Chapter V

OPTIMIZED GEOMETRY, VIBRATIONAL SPECTRAL ANALYSIS AND NON BONDED INTERACTION OF NONLINEAR OPTICAL CHROMOPHORE P-BROMOACETANILIDE

5.1 INTRODUCTION

Nonlinear optics is a frontier of science and technology playing a major role in the emerging field of photonics, which involves the applications of photons for information and image processing. The development of photonic and optoelectronic technologies rely heavily on the growth of NLO materials with high nonlinear optical responses, and the development of new and more efficient materials. In order to trace guidelines to fabricate NLO materials, much effort is being devoted to understand the origin of non-linearity in large systems and to relate NLO responses to electronic structure and molecular geometry [247]. Chirality and hydrogen bonding are the important factors in the design of NLO chromophores since the measurement of bulk NLO properties in the solid state is dependent on a non-centrosymmetric packing environment within the crystal lattice [304-307].

Many organic nonlinear optical (NLO) materials have been subject of investigated intensive research, as they are potential materials for photonic applications [245,308-310]. Moreover, organic materials have some advantages compared to inorganic materials such as a large and fast nonlinear response, processibility, and greater resistance to optical damage [311,312]. Donor (D)-acceptor (A) substituted organic molecules with large second-order nonlinear optical properties constitute a topic of burgeoning interest because of their possible applications in areas such as frequency doubling and photorefractive
polymers among others [30,313]. Organic molecules containing extended 
π-conjugated electrons and characterized by large values of molecular first 
hyperpolarizabilities show enhanced NLO properties. These molecules can 
show large first molecular hyperpolarizabilities (β) related to an electronic 
intramolecular charge transfer excitation between the ground and excited states of the molecules, and it has long been recognized that D-π-A NLO-phores with a 
dominantly aromatic ground state donor favour electronic polarization in an 
applied field, as a result of the decreased resonance energy upon charge 
transfer [314-316]. The second order NLO properties seem to be related with the 
existence of a large intramolecular charge transfer (ICT) at relatively low energy 
values which in turn depends on the efficiency of the π- electron delocalization 
through the bridge and electron-donor and electron-acceptor strength of end 
groups [317,318]. The C-H hydrogen bonded interactions also play an important 
role in many bio-organic systems as these systems contain a large number of 
C-H groups which can participate in C-H· · ·O, C-H· · ·π and C-H· · ·N interactions, 
thereby contributing towards certain structural preferences [319]. The Natural 
Bond Orbital (NBO) analysis can identify and confirm the possible intermolecular 
interactions between the units that would form the H-bonded dimer [320].

NIR-FT Raman spectroscopy [300,321-324] combined with quantum 
chemical computations has recently been used as an effective tool in the 
vibrational analysis of drug molecules [9], biological [10], natural products [6] and 
NLO active compounds [325], since fluorescence-free Raman spectra and 
computed results can help unambiguous identification of vibrational modes as 
well as the bonding and structural features of complex organic molecular 
systems. Vibrational spectroscopy has been recently employed to investigate the
structural features responsible for these NLO properties, which seem to be related to the existence of a larger intramolecular charge transfer at relatively low energy values, which in turn depends on the efficiency of the \( \pi \)-electron delocalization through the donor and the acceptor groups [326]. The present work deals with the FT-IR and NIR-FT Raman spectral study of the organic NLO material p-bromo acetanilide (PBA) to correlate the NLO activity with its structural and bonding features, nature of hydrogen bonding and charge transfer interactions supported by \textit{ab initio} computations and NBO analysis.

5.2 EXPERIMENTAL

5.2.1 Synthesis

Single crystals of PBA were grown by slow evaporation technique at 40°C. Recrystallization was accomplished by dissolving the grown crystal for supersaturation in methanol and the solution was kept at 40°C in a temperature bath having an accuracy of \( \pm 0.01 \)°C. Seed crystals were obtained by controlled slow evaporation of the solvent.

5.2.2 Crystal structure

Crystalline Acetanilide is an orthorhombic crystal characterized by soft hydrogen bonded chains of molecules which run through the crystal. PBA (Fig. 5.1) crystallizes in the space group \( P_{na2_1} \) and the cell has dimensions \( a = 9.70, \ b = 13.00, \ c = 6.67 \) Å and contains 4 molecules. The acetyl group has dimensions which agree better with those generally found in N-substituted amides (acetanilide). The halogenobenzene and acetyl groups are planar (Fig. 5.2) with the dihedral angle of \( 5.8^\circ \) between the planes [326].
5.2.3 IR and Raman Measurements

The IR spectrum (Fig. 5.3) of PBA was recorded using FT-IR spectrometer TENSOR (27) MICRO ATR accessory MIRACLE, Pike; ZnSe crystal over the full mid-IR range 400-4000 cm\(^{-1}\). The NIR FT-Raman spectrum (Fig. 5.4) was obtained using BRUKER RFS 100/s FT-Raman spectrometer. The SERS
Fig. 5.3 FT-IR spectrum of PBA

Fig. 5.4 NIR-FT Raman spectrum of PBA
spectrum (Fig. 5.5) of PBA was recorded in the stable colloid prepared by Lee-Meisel method [289] and the vibrational analysis is performed by comparing it with the IR and Raman spectra.

![SERS spectrum of PBA](image)

**Fig. 5.5 SERS spectrum of PBA**

### 5.3 COMPUTATIONAL DETAILS

Ab initio computations are performed at the HF/6-31G (d) level using Gaussian'98 program package [228] to derive the optimized geometry and vibrational frequencies of the normal modes of PBA. The optimum geometry is determined by minimizing the energy with respect to all geometrical parameters without imposing molecular symmetry constraints. The optimized bond lengths, bond angles and torsion angles are tabulated in Tables 5.1, 5.2 and 5.3 respectively.
Table 5.1 Optimized bond length (Å) of PBA

