CHAPTER V

Electronic transitions in symmetrical 1,3,5-trisubstituted benzenes
5.1. Introduction

Sponer\(^1\) had discussed the forbidden character of the vapour spectra of symmetric 1,3,5-trisubstituted benzene molecules. Appearance of 0,0 band and other features of the solid phase spectrum of 1,3,5-trichlorobenzene\(^2,3\) and 1,3,5-trimethylbenzene\(^4,5\) were also described. In this chapter results of investigations on the spectra of 1,3,5-triethyl- and 1,3,5-trihydroxybenzene in the vapour and solid states and in isobutyl alcohol rigid glass at low temperatures are described. Vibrational assignments of these molecules, not reported earlier, are also discussed.

5.2. I. Vibrational assignments of 1,3,5-triethyl- and 1,3,5-trihydroxybenzene

Before considering characteristics of the electronic spectra, assignments of the vibrational frequencies of 1,3,5-triethyl- and 1,3,5-trihydroxybenzene are taken up.

The Raman and infrared spectra of the first compound and the infrared spectrum of the second compound were recorded. The Raman data of Kohlrausch and Pongratz\(^6\) for the trihydroxy benzene were utilized and normal coordinate calculations of out-of-plane vibrations reported by Nonnenmacher and Mecke\(^7\) were considered.
Treating the substituent groups as point mass X, the symmetric 1,3,5-C₆H₃X₃ molecules may be assumed to have D₃h symmetry and the thirty phenyl ring vibrations in each molecule may be divided into

\[ 4a'_1 (R, p) + 3a''_2 + 7e' (I. r.; R, dp) + 3a''_1 (I. r.) + 3e''(R, dp) \]

The assignments of the phenyl ring vibrations are given in Table 5.1 and those of the vibrations of the substituent groups are given in Table 5.2.

5.2.1. 1,3,5-triethyl benzene

The totally symmetric a₁ vibrations are readily identified from the intensity and polarization character of the Raman lines. No attempt has been made to propose definite assignments for a₂ vibrations which inactive in both Raman and infrared.

Two weak Raman lines at 637 and 440 cm⁻¹ are observed in this work. These two could not be definitely assigned. But it may be mentioned that Bogomolov⁸ assigned a frequency 617 cm⁻¹ to a \( \sqrt{C_2H_6} \) mode in the case of m-diesthylbenzene. Further a frequency in the region 430-500 cm⁻¹ observed in the spectra of a few 1,3,5-C₆H₃X₃ molecules has been assigned to a₂' mode \( \gamma' \) by Green et al.⁹
The frequencies of vibrations associated with the stretching and the bending modes of CH$_3$ and CH$_2$ groups are generally accepted. Following Versanyi\textsuperscript{10}, the frequency 371 cm$^{-1}$ is assigned to C-C-C bending vibration. The very weak infrared band at 783 cm$^{-1}$ is proposed to have arisen from CH$_2$ rocking vibration\textsuperscript{11}.

5.2.2. 1,3,5-trihydoxy benzene

The strong infrared band at 1006 cm$^{-1}$ has been assigned at $\nu_{12}^{s} (e')$. On the basis of calculations of frequencies, Nonnenmacher and Mecke\textsuperscript{7} assigned the frequencies 566 and 249 cm$^{-1}$ to $e''$ modes $\nu_{19}^{s}$ and $\nu_{20}^{s}$ respectively. These assignments are retained. In regard to the assignment of the 566 cm$^{-1}$ Raman line it may be noted that the $e''$ mode $\nu_{19}^{s}$ has been reported to have frequency 577, 595, 530, 509 cm$^{-1}$ in the case of symmetric triethyl-, trifluoro- and tribromo benzene respectively. In accord with the results of Nonnenmacher and Mecke, the infrared bands at 810 and 660 cm$^{-1}$ are identified as $\nu_{15}^{s}$ and $\nu_{16}^{s}$ respectively. In accord with the analysis of the vibrational frequencies of 1,3,5-trimethyl benzene reported by Pitzer and Scott\textsuperscript{12} these two bands 810 and 660 cm$^{-1}$ may be considered to have originated from modes derived from $b_{2g}$ mode 5 and $b_{2g}$ mode 4 of benzene.
Table 5.1  Fundamental frequencies of 1,3,5-C_6H_3X_3

