61 \times 10^{23} \text{ cm}^{-3}$. The values of the polarizability for the $\nu_3$-mode is $15.14 \text{ Å}^3$ and that for the $\nu_2$-mode is $5.54 \text{ Å}^3$. Stoner has given the shape factor $0.191$ for the $\nu_3$-mode and $0.4045$ for the $\nu_2$-mode when the ratio $(a/b)$ is taken as $1.83$.

The calculated value of shape factors using eqn. (7.22) are given in Table 7.3. An examination of the table 7.3 shows that the interaction potential for the stretching infrared fundamental vibrational mode ($\nu_3$) is more than six times than the bending mode ($\nu_2$) in both the solid and liquid phases. Also, the interaction potential for the liquid phase is more than that in the solid phase, due to increasing value of the cavity factor in the liquid phase.

The approximation in eqn. (7.36) has mathematical justification if one puts $R_a = R_b = R_b'$, $l = 0 \cos \theta_i = 1$ ($i = a, b, b'$) in eqn. (7.33) and ionization potential for like molecules ($a = b = b'$) in eqn. (7.32). The assumption of moderate distance corresponds to $R = 2R_a$. Physically this approximation leads to the situation when the molecule $a$ is placed on the line joining $b$ and $b'$. Therefore the approximation is realistic and simplifies the calculation otherwise much more involved.
7.4 A THEORETICAL MODEL FOR DETERMINING OSCILLATOR STRENGTH USING A NON-SPHERICAL MOLECULAR CAVITY AND MEASUREMENT OF $H_e-N_e$ LASER LIGHT ABSORPTION COEFFICIENT IN AQUEOUS SOLUTION OF SODIUM CHLORIDE

In this section oscillator strengths have been calculated using principles of dielectric polarization and considering non-spherical molecular cavity and Buckingham's formula. Experimental measurement of He - Ne laser light absorption coefficient for aqueous solutions of sodium chloride at room temperature are done thereafter a co-relation between theoretical and experimental oscillator strengths has been used to estimate the shape of the molecular cavity.

Theoretical Formulation

Consider an electric dipole moment operator $\hat{d}$ which can be separated into a sum over electrons and a sum over nuclei. The electronic wave functions $\psi'_e$ and $\psi''_e$ are eigen functions of the Hermitian operator $H_e$ with different eigenvalues and therefore they are orthonormal. If we consider that the initial nuclear wave functions are normalized, it is possible to eliminate the nuclear wave functions. Under these conditions we can define the oscillator strength ($f$) of an electronic absorption transition in the gas phase as

$$f_g = \frac{8\pi^2 \nu m}{3\hbar^2} \left| \langle \psi'_e | \hat{d} | \psi''_e \rangle \right|^2 \quad (7.42)$$

where $\nu$ is an absorption transition frequency, $m$ is the mass of the electron, $e$ is the electronic charge and $h$ is Planck's constant.
Yamada and Person have defined an apparent oscillator strength for an oscillator imbedded in a solution which we can write as

$$M_l(f_s) = \int \ln \left( \frac{I_o}{I} \right) d\nu$$  \hspace{1cm} (7.43)

where $M$ represents the molar concentration, $l$ is the path length of light propagation. $I$ and $I_o$ are the intensity of light after and before the interaction with the absorbing sample. For a solvent, other than gas, the absolute oscillator strength can be obtained from eqn. (7.43) by letting $Ml \rightarrow 0$.