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Calculated values</th>
<th>Bond Lengths</th>
<th>Calculated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁ – C₂</td>
<td>1.3816</td>
<td>C₅ – H₁₁</td>
<td>1.0683</td>
</tr>
<tr>
<td>C₁ – C₆</td>
<td>1.3804</td>
<td>C₆ – H₁₂</td>
<td>1.0733</td>
</tr>
<tr>
<td>C₁ – Br₇</td>
<td>1.8988</td>
<td>N₁₀ – C₁₃</td>
<td>1.3671</td>
</tr>
<tr>
<td>C₂ – C₃</td>
<td>1.3809</td>
<td>N₁₀ – H₁₅</td>
<td>0.9946</td>
</tr>
<tr>
<td>C₂ – H₈</td>
<td>1.0731</td>
<td>C₁₃ – C₁₄</td>
<td>1.5150</td>
</tr>
<tr>
<td>C₃ – C₄</td>
<td>1.3923</td>
<td>C₁₃ – O₁₆</td>
<td>1.1960</td>
</tr>
<tr>
<td>C₃ – H₉</td>
<td>1.0766</td>
<td>C₁₄ – H₁₇</td>
<td>1.0854</td>
</tr>
<tr>
<td>C₄ – C₅</td>
<td>1.3911</td>
<td>C₁₄ – H₁₈</td>
<td>1.0854</td>
</tr>
<tr>
<td>C₄ – N₁₀</td>
<td>1.4058</td>
<td>C₁₄ – H₁₉</td>
<td>1.0794</td>
</tr>
<tr>
<td>C₅ – C₆</td>
<td>1.3852</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.2 Optimized bond angle (degrees) of PBA

<table>
<thead>
<tr>
<th>Bond angles</th>
<th>Calculated values</th>
<th>Bond angles</th>
<th>Calculated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂ – C₁ – C₆</td>
<td>120.2372</td>
<td>C₁ – C₆ – H₁₂</td>
<td>120.0371</td>
</tr>
<tr>
<td>C₆ – C₁ – Br₇</td>
<td>119.9899</td>
<td>C₅ – C₆ – H₁₂</td>
<td>119.4147</td>
</tr>
<tr>
<td>C₁ – C₂ – H₈</td>
<td>120.4461</td>
<td>C₄ – N₁₀ – H₁₅</td>
<td>114.8474</td>
</tr>
<tr>
<td>C₃ – C₂ – H₈</td>
<td>120.1536</td>
<td>C₁₃ – N₁₀ – H₁₅</td>
<td>116.0154</td>
</tr>
<tr>
<td>C₂ – C₃ – C₄</td>
<td>121.0108</td>
<td>N₁₀ – C₁₃ – C₁₄</td>
<td>113.5687</td>
</tr>
<tr>
<td>C₂ – C₃ – H₉</td>
<td>119.0407</td>
<td>N₁₀ – C₁₃ – O₁₆</td>
<td>124.1507</td>
</tr>
<tr>
<td>C₄ – C₃ – H₉</td>
<td>119.9484</td>
<td>C₁₄ – C₁₃ – O₁₆</td>
<td>122.2806</td>
</tr>
<tr>
<td>C₃ – C₄ – C₅</td>
<td>119.0879</td>
<td>C₁₃ – C₁₄ – H₁₇</td>
<td>110.7146</td>
</tr>
<tr>
<td>C₃ – C₄ – N₁₀</td>
<td>117.1018</td>
<td>C₁₃ – C₁₄ – H₁₈</td>
<td>110.7201</td>
</tr>
</tbody>
</table>
5.3.1 Hyperpolarizability and Thermodynamical Parameters

The first static hyperpolarizability ($\beta_0$) and its related properties ($\beta$, $\alpha_0$ and $\Delta\alpha$) have been calculated using HF/6-31G(d) based on finite field approach as explained in Chapter III. The value of second order optical susceptibility $\chi^{(2)}$ in a given NLO system depends on the molecular hyperpolarizability $\beta$, the number of chromophores and the degree of noncentrosymmetry. The computed first hyperpolarizability $\beta_{tot}$ of PBA is found to be $9.403069 \times 10^{-31}$ e.s.u., which is 6.6 times than that of urea. It is also seen from the HOMO-LUMO energy gap that there is an inverse relationship between hyperpolarizability and HOMO-LUMO energy gap.

<table>
<thead>
<tr>
<th>C$_5$ - C$<em>4$ - N$</em>{10}$</th>
<th>123.8103</th>
<th>C$<em>{13}$ - C$</em>{14}$ - H$_{19}$</th>
<th>108.6566</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_4$ - C$_5$ - C$_6$</td>
<td>119.7156</td>
<td>H$<em>{17}$ - C$</em>{14}$ - H$_{18}$</td>
<td>108.1278</td>
</tr>
<tr>
<td>C$_4$ - C$<em>5$ - H$</em>{11}$</td>
<td>120.2636</td>
<td>H$<em>{17}$ - C$</em>{14}$ - H$_{19}$</td>
<td>109.2987</td>
</tr>
<tr>
<td>C$_6$ - C$<em>5$ - H$</em>{11}$</td>
<td>120.0208</td>
<td>H$<em>{18}$ - C$</em>{14}$ - H$_{19}$</td>
<td>109.3005</td>
</tr>
<tr>
<td>C$_1$ - C$_6$ - C$_5$</td>
<td>120.5483</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ \text{HOMO energy} = -0.30730 \text{ a.u.} \]
\[ \text{LUMO energy} = 0.12704 \text{ a.u.} \]
\[ \text{HOMO} - \text{LUMO energy gap} = 0.43434 \text{ a.u.} \]

This study reveals that these novel molecular systems have large first static hyperpolarizabilities and have potential applications in the development of NLO devices. Furthermore, the decrease in the HOMO and LUMO energy gap explains the probable charge transfer taking place inside the chromophore.
Table 5.3 Optimized torsion angle (degrees) of PBA