( in cm\(^{-1}\) )

<table>
<thead>
<tr>
<th>X = C_2H_5</th>
<th>OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetry</td>
<td>R</td>
</tr>
<tr>
<td>a(_1^f)</td>
<td>(\nu_1)</td>
</tr>
<tr>
<td>R (p), - ,</td>
<td>(\nu_2)</td>
</tr>
<tr>
<td></td>
<td>(\nu_3)</td>
</tr>
<tr>
<td></td>
<td>(\nu_4)</td>
</tr>
<tr>
<td>a(_2^f)</td>
<td>(\nu_5)</td>
</tr>
<tr>
<td>- , - ;</td>
<td>(\nu_6)</td>
</tr>
<tr>
<td>e(_e^f)</td>
<td>(\nu_6)</td>
</tr>
<tr>
<td>R(dp), I.R</td>
<td>(\nu_7)</td>
</tr>
<tr>
<td></td>
<td>(\nu_{10})</td>
</tr>
<tr>
<td></td>
<td>(\nu_{11})</td>
</tr>
<tr>
<td></td>
<td>(\nu_{12})</td>
</tr>
<tr>
<td></td>
<td>(\nu_{13})</td>
</tr>
<tr>
<td></td>
<td>(\nu_{14})</td>
</tr>
</tbody>
</table>
Table 5.1 (contd.)

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>$X_5$</th>
<th>$X_6$</th>
<th>$X_7$</th>
<th>$X_8$</th>
<th>$X_{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a&quot;</td>
<td>866 (vs)</td>
<td>712 (1)</td>
<td>..</td>
<td>889 (2b)dp</td>
<td>577 (1)</td>
</tr>
<tr>
<td>R(dp), -</td>
<td>810 (s)</td>
<td>707 (vs)</td>
<td>..</td>
<td>889 (w)</td>
<td>..</td>
</tr>
<tr>
<td>b</td>
<td>660 (m)</td>
<td>..</td>
<td>..</td>
<td>..</td>
<td>566 (0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>249 (2)</td>
</tr>
</tbody>
</table>

a Kohlrausch and Pongratz (1934)
b Calculated (Nonnemacher and Mecke, 1961)
* liquid
** in nujol mull
Table 5.2 Internal vibrations of the substituent groups of 1,3,5-C_6H_3X_3 molecules
(Frequencies in cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Nature of vibrations</th>
<th>C_2H_5</th>
<th>OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_{as}(\text{CH}_3))</td>
<td>2966 (3)</td>
<td>-</td>
</tr>
<tr>
<td>(\nu_{as}(\text{CH}_2))</td>
<td>2940 (3P)</td>
<td>-</td>
</tr>
<tr>
<td>(\nu_{as}(\text{CH}_2))</td>
<td>2894 (2b)</td>
<td>-</td>
</tr>
<tr>
<td>(\nu_{as}(\text{CH}_2))</td>
<td>2950 (2bP)</td>
<td>-</td>
</tr>
<tr>
<td>(\delta_{as}(\text{CH}_3))</td>
<td>1436 (6dp)</td>
<td>-</td>
</tr>
<tr>
<td>(\nu_{as}(\text{CH}_3))</td>
<td>1385 (1)</td>
<td>1380 (s)</td>
</tr>
<tr>
<td>CH_2 wag</td>
<td>1336 (3P)</td>
<td>1325 (s)</td>
</tr>
<tr>
<td>CH_2 twist</td>
<td>1245 (2)</td>
<td>-</td>
</tr>
<tr>
<td>CH_3 rock</td>
<td>1064 (1bP)</td>
<td>1060 (s)</td>
</tr>
<tr>
<td>CH_2 rock</td>
<td>790 (1)</td>
<td>783 (w)</td>
</tr>
<tr>
<td>(\delta(\text{CCC}))</td>
<td>317 (1b)</td>
<td>-</td>
</tr>
<tr>
<td>(\delta(\text{OH}))</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
respectively. The former is an X-sensitive $\gamma$ (CH) mode and the latter a $\phi$ (CC) mode. These bands of low frequency arising from such out-of-plane vibrations are not expected to exhibit any marked solvent effect and actually the frequencies observed in nujol mull are in good agreement with those in KBr reported by Nonnenmacher and Mecke\textsuperscript{7}. A very weak infrared band is observed at 885 cm\textsuperscript{-1} and this has been assigned to e" mode $\nu_{18}$. The calculated frequency is 923 cm\textsuperscript{-1}.