Buckingham has formulated a relation for the ratio $(f_s/f_g)$ based on the dielectric polarization which can be expressed by the following equation

$$(f_s/f_g)^{1/2} = \left\{ \frac{\kappa^{2}}{n_{12}^{2}(1-g_p \alpha_p)^{-1}} \right\} / \left\{ (n)^{1/2} - \left[ (n_{12}^{2} - (n_{12}^{2} - 1)Sp \right) \right\}$$  \hspace{1cm} (7.44)

where a monochromatic source of light e.g., He-Ne laser light, is used for interaction with the solution, one can then ignore the contribution of oriental polarizability because, for frequencies in the visible part of the spectrum, the electronic and atomic polarizability become dominant mechanisms. Therefore we can write

$$(f_s/f_g)^{1/2} = \left\{ \frac{\kappa^{2}}{n_{12}^{2}(1-g_p \alpha_p)^{-1}} \right\} / \left\{ (\epsilon_{\omega_{12}}^{1/4}) \left[ (\epsilon_{\omega_{12}} - 1)Sp \right] \right\}$$  \hspace{1cm} (7.45)

where $Sp$ is the shape factor for a non-spherical molecular cavity model and $\alpha_p$ is the polarizability of the ellipsoid taken out of the solution medium for the principal axis system. The quantity $g_p$ is the reaction field factor, $\epsilon_{\omega_{12}}$ is the high frequency
permittivity of the solution and $\varepsilon_{w1}$ is that of the solvent.

Scholte has derived an expression for $\alpha_p$ and $g_p$ which is given below (in SI units) as

$$a_p = (abc/3) \sum_j N_j \alpha_j \quad (7.46)$$

and

$$g_p = [3/abc] \left( \varepsilon_{w1}^2 - 1 \right) \mathrm{Sp}(1 - \mathrm{Sp}) / \left[ \varepsilon_{w1} - (\varepsilon_{w1} - 1) \mathrm{Sp} \right] \quad (7.47)$$

where $\alpha_j$ is the polarizability of the molecule of the $j$th component and $N_j$ is the number of molecules per unit volume. Therefore, from eqn. (7.46) and eqn. (7.47) we get

$$1 - \alpha_p g_p = 1 \left\{ \left( \varepsilon_{w1}^2 - 1 \right) \mathrm{Sp}(1 - \mathrm{Sp}) / \left[ \varepsilon_{w1} - (\varepsilon_{w1} - 1) \mathrm{Sp} \right] \right\} \sum_j N_j \alpha_j \quad (7.48)$$

To determine the summation $\sum N_j \alpha_j$ over $j$ we need to consider the internal field $E_s$ that acts at the site of the molecule (or ion) which is significantly different from the value of the macroscopic electric field $E$ and is written as (in SI units).

$$E_s = E_o + \sum_i \left\{ 3(\mu_i \cdot \gamma_i) \gamma_i - \gamma_i^2 \cdot \mu_i \right\} / \left[ 4\pi \varepsilon_0 \gamma_i^5 \right] \quad (7.49)$$

where $\varepsilon_0$ is the permittivity of the vacuum ($8.8542 \times 10^{-12}$ F/m) and $E_o$ is the electric field produced by the field charges external to the body. The second term in the right hand side of eqn. (7.49) includes the polarization electric field $E_1$ from a surface charge density on the outer surface of the specimen and the field $E_2$ arises from polarization charges on the inside of a cavity "cutout" of the specimen and the field $E_3$ is due to molecules inside of the hypothetical sphere concentric with the
reference molecule, which vanishes at the reference site under cubic symmetry.

Defining \( E = E_0 + E_1 \) as the macroscopic field, we can relate the dielectric constant to the polarizability through \( E_2 \) as given below

\[
E_2 = Sp \frac{P}{\varepsilon_0}
\]

Therefore, the internal field is represented as

\[
E_S = E + Sp \frac{P}{\varepsilon_0}
\]

The polarization of the solution \( P \) may be expressed approximately as the product of the polarizabilities of the molecules times the internal or local electric field i.e.

\[
P \approx \varepsilon_0 N_j \mu_j = \varepsilon_0 \sum_j N_j \alpha_j (E_j(j)),
\]

where \( \alpha_j \) is the polarizability of the molecules, \( \mu_j \) is the dipole moment and \( E_j(j) \) is the local electric field. The suffix \( j \) designates the molecular site.