<table>
<thead>
<tr>
<th>Torsion Angles</th>
<th>Calculated values</th>
<th>Torsion Angles</th>
<th>Calculated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$ - C$_1$ - C$_2$ - H$_8$</td>
<td>179.9</td>
<td>C$<em>5$ - C$<em>4$ - N$</em>{10}$ - C$</em>{13}$</td>
<td>-0.0</td>
</tr>
<tr>
<td>Br$_7$ - C$_1$ - C$_2$ - C$_3$</td>
<td>179.0</td>
<td>C$<em>5$ - C$<em>4$ - N$</em>{10}$ - H$</em>{15}$</td>
<td>179.9</td>
</tr>
<tr>
<td>Br$_7$ - C$_1$ - C$_2$ - H$_8$</td>
<td>0.0</td>
<td>C$_4$ - C$_5$ - C$<em>6$ - H$</em>{12}$</td>
<td>-179.9</td>
</tr>
<tr>
<td>C$_2$ - C$_1$ - C$<em>6$ - H$</em>{12}$</td>
<td>-179.9</td>
<td>H$_{11}$ - C$_5$ - C$<em>6$ - H$</em>{12}$</td>
<td>-0.0</td>
</tr>
<tr>
<td>Br$_7$ - C$_1$ - C$<em>6$ - H$</em>{12}$</td>
<td>0.0</td>
<td>C$<em>4$ - N$</em>{10}$ - C$<em>{13}$ - C$</em>{14}$</td>
<td>-179.9</td>
</tr>
<tr>
<td>H$_8$ - C$_2$ - C$_3$ - C$_4$</td>
<td>179.9</td>
<td>C$<em>4$ - N$</em>{10}$ - C$<em>{13}$ - O$</em>{16}$</td>
<td>0.0</td>
</tr>
<tr>
<td>H$_8$ - C$_2$ - C$_3$ - H$_9$</td>
<td>0.0</td>
<td>H$<em>{15}$ - N$</em>{10}$ - C$<em>{13}$ - O$</em>{16}$</td>
<td>179.9</td>
</tr>
<tr>
<td>C$_2$ - C$_3$ - C$<em>4$ - N$</em>{10}$</td>
<td>179.9</td>
<td>N$<em>{10}$ - C$</em>{13}$ - C$<em>{14}$ - H$</em>{18}$</td>
<td>-59.9</td>
</tr>
<tr>
<td>H$_9$ - C$_3$ - C$_4$ - C$_5$</td>
<td>-179.9</td>
<td>N$<em>{10}$ - C$</em>{13}$ - C$<em>{14}$ - H$</em>{19}$</td>
<td>-179.9</td>
</tr>
<tr>
<td>H$_9$ - C$_3$ - C$<em>4$ - N$</em>{10}$</td>
<td>-0.0</td>
<td>H$<em>{15}$ - N$</em>{10}$ - C$<em>{13}$ - C$</em>{14}$</td>
<td>-0.0</td>
</tr>
<tr>
<td>N$_{10}$ - C$_4$ - C$_5$ - C$_6$</td>
<td>-179.9</td>
<td>O$<em>{16}$ - C$</em>{13}$ - C$<em>{14}$ - H$</em>{17}$</td>
<td>-120.0</td>
</tr>
<tr>
<td>N$_{10}$ - C$_4$ - C$<em>5$ - H$</em>{11}$</td>
<td>0.0</td>
<td>O$<em>{16}$ - C$</em>{13}$ - C$<em>{14}$ - H$</em>{18}$</td>
<td>120.0</td>
</tr>
<tr>
<td>C$<em>3$ - C$<em>4$ - N$</em>{10}$ - C$</em>{13}$</td>
<td>179.9</td>
<td>O$<em>{16}$ - C$</em>{13}$ - C$<em>{14}$ - H$</em>{19}$</td>
<td>0.03</td>
</tr>
<tr>
<td>C$<em>3$ - C$<em>4$ - N$</em>{10}$ - H$</em>{15}$</td>
<td>-0.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The calculated values of some of the important thermodynamic parameters are listed below.

i) Self-consistent field (SCF) energy  = -30006.8271 a.u

ii) Zero-point vibrational energy  = 409.68 Kcal mol$^{-1}$

iii) Entropy  = 443.6 cal mol$^{-1}$K$^{-1}$

iv) $C_V$  = 149.54 cal mol$^{-1}$K$^{-1}$
5.4 NATURAL BOND ORBITAL ANALYSIS

The Natural Bond Orbital Analysis (NBO) has been performed to identify and confirm the possible intra- and intermolecular interactions between the units that would form the proper and improper (blue shifting) hydrogen bonding occurring upon dimerization [291,327]. The importance of hyperconjugative interaction and electron density transfer (EDT) from lone electron pairs of the Y atom to the X-H antibonding orbital in the X-H · · · Y system have been analyzed [328] and the results are presented in the Tables 5.4, 5.5 and 5.6. The NBO analysis clearly shows the existence of two strong C-H · · · O intramolecular and N-H · · · O intermolecular hydrogen bonding in PBA dimer. The intermolecular N-H · · · O hydrogen bonding is formed due to the orbital overlap between n (O 16) and σ*(N 31-H 33) which results in ICT causing stabilization of H-bonded systems. Thus the nature and strength of intermolecular hydrogen bonding can be explored by studying the changes in electron densities (ED) in the vicinity of N · · · H hydrogen bonds, which leads to an increase in ED of N-H antibonding orbital. The increase in population of the N-H antibonding orbital weakens the N-H bond. The NBO analysis of PBA dimer clearly reveals the formation of H-bonded interaction between n (O 16) and σ*(N 31-H 33) antibonding orbitals. The difference in stabilization energy E(2) associated with the hyperconjugative interaction n 1 (O 16) → σ*(N 31-H 33), and n 2(O 16) → σ*(N 31-H 33) are 49.20 and 66.23 KJmol⁻¹ respectively, which is due to the accumulation of electron density in the N-H bond drawn not only from n(O) of the hydrogen-acceptor but from the entire molecule leading to its elongation and concomitant red shift of the N-H stretching wavenumber [328].
Table 5.4 Second-order perturbation theory analysis of Fock matrix in NBO basis corresponding to the intramolecular C-H⋯O hydrogen bonds in PBA monomer

<table>
<thead>
<tr>
<th>Donor NBO (i)</th>
<th>Acceptor NBO (j)</th>
<th>(E(2)) kJ/ mol</th>
<th>(E(j)-E(i)) a.u.</th>
<th>(F(i,j)) a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(LP_{2}O_{16})</td>
<td>(\sigma^*C_{6}-H_{11})</td>
<td>4.85</td>
<td>1.27</td>
<td>0.035</td>
</tr>
<tr>
<td>(LP_{2}O_{16})</td>
<td>(\sigma^*C_{13}-C_{15})</td>
<td>78.12</td>
<td>1.06</td>
<td>0.128</td>
</tr>
<tr>
<td>(LP_{2}O_{35})</td>
<td>(\sigma^*C_{25}-H_{30})</td>
<td>9.12</td>
<td>1.23</td>
<td>0.047</td>
</tr>
<tr>
<td>(LP_{2}O_{35})</td>
<td>(\sigma^*C_{32}-C_{34})</td>
<td>108.16</td>
<td>1.02</td>
<td>0.148</td>
</tr>
</tbody>
</table>

Table 5.5 Second-order perturbation theory analysis of Fock matrix in NBO basis corresponding to the intermolecular N-H⋯O hydrogen bonds in PBA dimer

<table>
<thead>
<tr>
<th>Donor NBO (i)</th>
<th>Acceptor NBO (j)</th>
<th>(E(2)) kJ/ mol</th>
<th>(E(j)-E(i)) a.u.</th>
<th>(F(i,j)) a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(LP_{1}O_{16})</td>
<td>(\sigma^*N_{31}-H_{33})</td>
<td>49.29</td>
<td>1.71</td>
<td>0.127</td>
</tr>
<tr>
<td>(LP_{2}O_{16})</td>
<td>(\sigma^*N_{31}-H_{33})</td>
<td>66.23</td>
<td>1.26</td>
<td>0.128</td>
</tr>
</tbody>
</table>

\(E(2)\) - Energy of hyperconjugative interactions (stabilization energy)
\(E(j)-E(i)\) - Energy difference between donor i and acceptor j NBO orbitals
\(F(i,j)\) - Fock matrix element between i and j NBO orbitals.