The assignments of 1291 and 1158 cm\textsuperscript{-1} (Table 5.2) are made following Wilson\textsuperscript{13}.

5.3. Analysis of the electronic spectra

5.3.1. 1,3,5-triethylbenzene

The absorption spectra of 1,3,5-triethylbenzene in the vapour and solid phases and in an isobutyl alcohol rigid glass at 90\textdegree{}K have been analysed. The f-value of the transition, measured in isobutyl alcohol solution is about 4.58 x 10\textsuperscript{-3}. The vapour spectrum consists of weak broad bands (Fig.5.12). The first two prominent bands at 36975 and 37913 cm\textsuperscript{-1} are separated by about 938 cm\textsuperscript{-1}. An examination of the rigid glass spectrum (Fig.5.12) reveals that the 0,0 transition can be identified with the weak band at 36593 cm\textsuperscript{-1} whose appearance should probably be attributed to some environmental
Solution spectra of 1,3,5-triethylbenzene in isobutyl alcohol — see after page 124
Fig. 5.12 Near ultraviolet absorption spectra of 1,3,5-triethyl benzene
a) Thin film at 90°K  b) Thin film at 300°K
c) Isobutyl alcohol rigid glass at 90°K
d) Isobutyl alcohol solution at 300°K
e) Vapour
perturbation. In the rigid glass spectrum the second strong band at 37014 cm\(^{-1}\) involves an excited state frequency 421 cm\(^{-1}\) which may be reasonably correlated with the e\(^t\) vibration of frequency 517 cm\(^{-1}\) in the ground state. If the frequency separation 938 cm\(^{-1}\) in the vapour spectrum be expressed at 517 + 421 then the 36975 cm\(^{-1}\) may be interpreted as a 0\(\leftarrow\)1 transition involving one quantum of the e\(^t\) ground state frequency 517 cm\(^{-1}\) while the 37913 cm\(^{-1}\) band may be attributed to a 1\(\leftarrow\)0 transition involving the same mode having frequency 421 cm\(^{-1}\) in the excited state. On this basis the calculated position of the 0,0 band, band due to vapour would be at 37492 cm\(^{-1}\). Actually a weak absorption is present in this region in the vapour spectrum.

A further examination of the rigid glass spectrum shows the presence of a moderately strong band at 37512 cm\(^{-1}\) apparently representing an excited state frequency 920 cm\(^{-1}\) which, at the first sight, may be thought of as representing the a\(^t\) "breathing" vibration that has frequency 1001 cm\(^{-1}\) in the ground state (Table 5.1). But the large intensity of the band is in conflict with this assignment. Alternatively 920 cm\(^{-1}\) may be expressed as 421 + 498 where the excited state frequency 498 cm\(^{-1}\) may be correlated with the ground state vibration of frequency 541 cm\(^{-1}\) observed in the Raman spectrum\(^{14}\). Following Pitzer and Scott\(^{12}\) this may be thought
of as being derived from the $b_{1u}$ mode 12 of benzene representing C-C-C angle of deformation. On the basis of above observations it may be argued that coupling of the aforesaid $e'$ vibration with the electronic transition $1_{A_2} \leftarrow 1_{A_1}$ is mainly responsible for the observed spectrum and the $a$ vibration 498 cm$^{-1}$ is combined with integral number of quanta significantly odd as well as even, of this $e'$ vibration.