From Eqns. (7.51) and (7.52) we can write

\[
P \approx \varepsilon_0 \sum_j N_j \alpha_j (E + Sp \frac{P}{\varepsilon_0})
\]

Using Maxwell’s equations, the ratio of \( P \) and \( E \) obtained from Eq. (7.53) may be related to Drude’s expression as given below

\[
\frac{P}{E} = \left[ \varepsilon_0 \sum_j N_j \alpha_j \right] / \left[ 1 - Sp \sum_j N_j \alpha_j \right] = \varepsilon_0 (\varepsilon_{\infty 2} - 1)
\]

Equation (7.54) may be solved for the summation \( \sum_j N_j \alpha_j \) to give the result

\[
\sum_j N_j \alpha_j = (\varepsilon_{\infty 2} - 1) / [1 + Sp(\varepsilon_{\infty 2} - 1)]
\]
If we substitute Eqn. (7.55) into Eqn. (7.48), the following equation is produced

\[(1 - \alpha g_p) = [\epsilon_{\infty 12} - (\epsilon_{\infty 12} - 1)sp][1 + (\epsilon_{\infty 12} - 1)sp]/\epsilon_{\infty 12} \quad (7.56)\]

Then, by combining Eqn. (7.56) with Eqn. (7.45) the ratio of the apparent oscillator strength in solution to that of the oscillator strength in the gas phase is given by the equation

\[\left(\frac{f_s}{f_g}\right)^{1/2} = \left\{\frac{[1 + sp(\epsilon_{\infty 12} - 1)]/(\epsilon_{\infty 1})^{1/4}}{\epsilon_{\infty 1}}\right\} \quad (7.57)\]

Eqn. (7.57) is applicable when the surrounding medium of the solute molecule is non-polar for the medium is in the gas phase. When aqueous electrolytic solution systems are to be studied, Eqn. (7.57) needs to be modified to take the following form

\[\left(\frac{f_s}{f_g}\right)^{1/2} = \left[\epsilon_{\infty 1} + (\epsilon_{\infty 12} - \epsilon_{\infty 1})Sp\right] / (\epsilon_{\infty 1})^{5/4} \quad (7.58)\]

The atomic polarizability, in general, does not contribute significantly in comparison to the electronic polarizability. Under this assumption, Eqn. (7.58) can be rewritten, with \(\epsilon_{\infty 12} \approx n_{12}^2\) and \(\epsilon_{\infty 1} = n_1^2\), as

\[\left(\frac{f_s}{f_g}\right)^{1/2} = \left[\frac{n_1^2 + (n_{12}^2 - n_1^2)Sp}{(n_1)}\right] / (n_1)^{5/2} \quad (7.59)\]

Therefore

\[f_s^{1/2} = (f_g/n_1)^{1/2} \left[(n_{12}^2 - n_1^2)Sp\right] / (n_1)^2 + (f_g/n_1)^{1/2} \quad (7.60)\]

In Eqn. (7.60), \(n_1\) is the refractive index of the solvent (for water \(n = 1.3333\)) and \(n_{12}\) is that for the solution. The
derivation of eqn. (7.60) represents an alternate method which is useful to determine the shape factor $S_p$ from the experimental data. Moreover the equation has general application into the visible part of the electromagnetic spectrum where orientational polarizability may be neglected.

**EXPERIMENTAL DESIGN**

The experimental arrangement used to conduct the present experiment is outlined in Figure 7.1. The amount of light scattered perpendicular to the laser beam was shielded by means of an opaque cylinder surrounding the laser beam over the path length. The source of laser light was a He-Ne laser (model 125 by Spectra Physics) lasing at 6328 Å and with a power output of 60 mW. The laser beam was directed normal to the surface of the optically ground cell. The optically ground parallel faces were separated by 10 mm for the path length of the laser beam within the sample contained in the cell. The cells were sealed with polyethylene caps to reduce contamination and to lower the evaporation rate of the solvent. The focal zone of the laser beam was confined to a cross-sectional area of about 1 mm$^2$. The emergent beam passed through the monochromator (Model 0200, Jarrell-Ash, Division of Fisher Scientific Co.) and into the photo multiplier tube for analysis and detection. The output signals were monitored both by display onto an oscilloscope and recorded on a single pen constant rate chart recorder for a permanent record.
CHART RECORDER  →  CATHODE RAY OSCILLOSCOPE