The existence of intramolecular C-H⋯O hydrogen bonds due to the interaction between the lone pair of oxygen \(LP_{2}O_{16}\) and \(LP_{2}O_{35}\) with the antibonding orbital \(\sigma^* (C_{13}-H_{11})\) and \(\sigma^* (C_{25}-H_{20})\) has been confirmed by the results of NBO analysis. Notwithstanding the fact that the energetic contribution of hyperconjugative interactions is weak, the \(E(2)\) values are chemically significant and are used as a measure of the intermolecular delocalization. The strengthening and contraction of C-H bonds is due to rehybridization [329], which
is revealed by the low value of electron density (0.01253e and 0.01315e) in the 
σ* (C₆-H₁₁) and σ* (C₂₅-H₃₀) orbitals respectively.

<table>
<thead>
<tr>
<th>Bond (A-B)</th>
<th>ED/Energy (a.u.)</th>
<th>ED_A%</th>
<th>ED_B%</th>
<th>NBO</th>
<th>S%</th>
<th>P%</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ C₆ - H₁₁</td>
<td>1.97971 -0.71512</td>
<td>63.70</td>
<td>-</td>
<td>0.793 (sp².23) C + 0.6025 (s) H</td>
<td>30.95</td>
<td>68.92</td>
</tr>
<tr>
<td></td>
<td>0.01253 -0.7724</td>
<td>36.30</td>
<td>36.30</td>
<td>0.6025 (sp².23) C - 0.7981 (s) H</td>
<td>27.35</td>
<td>72.52</td>
</tr>
<tr>
<td>σ* C₆ - H₁₁</td>
<td>1.99654 -1.41707</td>
<td>33.39</td>
<td>66.61</td>
<td>0.5778 (sp².05) C + 0.8162 (sp¹.31) O</td>
<td>32.72</td>
<td>67.00</td>
</tr>
<tr>
<td>σ C₁₃ - O₁₆</td>
<td>0.01154 0.85493</td>
<td>66.61</td>
<td>33.39</td>
<td>0.8162 (sp².05) C - 0.5778 (sp¹.31) O</td>
<td>32.72</td>
<td>67.00</td>
</tr>
<tr>
<td>σ* C₁₃ - O₁₆</td>
<td>0.99229 -0.56573</td>
<td>24.63</td>
<td>75.37</td>
<td>0.4962 (p) C + 0.8682(p) O</td>
<td>-</td>
<td>99.99</td>
</tr>
<tr>
<td>σ C₂⁻⁻ - O₁₆</td>
<td>0.20256 0.15591</td>
<td>75.37</td>
<td>24.63</td>
<td>0.8682 (p) C - 0.4962 (p) O</td>
<td>-</td>
<td>99.99</td>
</tr>
<tr>
<td>σ* C₂⁻⁻ - O₁₆</td>
<td>0.99246 -0.68308</td>
<td>63.89</td>
<td>36.11</td>
<td>0.7993 (sp².22) C + 0.6009 (s) H</td>
<td>30.99</td>
<td>68.88</td>
</tr>
<tr>
<td>σ C₂₅⁻⁻ - H₃₀</td>
<td>0.01315 0.80513</td>
<td>36.11</td>
<td>63.89</td>
<td>0.6009 (sp².22) C - 0.7993 (s) H</td>
<td>30.99</td>
<td>68.88</td>
</tr>
<tr>
<td>σ* C₂₅⁻⁻ - H₃₀</td>
<td>1.99694 -1.37183</td>
<td>33.69</td>
<td>66.31</td>
<td>0.5804 (sp².02) C + 0.8143 (sp¹.30) O</td>
<td>33.03</td>
<td>66.70</td>
</tr>
<tr>
<td>σ C₃₂⁻⁻ - O₃₅</td>
<td>0.01051 0.90810</td>
<td>66.31</td>
<td>33.69</td>
<td>0.8143 (sp².02) C - 0.5804 (sp¹.30) O</td>
<td>33.03</td>
<td>66.70</td>
</tr>
<tr>
<td>σ* C₃₂⁻⁻ - O₃₅</td>
<td>1.99208 -0.50984</td>
<td>26.85</td>
<td>73.15</td>
<td>0.5182 (p) C + 0.8553 (p) O</td>
<td>-</td>
<td>99.99</td>
</tr>
<tr>
<td>σ C₃₃⁻⁻ - C₃₅⁻⁻</td>
<td>0.18248 0.21378</td>
<td>73.15</td>
<td>26.85</td>
<td>0.8553 (p) C - 0.5182 (p) O</td>
<td>-</td>
<td>99.99</td>
</tr>
<tr>
<td>σ N₃₁⁻⁻ - H₃₃</td>
<td>1.98342 -0.85333</td>
<td>74.47</td>
<td>25.53</td>
<td>0.8630 (sp².31) N + 0.5052 (s) H</td>
<td>30.14</td>
<td>69.74</td>
</tr>
<tr>
<td>σ* N₃₁⁻⁻ - H₃₃</td>
<td>0.03805 0.76130</td>
<td>25.53</td>
<td>74.47</td>
<td>0.5052 (sp².31) N - 0.8630 (s) H</td>
<td>30.14</td>
<td>69.74</td>
</tr>
<tr>
<td>LP₁ O₁₆</td>
<td>1.96002 -0.95038</td>
<td>-</td>
<td>-</td>
<td>sp⁰.⁸³</td>
<td>54.46</td>
<td>45.46</td>
</tr>
<tr>
<td>LP₂ O₁₆</td>
<td>1.89026 -0.49849</td>
<td>-</td>
<td>-</td>
<td>p</td>
<td>-</td>
<td>97.42</td>
</tr>
<tr>
<td>LP₁ O₃₅</td>
<td>1.97484 -0.91849</td>
<td>-</td>
<td>-</td>
<td>sp⁰.⁷⁶</td>
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<td>43.30</td>
</tr>
<tr>
<td>LP₂ O₃₅</td>
<td>1.89500 -0.41993</td>
<td>-</td>
<td>-</td>
<td>p</td>
<td>-</td>
<td>99.78</td>
</tr>
</tbody>
</table>
5.5 VIBRATIONAL SPECTRAL ANALYSIS

The vibrational analysis of PBA is performed based on the characteristic vibrations of phenyl ring, imino, methyl and carbonyl groups. The computed vibrational wavenumbers, their IR and Raman activities, depolarization ratios, force constants and the atomic displacements corresponding to the different normal modes have been used to identify the vibrational modes unambiguously. The calculated vibrational wavenumbers, measured infrared and Raman band positions and their tentative assignments are given in Table 5.7. Atomic displacements corresponding to selected vibrational modes of PBA are sketched in Fig. 5.6.