The general features of the spectrum are thus broadly brought out on an approximation $D_{3h}$ model. But as was pointed out there is actually a weak absorption in the calculated position of the 0,0 band is the vapour spectrum. It seems that the possibility that the symmetry of the molecule may be lower than $D_{3h}$ because of actual equilibrium position of the ethyl groups which may be unsymmetric can not be discounted. In this connection, the situation in the case of hexamethylbenzene discussed by Schnepp$^{15}$ may be recalled.

The spectrum of solid 1,3,5-triethylbenzene at 90$^\circ$K resembles the rigid glass spectrum. In both cases the bands are quite broad and it appears that a study of the spectrum at lower temperature and under higher resolution might bring out more details of the vibrational structure leading to a better understanding of the electronic transition and symmetry of the molecule.
### Table 5.3 Absorption bands of 1,3,5-triethylbenzene

<table>
<thead>
<tr>
<th>Wave No. (cm⁻¹) &amp; intensity</th>
<th>Assignment</th>
<th>Solid at 90°K</th>
<th>Rigid glass in isobutyl alcohol at 90°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>36975 m</td>
<td>0 - 517</td>
<td>36539 m</td>
<td>36593 m</td>
</tr>
<tr>
<td>(37492)</td>
<td>(0-0)</td>
<td>36971 s</td>
<td>37014 s + 0 + 421</td>
</tr>
<tr>
<td>37913 s</td>
<td>0 + 419</td>
<td>37477 s + 0 + 432</td>
<td>37512 s + 0 + 421 + 498</td>
</tr>
<tr>
<td>38300</td>
<td>Weak broad</td>
<td>37896 s + 0 + 2x</td>
<td>37925 s + 0 + 2x + 421 + 498</td>
</tr>
<tr>
<td>bands, position uncertain</td>
<td></td>
<td>38421 s, b + 2x</td>
<td>38838 s, b + 3x + 421 + 2x + 498</td>
</tr>
<tr>
<td>39900</td>
<td>sb</td>
<td>38376 s + 0 + 2x</td>
<td>38838 s, b + 3x + 421 + 2x + 498</td>
</tr>
</tbody>
</table>

( ) calculated value

### Table 5.4 Fundamental frequencies of 1,3,5-triethylbenzene

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Ground state</th>
<th>Excited state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R</td>
<td>IR</td>
</tr>
<tr>
<td>e'</td>
<td>517</td>
<td>..</td>
</tr>
<tr>
<td>a₁</td>
<td>544</td>
<td>..</td>
</tr>
</tbody>
</table>
5.3.2. 1,3,5-trihydroxybenzene

The spectra of the molecule in the vapour and solid states and in isobutyl alcohol at 77°C were recorded. The results are discussed below.

The absorption spectrum of 1,3,5-trihydroxybenzene in the vapour phase is of diffused nature. The spectrum of the compound in isobutyl alcohol solution at room temperature (Fig. 5.21) exhibits a few broad but resolved bands and the measured f-value of the transition is about $6.97 \times 10^{-3}$ (Table 5.5). The f-value compares favourably with the f-values of other 1,3,5-trisubstituted benzenes as is shown in Table 5.6 and is of magnitude expected for a forbidden transition.