PHOTOMULTIPLIER TUBE

SAMPLE HOLDER

MONOCHROMATOR

HELIUM-NEON LASER

SCATTERED LIGHT

Fig. 7.1. A Schematic diagram of the basic experimental apparatus used to make the measurements of absorption coefficients and oscillator strength using He-Ne laser light.
The amplitude of the signal profile obtained in the neighbourhood of 6328 Å wavelength was determined in the absence of the sample in the absorption cell and then with the samples in place in the optical cells. Thus, the difference between the absorbing sample and the background could be established. A simple model can be developed for the intensity behaviour of the laser beam as it passes through the absorbing medium in the absorption cell as follows.

Consider an electromagnetic wave of frequency $\omega$ propagating in the $Z$-direction through a medium whose refractive index is $n_{12}$. The electric field of the wave is given by

$$E = E_0 \exp \left[ i \omega (t - n_{12} Z/c) \right], \quad (7.61)$$

where $c$ is the speed of light in vacuum. The refractive index is complex and is given by

$$n_{12} = n'_{12} - jn''_{12} \quad (7.62)$$

where $n'_{12}$ and $n''_{12}$ are the real and imaginary parts of the index of refraction, respectively.

If both sides of Eq. (7.61) are square and the replacement $I = |E|^2$ and $I_0 = |E_0|^2$ are made, the intensity relationship for absorption is

$$I = I_0 \exp \left[ -2n''_{12} \omega Z/c \right] \quad (7.63)$$

or

$$I = I_0 \exp \left[ -\beta_{12} Z \right], \quad \text{with} \quad \beta_{12} \equiv 2n''_{12} \omega/c \quad (7.64)$$
Eqn. (7.64) shows that \( \beta_{12} \), the absorption coefficient per unit length of propagation, is directly proportional to \( n_{12}'' \). Thus the absorption at a given wavelength can be calculated using the following relation:

\[
\beta(\lambda) = \beta_{12} \times \lambda = (\lambda/d) \ln \left( \frac{I_0}{I} \right)
\]  

(7.65)

where \( \lambda \) is the wavelength of the incident radiation, \( d \) is the thickness of the sample, \( I_0 \) is the undiminished light intensity and \( I \) is the intensity of the light after it has passed through the absorbing material.

Discussion of Correlations Between Theoretical and Experimental Results

From eqn. (7.43) the oscillator strength can be obtained from the integrated absorption coefficient per unit concentration (g/mole/cm) over a unit path length of propagation. For infinitely sharp absorption lines which we can assume for monochromatic sources of light, e.g., He-Ne lasers, the ratio of the molar integrated absorption coefficient in solution of that in the gas phase may be approximated as equal to the ratio of \( \beta_{12} \) of the solution to \( \beta_1 \) of the solvent. Therefore, we can write from eqn. (7.60) and eqn. (7.65) the following relationship:

\[
(\beta_{12})^{1/2} \approx (\beta_1/n_1)^{1/2} \left[ \left( \frac{n_{12}^2 - n_1^2}{n_1^2} \right) \right]_{Sp} + (\beta_1/n_1)^{1/2}
\]  

(7.66)

Inspection of eqn. (7.66) shows that if the two variables \( (\beta_{12})^{1/2} \) and \( (n_{12}^2 - n_1^2)/n_1^2 \) are defined, in the standard way, and the plot of \( (\beta_{12})^{1/2} \) vs. \( (n_{12}^2 - n_1^2)/n_1^2 \) is fitted to a linear least-square
regression, the shape factor $Sp$, if the slope is taken as $(\beta_{12})^{1/2}$ $Sp$, is given by the following ratio

$$Sp = \left[\frac{\text{Line Slope}}{\text{Line Intercept}}\right]$$  \hspace{1cm} (7.67)