5.5.1 Imino Vibrations

The N-H stretching vibrations generally give rise to bands at 3500-3300 cm\(^{-1}\) [84,330]. The width and fine structure are partly explained by the large anharmonicity and strong coupling of \(\nu(N-H)\) stretching with the \(\nu(N-H\cdot\cdot\cdotO)\) (also called hydrogen bond strain) and the other intermolecular interactions of the chain. The bands corresponding to N-H stretching appear at 3294 and 3253 cm\(^{-1}\) in the IR with a strong intensity and at 3313 and 3275 cm\(^{-1}\) in the Raman with a weak intensity.

The observed splitting by 41 cm\(^{-1}\) (IR) and 38 cm\(^{-1}\) (Raman) is due to strong intermolecular hydrogen bonding. Furthermore, the N-H stretching wavenumber is red shifted by 174 cm\(^{-1}\) in IR with a strong intensity from the computed wavenumbers which indicates the weakening of the N-H bond resulting in proton transfer to the neighbouring oxygen [331]. In the PBA dimer, the calculated N-H stretching wavenumbers are lowered to 3244 cm\(^{-1}\), which also
reveals the existence of strong N-H· · · O intermolecular hydrogen bonding. The bond distance and bond angle between the N_{31} atom of one PBA molecule and the O_{16} of the other molecule is calculated to be 3.101 Å and 167° respectively, which are in good agreement with XRD data (2.87±3 Å) confirming the presence of strong N-H· · · O intermolecular hydrogen bonding. The presence of strong N_{31}-H_{33}· · · O_{16} intermolecular hydrogen bonding is also substantiated by the NBO analysis and computations.

The N-H in-plane and out of plane bending bands have been identified and analyzed. The C-N stretching vibrations expected to occur as two intense bands around 1180-1360 cm\(^{-1}\) are observed at 1290 (IR), 1264 cm\(^{-1}\) (Raman), and 1317 (IR) and 1319 cm\(^{-1}\) (Raman) [330,331].

Table 5.7 Calculated vibrational wavenumbers, measured IR and Raman band positions (cm\(^{-1}\)) and assignments of PBA

<table>
<thead>
<tr>
<th>(v_{\text{cal}})</th>
<th>(v_{\text{IR}})</th>
<th>(v_{\text{Ram}})</th>
<th>Depol. ratio</th>
<th>Force const.</th>
<th>Assignments</th>
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<tr>
<td>121</td>
<td>111s</td>
<td></td>
<td>0.5217</td>
<td>0.0695</td>
<td>(\gamma C_{13} = O_{16})</td>
</tr>
<tr>
<td>515</td>
<td>504s</td>
<td></td>
<td>0.7500</td>
<td>0.4799</td>
<td>(\nu C_{1}-Br_{7})</td>
</tr>
<tr>
<td>622</td>
<td>626vw</td>
<td>617vw</td>
<td>0.7329</td>
<td>1.9932</td>
<td>6a ring bend ((\delta)CCC)</td>
</tr>
<tr>
<td>673</td>
<td>687m</td>
<td>701m</td>
<td>0.1552</td>
<td>1.9308</td>
<td>11 ring bend,((\gamma)C-H)</td>
</tr>
<tr>
<td>711</td>
<td>740s</td>
<td>752vw</td>
<td>0.7500</td>
<td>1.2020</td>
<td>4 ring bend,((\gamma)CCC)</td>
</tr>
<tr>
<td>809</td>
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<td></td>
<td>0.1545</td>
<td>2.2297</td>
<td>(\gamma C-N-H)</td>
</tr>
<tr>
<td>832</td>
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<td></td>
<td>0.7500</td>
<td>0.7114</td>
<td>(\gamma C-N-H)</td>
</tr>
<tr>
<td>864</td>
<td>845w</td>
<td>854w</td>
<td>0.7500</td>
<td>0.7691</td>
<td>10b ring bend ((\gamma)C-H)</td>
</tr>
<tr>
<td>936</td>
<td>943w</td>
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<td>0.1790</td>
<td>4.0920</td>
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</tr>
<tr>
<td>973</td>
<td>967w</td>
<td>977vw</td>
<td>0.7500</td>
<td>0.9623</td>
<td></td>
</tr>
<tr>
<td>1005</td>
<td>1007s</td>
<td>1023 wsh</td>
<td>0.7500</td>
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<tr>
<td>1061</td>
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<td>1176m</td>
<td>0.1155</td>
<td>2.1488</td>
<td></td>
</tr>
<tr>
<td>1174</td>
<td>1188s</td>
<td>1213 msh</td>
<td>0.1537</td>
<td>1.1731</td>
<td></td>
</tr>
<tr>
<td>1213</td>
<td>1209 msh</td>
<td>1257 s1249m</td>
<td>0.1989</td>
<td>3.7855</td>
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<tr>
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<tr>
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<td>1309vs</td>
<td>1317 wsh</td>
<td>1423 m1404 vv</td>
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</tr>
<tr>
<td>1368</td>
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<td>1423 m1404 vv</td>
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<td>2.2819</td>
<td></td>
</tr>
<tr>
<td>1396</td>
<td>1394vs</td>
<td>1497 1503 w</td>
<td>0.6994</td>
<td>2.6919</td>
<td></td>
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</tr>
<tr>
<td>1605</td>
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<td>1605 vvs</td>
<td>0.7033</td>
<td>6.8548</td>
<td></td>
</tr>
<tr>
<td>1777</td>
<td>1669vs</td>
<td>1669v vs</td>
<td>0.1978</td>
<td>20.0942</td>
<td></td>
</tr>
<tr>
<td>2879</td>
<td>2870 vv</td>
<td>2992 vv</td>
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<td>6.3377</td>
<td></td>
</tr>
<tr>
<td>2992</td>
<td>2930 vv</td>
<td>3047 w3066w</td>
<td>0.7500</td>
<td>6.9617</td>
<td></td>
</tr>
<tr>
<td>3047</td>
<td>3052w</td>
<td>3105 w3115m</td>
<td>0.2214</td>
<td>7.4715</td>
<td></td>
</tr>
<tr>
<td>3105</td>
<td>3115m</td>
<td>3100w</td>
<td>0.2226</td>
<td>7.7494</td>
<td></td>
</tr>
</tbody>
</table>