In the spectrum of 1,3,5-trihydroxybenzene in isobutyl alcohol rigid glass at 77°C several fairly resolved bands are observed and of these, the first band on the long wave length side has been taken as the 0,0 band which possibly appears due to environmental perturbation as the following discussion indicates. The main feature of the spectrum is an excited state fundamental frequency 480 cm$^{-1}$ which may be reasonably attributed to an e' vibration derived from the e$_{2g}$ mode of benzene that has frequencies
Fig. 5.21 Solution spectra of 1,3,5-trihydroxy benzene
(solvent - isobutyl alcohol)
Fig. 5.22 Near ultraviolet absorption spectra of 1,3,5-trihydroxy benzene
a) Thin film at 77°K
b) Isobutyl alcohol rigid glass at 77°K
c) Isobutyl alcohol solution at 300°K
606 and 520 cm\(^{-1}\) in the ground and excited states respectively\(^{16}\). It can be seen from Table 5.7 that several odd quanta of this \(e'_v\) vibration appear in the spectrum. A list of \(e'_v\) vibrational frequencies excited in the absorption spectra of some \(1,3,5-\text{C}_6\text{H}_3X_3\) molecules is given in Table 5.8 for comparison. It is known that for molecules of \(D_3h\) symmetry the electronic transition is \(^1A_2'^{\prime}\) \(\leftrightarrow\) \(^1A_1^{\prime}\) corresponding to the \(^1B_{2u}\) \(\leftrightarrow\) \(^1A_{1g}\) transition of benzene and is symmetry forbidden\(^{17}\). The spectrum may appear through excitation of vibration of \(e'_v\) symmetry with the transition moment in the plane of the molecule. Following Herzberg and Teller's idea\(^{18}\) it may be argued that in this trihydroxy benzene molecule, vibronic mixing of \(^1A_2'^{\prime}\)-level under consideration with an upper excited electronic state \(^1E_1^{\prime}\) corresponding to \(^1E_{1u}\) state of benzene is possible through interaction of the \(e'_v\) vibration and this may lead to borrowing of intensity by the forbidden \(^1A_2'^{\prime}\) \(\leftrightarrow\) \(^1A_1^{\prime}\) transition from the allowed electronic transition \(^1E_1^{\prime}\) \(\leftrightarrow\) \(^1A_1^{\prime}\). A significant contribution to the intensity of the absorption system probably comes through such intensity borrowing.

Another prominent excited frequency 550 cm\(^{-1}\) appears in the spectrum not as a fundamental, but only in
Table 5.5  Absorption bands of 1,3,5-trihydroxybenzene in isobutyl alcohol at 300°K

<table>
<thead>
<tr>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{max}}$</th>
<th>(Assignment)</th>
<th>f-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>36274</td>
<td>297</td>
<td>(0-0)</td>
<td></td>
</tr>
<tr>
<td>36740</td>
<td>387</td>
<td>(0 + 466)</td>
<td>6.97 x 10^{-3}</td>
</tr>
<tr>
<td>37261</td>
<td>427</td>
<td>(0 + 466 + 521)</td>
<td></td>
</tr>
<tr>
<td>37740</td>
<td>375</td>
<td>(0 + 466 + 2 x 521)</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.6  f-value of $^1A_2 \leftrightarrow ^1A_1$ transition in $1,3,5$-$C_6H_3X_3$ molecules

<table>
<thead>
<tr>
<th>X = (H)</th>
<th>f = (1.6 x 10^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>3.5 x 10^{-3}</td>
</tr>
<tr>
<td>F</td>
<td>2 x 10^{-3}</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>7.1 x 10^{-3}</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>2.1 x 10^{-3}</td>
</tr>
<tr>
<td>C$_2$H$_5$</td>
<td>4.58 x 10^{-3}</td>
</tr>
<tr>
<td>OH</td>
<td>6.97 x 10^{-3}</td>
</tr>
</tbody>
</table>

a Sklar 19  b Sponer 20  c Present work
## Table 5.7  Absorption bands of 1,3,5-trihydroxybenzene