It is worth noting that the molecular polarizability is not a scalar quantity but is a tensor quantity when the molecule is not completely spherical. For practical purposes, however, the effect of this so-called anisotropy of the polarizability is small and the tensor $\alpha$ may be replaced by a scalar polarizability $\alpha = [(1/3)\text{Tr}(\alpha)]$ as was also pointed out by Bottcher$^3$. When an ellipsoid has a spherical form, $Sp = 1/3$ for any axis. If the final form is a thin slab (normal), $Sp = 1$, a thin slab (in plane), $Sp = 0$, a long circular cylinder (longitudinal), $Sp = 0$ and for a long circular cylinder (transverse), $Sp = 1/2$. These values are given in S.I. units and $0 \leq Sp \leq 1$.\textsuperscript{20} For the perfect sphere, $Sp = 1/3$, Eqn. (7.66) reduces to

$$(\beta_{12})^{1/2} = (\beta_1/n_1)^{1/2} \left[\frac{(n_{12}^2/n_1^2)+2}{3}\right]$$ \hspace{1cm} (7.68)

The model has been applied to aqueous solution of NaCl at various concentrations. The coefficients of light absorption $\beta_{12}$ for various concentrations of NaCl are given in Table 7.4. The value of the refractive index at each of these concentrations given in Table 7.4 have been obtained by interpolation of those from the literature\textsuperscript{23} for aqueous solutions of NaCl. The least-squares regression of $(\beta_{12})^{1/2}$ versus $(n_{12}^2-n_1^2)/n_1^2$ yields a slope of $-0.3585$ and an intercept of $1.174$ with a 98\%
Table 7.4 List of coefficients for He-Ne laser light absorption in aqueous solutions of NaCl and refractive index at various ionic concentrations. The temperature was kept at room temperature during measurement of the light absorption coefficients at each concentration.

<table>
<thead>
<tr>
<th>Concentration (gm-mole/cm³) x10⁴</th>
<th>β₁₂ x10⁴</th>
<th>(β₁₂)¹/₂ x10²</th>
<th>n₁₂</th>
<th>(n₁₂^n²/n₁^n²) x10⁴/n₁²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0170</td>
<td>1.3491</td>
<td>1.1615</td>
<td>1.3332</td>
<td>-1.6876</td>
</tr>
<tr>
<td>0.4278</td>
<td>1.7052</td>
<td>1.3058</td>
<td>1.3334</td>
<td>1.6876</td>
</tr>
<tr>
<td>0.6845</td>
<td>1.3847</td>
<td>1.1767</td>
<td>1.3344</td>
<td>6.1878</td>
</tr>
<tr>
<td>1.3689</td>
<td>1.2100</td>
<td>1.1000</td>
<td>1.3337</td>
<td>16.3133</td>
</tr>
<tr>
<td>7.7002</td>
<td>0.4081</td>
<td>0.6388</td>
<td>1.3407</td>
<td>111.3806</td>
</tr>
<tr>
<td>11.9781</td>
<td>0.2494</td>
<td>0.4994</td>
<td>1.3446</td>
<td>169.8835</td>
</tr>
<tr>
<td>21.3895</td>
<td>0.0250</td>
<td>0.1581</td>
<td>1.3537</td>
<td>308.2654</td>
</tr>
</tbody>
</table>
correlation factor. The ratio of the slope to intercept gives a value for Sp of 0.30. The negative sign before the slope indicates a decrement in the dielectric value with increasing concentrations of ions. This effect was expected and has already been reported by Winsor and Cole\textsuperscript{24} at microwave frequencies and Hubbard et al\textsuperscript{25} at radio frequencies.
REFERENCES