17a ring bend ($\gamma$C-H)
5 ring bend, ($\gamma$C-H)
1 ring bend, ($\delta$CCC)
18a ring bend, ($\delta$C-H)
15 ring bend, ($\delta$C-H)
9a ring bend, ($\delta$C-H)
$\delta$N$_{10}$-H$_{15}$
$\nu$C$_{13}$-N$_{10}$
14 ring stretch, ($\nu$C-C)
$\nu$C$_{13}$-N$_{10}$
$\nu$C$_{14}$H$_{17}$,18,19
$\nu$C$_{14}$H$_{17}$,18,19
$\nu$C$_{14}$H$_{17}$,18,19
$\delta$C-N-H
$\delta$C-N-H
8b Ring stretch, ($\nu$C=C)
5.5.2 Phenyl Ring Vibrations

In PBA molecule, the aromatic ring is asymmetrically para-disubstituted. The selection rules allow five normal modes 8a, 8b, 19a, 19b and 14 for tangential C-C stretching mode in asymmetrically disubstituted [332] benzene derivatives. It is well established that the wavenumber of mode 8b, which is less substituent sensitive, is lower than that of 8a. The phenyl ring mode 8a manifests as very strong bands in the IR and Raman spectra at 1601 cm\(^{-1}\) and its relatively weaker companion 8b is identified at 1587 cm\(^{-1}\) in IR spectrum as strong band. The intensity of this mode is dependent on the algebraic difference of the electronic effects of the substituents, which is justified by the large intensity difference observed between 8a and 8b modes in the IR spectra. Moreover, the wavenumber of 8a mode is found to be lower than the computed result, which indicates the weakening of C-C bonds of the phenyl ring in crystalline state[36,299,332,333]. The mode 8a appears in both IR and Raman with high intensity at 1601 cm\(^{-1}\). This can be interpreted to be the results of intramolecular charge transfer, which contributes to the hyperpolarizability enhancement responsible for NLO activity, between \(\pi\)-electron donor and acceptor through conjugated path [323]. The simultaneous IR and Raman activation of the phenyl ring mode 8a provides evidence for the charge transfer interaction between the

<table>
<thead>
<tr>
<th></th>
<th>3186m</th>
<th>3188vw</th>
<th>3253m</th>
<th>3275vw</th>
<th>7b ring stretch ((\nu)C-H)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3468</td>
<td>3294s</td>
<td>3313vw</td>
<td>0.1675</td>
<td>9.5294</td>
</tr>
<tr>
<td></td>
<td>33294s</td>
<td>3313vw</td>
<td>0.1675</td>
<td>9.5294</td>
<td>(\nu_{as}) N(<em>{10})-H(</em>{15})</td>
</tr>
</tbody>
</table>
Fig. 5.6 Atomic displacements corresponding to selected vibrational modes of PBA monomer
donor and the acceptor group through the $\pi$-system subsequently leading to hyperpolarizability enhancement. With donor substituents, the 19a mode in $p$-disubstituted benzene is generally observed above 1500 cm$^{-1}$ and 19b mode around 1400 cm$^{-1}$ and are expected to interact slightly with methyl umbrella modes. The bands corresponding to 19a and 19b are identified at 1503 and 1408 cm$^{-1}$ in the Raman spectrum with a weak intensity and the intense IR band at 1309 cm$^{-1}$ and Raman band at 1304 cm$^{-1}$ are attributed to the Kukule C-C stretching mode 14 [85,333].

For the $p$-substituted phenyl ring, the aromatic C-H stretching vibrations usually give rise to bands in the region 3100-3000 cm$^{-1}$ [79, 85,299,333]. Of the four allowed C-H stretching modes 7b, 20a, and 20b for $p$-disubstituted ring, 7b, 20b and 20a are found to be active. The 20a ring stretching bands are observed at 3115 cm$^{-1}$ in IR and 3100 cm$^{-1}$ in Raman and the bands at 3052 (IR) and 3066 (Raman) cm$^{-1}$ are correlated to 20b ring stretching. The C-H in-plane bending modes 3, 9a, 15, 18a and 5 expected in the region 1300-1000 cm$^{-1}$ are identified and analyzed. It is found that the bands 3, 5 and 15 have strong intensities and the modes 9a and 18a are weak. The C-H out-of-plane bending vibrations 17a, 17b and 10b are expected to occur in the region 1000-675 cm$^{-1}$. The 17a, 17b and 10b modes are observed at 967, 943 and 845 cm$^{-1}$ in IR and the Raman bands corresponding to 17a and 10b appear at 977 and 854 cm$^{-1}$ respectively [334]. The IR bands at 626 cm$^{-1}$ (medium) and at 740 cm$^{-1}$ (strong) and the Raman bands at 617 and 752 cm$^{-1}$ correspond to ring modes 6a and 4 respectively.
5.5.3 Methyl Vibrations