<table>
<thead>
<tr>
<th>Isobutyl alcohol rigid glass at 77°K Wave No.(cm⁻¹)</th>
<th>Assignment and intensity</th>
<th>Solid (thin film) at 77°K Wave No.(cm⁻¹)</th>
<th>Assignment and intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>36274 w</td>
<td>0-0</td>
<td>36300 w</td>
<td>0-0</td>
</tr>
<tr>
<td>36754 s</td>
<td>0 + 480</td>
<td>36767 m</td>
<td>0 + 467</td>
</tr>
<tr>
<td>37302 s</td>
<td>0 + 480 + 550</td>
<td>37344 m</td>
<td>0+467+577</td>
</tr>
<tr>
<td>37654 vs</td>
<td>0+3x480</td>
<td>37696 m</td>
<td>0 + 3 x 467</td>
</tr>
<tr>
<td></td>
<td>0 + 1380</td>
<td>0 + 1396</td>
<td></td>
</tr>
<tr>
<td>37610 s</td>
<td>0+480+2x550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38215 vsb</td>
<td>0+3x480+550</td>
<td>38273 m</td>
<td>0+3x467+577</td>
</tr>
<tr>
<td>38673 s</td>
<td>0+5x480</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38763 s</td>
<td>0+3x480+2x550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39219 m</td>
<td>0+5x480+550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39860 svb</td>
<td>0+3x480+4x550</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## Table 5.8  Perturbing e' vibrations in 1,3,5-C₆H₃X₃ molecules

<table>
<thead>
<tr>
<th>X = ( II )a</th>
<th>Ground state</th>
<th>Excited state</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 606 )</td>
<td>( 520 )</td>
<td></td>
</tr>
<tr>
<td>Clb</td>
<td>425</td>
<td>371</td>
</tr>
<tr>
<td>CH₃c</td>
<td>516</td>
<td>443</td>
</tr>
<tr>
<td>C₂H₅d</td>
<td>517</td>
<td>421**</td>
</tr>
<tr>
<td>OHd</td>
<td>535</td>
<td>480**</td>
</tr>
</tbody>
</table>

a Ref.16  
b Ref.17  
c Ref.21  
d Present work

** Rigid glass
combination with odd quanta of the $e'$ vibration 480 cm$^{-1}$.
This in all probability represents deformation of C-C-C angle and corresponds to the $b_{1u}$ mode 12 of benzene. It can be seen from Table 5.7 that the band at 37654 cm$^{-1}$ may be alternatively assigned as $0 + 1380$ cm$^{-1}$ when 1380 cm$^{-1}$ may represent an $e'$ vibration (\(\nu_{CC}^e\)) the corresponding ground state frequency being 1496 cm$^{-1}$.

It is to be noted that though the 0-0 band which is of electronic origin appears in the rigid glass spectrum at 77$^\circ$K, the spectrum does not have an "allowed part" i.e. no totally symmetric vibration appears as fundamental. In particular, no frequency corresponding to "ring breathing" mode can be identified. Thus it is to be concluded that in isobutyl alcohol matrix at 77$^\circ$K there is no departure from $D_{3h}$ symmetry of the molecule and the appearance of the 0-0 band must be attributed to environmental perturbation, one possible cause for which may be intermolecular hydrogen bonding between the solvent isobutyl alcohol and the solute trihydroxybenzene molecules. Even in the case of solution in isobutyl alcohol at room temperature the solvent perturbation is quite strong as can be seen from the presence of weak
absorption in the position of the 0-0 band (Fig. 522c) and the essential features of the spectrum are the same.

Table 5.9  Fundamental frequencies of 1,3,5-trihydroxy benzene

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Ground state</th>
<th>Excited state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R</td>
<td>IR</td>
</tr>
<tr>
<td>e'</td>
<td>-</td>
<td>535</td>
</tr>
<tr>
<td>a'</td>
<td>598</td>
<td>-</td>
</tr>
<tr>
<td>l</td>
<td>1496</td>
<td>-</td>
</tr>
</tbody>
</table>

as those of the rigid glass spectrum at 77°C.

The spectrum of thin film of solid (polycrystalline) 1,3,5-trihydroxybenzene at 77°C is closely similar to the rigid glass spectrum and there is no noticeable crystal field effects on the electronic transition at the low temperature.
References

   Wiss. Wien., 143, 358 (1934).
   17, 1049 (1961).
8. A. M. Bogomolov, Optics and Spectroscopy, 13, 90
   (1962).
9. J.H.S. Green, D.J. Harrison and W. Kynaston,
10. G. Varsanyi, Vibrational spectra of benzene derivatives
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    65, 803 (1943).
14. P. K. Mallick, S. Chakraborty and S. B. Banerjee,
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