Methyl groups are generally referred to as electron-donating substituents in the aromatic ring system [335]. The asymmetric stretching mode of CH$_3$ is expected in the region around 2980 cm$^{-1}$ and the symmetric around 2870 cm$^{-1}$ [36,79,332,333]. Absorption intensities, in the infrared region, provide much information on the nature of the chemical bonds and the effects due to intramolecular environment. Different theoretical models have been proposed for infrared intensities, which can reveal a picture of the charge distribution and charge mobility in molecules. The best-known and most widely used parameters are atomic polar tensors (APT), electro-optical parameters (EOP) and equilibrium charge and charge fluxes (ECCF). Using ECCF, the charge distribution in molecules in terms of equilibrium point charges on the nuclei (q$_0^\alpha$) and of their variation with internal valence coordinates ($\partial q_\alpha/\partial R_i$) may be obtained. To obtain ECCF correctly absolute, well-separated infrared intensities for all the infrared active normal modes of a given molecule must be available along with a reliable force field. It has been shown that ECCF from infrared spectra account quantitatively for several intramolecular electronic effects including induction and hyperconjugation. The electronic effect, hyperconjugation, usually means the interaction of the orbitals of a methyl or methylene group with the π-orbitals of an adjacent C-C bond. When the hydrogen bonds become more acidic because of release of electronic charge, the infrared C-H stretching intensity decreases and bending intensity increases [83]. The observed bands at 2930 and 2870 cm$^{-1}$ in IR and 2938 and 2850 cm$^{-1}$ in Raman are assigned to asymmetric and symmetric stretching modes of CH$_3$ respectively. This happens because of hyperconjugation of the methyl group with the π-electrons in the aromatic ring, where the injection
of negative electronic charge takes place from the CH$_3$ group to an adjacent portion of the molecule that contains $\pi$-electrons. In PBA, the methyl hydrogen atoms are subjected simultaneously to hyperconjugation and induction, which cause the decrease of infrared intensities as reported in the literature for similar molecular systems [336]. Thus hyperconjugation and induction of the methyl group, causing changes in intensity in infrared spectrum, clearly indicates that methyl hydrogens are directly involved in the donation of electronic charge. The asymmetric and symmetric bending vibrations of methyl groups are normally expected to occur in the region 1465-1440 cm$^{-1}$ and 1390-1370 cm$^{-1}$ respectively. The asymmetric bending modes of CH$_3$ appear at 1446 and 1487 cm$^{-1}$ and the symmetric bending modes at 1394 cm$^{-1}$ in the IR with strong intensity. The enhancement in intensity of the bending modes are due to the presence of C=O adjacent to CH$_3$ group [85], which is in good agreement with the calculated values. The relatively large value of IR intensity of the symmetric bending mode suggests a large positive charge localized on the hydrogen, which further supports the occurrence of hyperconjugation.

Hydrogen bonding originates from an attractive interaction between the electron deficient hydrogen donor group (A-H) and a region of high electron density acceptor atom (B), leading to the variation of H··B distance than the Van der Waals radii of the isolated H and B atoms. Although the interaction energy of a C-H··O hydrogen bond is less than those of typical N-H··O and O-H··O type bonds, the C-H type hydrogen bond plays an important role in determining higher order structure in proteins, molecular structure conformation and crystal packing. The complexes involving this shift are often accompanied by a significant decrease in its infrared intensity [63,319-321]. In C-H··O hydrogen
bond, a charge transfer from the lone pairs of the electron donor is directed mainly to the antibonding orbitals in the remote part of the complex, thus causing elongation in that part of a complex. This primary effect of elongation is accompanied by a secondary effect of structural reorganization of the proton donor, leading to contraction of the C-H bond. Therefore, a C-H· · ·O hydrogen bond is considered an ‘improper hydrogen bond or blue-shifting H-bond’. Blue shifting hydrogen bonds are characterized by a contraction or strengthening of the C-H distance, a blue shift of the C-H stretching vibrational mode, and a reduction of its infrared intensity, features which are in sharp contrast to those rooted to the conventional hydrogen bonds. The aromatic C-H stretching modes 20a and 20b appear at 3115 and 3052 cm\(^{-1}\) in IR as weak bands. The corresponding stretching modes are computed at 3105 and 3047 cm\(^{-1}\), which explains that the observed vibrational wavenumbers are larger by 10 and 5 cm\(^{-1}\) than the computed values from their normal coordinates. The bond lengths of C_5-H_11, C_3-H_6, C_2-H_8 and C_6-H_{12} are calculated to be 1.06, 1.07, 1.07 and 1.07 Å, respectively, from the optimized geometry. The C-H bond length corresponding to C_5-H_{11} is shortened by 0.01 Å over the other calculated C-H bond lengths confirming the existence of blue shifting hydrogen bond, which is further ascertained by the NBO analysis.

5.5.4 Carbonyl Group Vibrations

Carbonyl group vibrations in ketones are the best characteristic bands in the vibrational spectra, and for this reason, such bands have been the subject of extensive studies [36,332,333]. The intensity of these bands can increase because of conjugation or formation of hydrogen bonds. The increase of
conjugation, therefore, leads to the intensification of the Raman lines as well as the increased infrared band intensities. The carbonyl stretching \( \text{C}_{13}=\text{O}_{16} \) vibrations in ketones [85] are expected to occur in the region 1715-1680 cm\(^{-1}\) and this mode appears at 1669 cm\(^{-1}\) in IR and at 1679 cm\(^{-1}\) in Raman as intense bands. The conjugation and influence of intermolecular hydrogen bonding network in the crystal results in the lowering of the stretching wavenumbers. The bands associated with the \( \text{C}_{13}=\text{O}_{16} \) stretching mode are found to be strongly and simultaneously active in both IR and Raman spectra. This phenomenon is quite unusual, since generally, even in the absence of inversion symmetry, the infrared and Raman spectra are complimentary: in most cases, the strongest bands in the Raman are weak in the IR and vice versa. However, the ICT from the donor to acceptor group through a single-double bond conjugated path can induce large variations of both the molecular dipole moment and molecular polarizability, making IR and Raman activity strong at the same time.

Thus in PBA, simultaneous IR and Raman activation of \( \text{C}_{13}=\text{O}_{16} \) stretching modes clearly explains the charge-transfer interaction between donor and acceptor through the \( \pi \)-conjugated path [90,323].

Considering the soliton theory of Davydov, the origin of the anomalous band at 1679 cm\(^{-1}\) has been assigned to a “self trapped state” in which C=O vibrational energy is localized near a single acetanilide molecule through interaction with lattice phonons. The relevant parameter of the “soliton” model [308] is \( \delta = X^2/W \), where ‘\( X \)’ is the nonlinear coupling between the C=O excitations and a low frequency mode (\( \nu_0 \) frequency about 111cm\(^{-1}\) for PBA) and \( W \) is the force constant. Especially ‘\( \delta \)’ is related to the shift ‘\( \Delta \)’ of the anomalous band with respect to the C = O mode, which is given by:
\[ \Delta = \nu_{c=0} - \nu = \delta / 2 - 2J \]

where, 'J' is the strength of dipole-dipole interaction between nearest neighbors.

### 5.5.5 Low Wavenumber Hydrogen Bond Vibrations

The attractive interaction between the hydrogen donor group and the acceptor moiety leads to the occurrence of new vibrational degrees of freedom, the so called hydrogen bond modes [255]. The H-bond strain usually appears between 100 and 150 cm\(^{-1}\) as intense bands [304]. An interesting feature of these vibrations is the occurrence of an intense Raman band in the low wavenumber region ca 111 cm\(^{-1}\) corresponds to the N···O stretching H-bonds vibrations and these hydrogen bonds are named as “ionic hydrogen bonds”, through which the charge transfer can take place inside the crystal making the molecule NLO active.

### 5.6 SERS SPECTRAL INVESTIGATIONS

The calculated vibrational wavenumbers, measured SERS, Raman and IR band positions and the tentative assignments are given in Table 5.8. The adsorption mechanism of an adsorbate can be deduced from the SERS spectrum. The orientation of the adsorbate and the metal surface will depend on the active sites through which the interaction takes place. The chemically possible orientation of PBA molecular ion with respect to the silver surface can be envisaged: ‘flat’ or lying down on the metal surface through bonding with the ring system or ‘standing up’ (end-on) with bonding with the lone pair of oxygen atom with silver [338-340].
Table 5.8 Calculated IR, Raman and SERS spectral data (cm$^{-1}$) and band assignments for PBA

<table>
<thead>
<tr>
<th>$\nu_{cal}$</th>
<th>$\nu_{IR}$</th>
<th>$\nu_{Raman}$</th>
<th>$\nu_{SERS}$</th>
<th>Assignments</th>
</tr>
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<td>3294 s</td>
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<td>3321 vw</td>
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<tr>
<td>3186 m</td>
<td>3188 vw</td>
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<td>3089 vw</td>
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</tr>
<tr>
<td>3047</td>
<td>3052 w</td>
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<td>3048 vw</td>
<td>$20b$ ring stretch ($\nu$ C-H)</td>
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<tr>
<td>2992</td>
<td>2930 vw</td>
<td>2938 w</td>
<td>2968 w</td>
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<tr>
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<td>2870 vw</td>
<td>2850 vw</td>
<td>2851 w</td>
<td>$\nu_{s}$ CH$_3$</td>
</tr>
<tr>
<td>1580</td>
<td>1587 s</td>
<td>1570 s</td>
<td></td>
<td>$8b$ ring stretch ($\nu$ C-H)</td>
</tr>
<tr>
<td>1317 wsh</td>
<td>1319 s</td>
<td>1322 w</td>
<td></td>
<td>$\nu$ C - N</td>
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<tr>
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<td>1255 s</td>
<td>1249 m</td>
<td>1266 w</td>
<td>$\delta$ N - H</td>
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<tr>
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<td>1176 m</td>
<td>1188 s</td>
<td>1150 m</td>
<td>15 ring bend ($\delta$ C-H)</td>
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<td>1023 wsh</td>
<td>1020 w</td>
<td>1021 vs</td>
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<tr>
<td>864</td>
<td>845 w</td>
<td>854 w</td>
<td>858 m</td>
<td>$10b$ ring bend ($\gamma$C-H)</td>
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<tr>
<td>711</td>
<td>740 s</td>
<td>752 vw</td>
<td>728 m</td>
<td>4 ring bend ($\gamma$CCC)</td>
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<tr>
<td>673</td>
<td>687 m</td>
<td>701 m</td>
<td>643 s</td>
<td>11 ring bend ($\gamma$C-H)</td>
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<tr>
<td>515</td>
<td>504 s</td>
<td>504m</td>
<td></td>
<td>$\nu$ C - Br</td>
</tr>
<tr>
<td>111 s</td>
<td>285 vs</td>
<td></td>
<td></td>
<td>$\gamma$ C = O</td>
</tr>
</tbody>
</table>

vs - very very strong, s- strong, m - medium, w - weak, vw - very weak, vvw - very very weak, $\delta$ - in-plane bending, $\gamma$ - out-of-plane bending, $\nu_{s}$ - symmetric stretching, $\nu_{as}$ - asymmetric stretching.

The orientation of the molecule on the silver surface can be inferred from aromatic C-H stretching vibrations, ring stretching vibrations, ring breathing mode, in-plane and out-of-plane vibrations and SERS surface selection rule. It is well known [341,342] that there are two possibilities of molecular adsorption on the metal surface: physisorption and chemisorption. When the molecules are physisorbed on the metal surface the SERS spectra are very similar to those of the free molecules, the electromagnetic mechanism being the main mechanism.
of the Raman enhancements [83]. In the case of chemisorption, a new metal-
molecule SERS complex is formed that leads to drastic changes of the position
and relative intensity of the SERS band related to their corresponding Raman
bands. In this case, the charge transfer effect is the dominant mechanism of the
Raman enhancements [342]. The out of plane bending modes will be more
enhanced when compared with its in-plane bending mode, when the molecule is
adsorbed flat on the silver surface and vice versa, when it is adsorbed
perpendicular to the surface. Further, vibrations involving atoms that are close to
the silver surface will be enhanced.

By looking at the geometry of the molecule, one can assume that it may
be bound to the silver surface either through the π*-orbitals of the phenyl rings or
through the lone pair electron of the oxygen atoms-metal interaction being
sterically hindered. The observed aromatic out-of-plane bending mode at 643,
728 and 858 cm\(^{-1}\) are much more intense with respect to the in-plane bending
mode at 1150 cm\(^{-1}\). From these results it may be inferred that the intensity of
the aromatic out-of-plane C-H bands with respect to the in-plane bending mode
increases as the molecule is adsorbed flat on to the silver surface as shown in
Fig. 5.7.

![Fig. 5.7 Schematic model for the adsorption geometry of PBA on a colloidal silver surface](image)
5.7 CONCLUSION

Single crystals of PBA have been grown by the slow-evaporation technique and the vibrational spectral analysis is carried out using NIR-FT Raman and FT-IR spectroscopy. *Ab initio* molecular orbital computations have been performed at HF/6-31G (d) level to derive equilibrium geometry, vibrational wavenumbers, IR and Raman intensities and first hyperpolarizability. The calculated first hyperpolarizability of PBA is found to be 9.403069 x 10^{-31} e.s.u., which is 6.6 times that of urea. The resemblance between IR and Raman spectra reveals the existence of intramolecular charge transfer (ICT), thus the molecule behaves as an effective push-pull NLO system. The appearance of strong band at 1601 cm⁻¹ in both IR and Raman spectra corresponds to the in-phase symmetric stretching of the C=C bonds of the phenyl ring of the π-conjugated system. The vibration spreads over the whole π-conjugated path with relevant vibrational amplitudes from all the parts of PBA π-conjugated system. This analysis shows that the N-H stretching bands are lowered from the computed frequencies due to the intra- and intermolecular N-H⋯O hydrogen bond interactions throughout the crystal. *Ab initio* quantum chemical computations predict the existence of intramolecular C-H⋯O bonds. NBO analysis confirms the presence of strong intermolecular N-H⋯O hydrogen bonds in PBA dimer. The SERS spectra predict that the PBA molecule is adsorbed perpendicular to the silver surface.