Spectroscopic characterization of metal decorated benzene and boron/nitrogen substituted benzene

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This work reports theoretical vibrational spectra of Li, Be and Ti doped benzene using second ordered Møller-Plesset method (MP2) with 6-311++G** basis set. Effect of boron/nitrogen atom substitution on the vibrational frequencies of pristine benzene has also been studied using vibrational spectra obtained from quantum chemical method. Two boron/nitrogen atoms have been substituted for exactly opposite carbon atoms in a benzene ring. An influence of metal doping on the vibrational frequencies of boron/nitrogen substituted benzene complexes has been studied and compared with the metal doped pristine benzene complexes. Vibrational frequencies obtained for the isolated benzene have been significantly altered after metal doping and B/N substitution.

Keywords: Vibrational spectra, Benzene, Metal doping, Boron/nitrogen substituted benzene

1 Introduction

Infrared (IR) spectroscopy has a wide range of applications in organic as well as inorganic chemistry. IR energy corresponds to bond vibration in a molecule. Vibrational spectroscopy is found to be a powerful technique to study different materials like protein\textsuperscript{1} and interstellar molecules\textsuperscript{2}. Singh \textit{et al.} have studied vibrational spectra of muscovite and biotite layered phyllosilicates\textsuperscript{3}. Naganathappa \textit{et al.} have performed spectroscopic characterization of several interstellar molecules using theoretically obtained vibrational spectra\textsuperscript{4,5}. Sen \textit{et al.} have carried out vibrational spectral analysis of isotopic species of hydrogen sulfide, hydrogen selenide and water\textsuperscript{6}. Hajlaoui \textit{et al.} have studied vibrational spectra of organic-inorganic compounds\textsuperscript{7}.

Benzene is a six membered carbon ring and the simpler aromatic system. The vibrational spectra of benzene can be useful to account different types of bonding and vibrational modes for the benzene. Chemical properties of benzene can be altered by doping and substitution of foreign atom and this variation can be analyzed with the help of vibrational spectrum. Raja \textit{et al.} have investigated different vibrations in benzene derivatives using quantum chemical methods\textsuperscript{8}. Theoretical vibrational spectrum of fluobenzene has been calculated by Fogarasi \textit{et al.}\textsuperscript{9}. Properties of benzene can be altered by substituting boron(B)/nitrogen(N) atoms due to their similar atomic radii. Analog structures of benzene have interesting chemical and physical properties\textsuperscript{10}. Song \textit{et al.} have synthesized and characterized the B and N containing graphene complexes\textsuperscript{11}.

Here, we have carried out spectroscopic analysis of benzene using vibrational spectroscopy. Benzene ring is modified by replacing two carbon atoms by two B/N atoms. The vibrational spectra of pristine, boron and nitrogen substituted benzene are compared with the help of electronic structure calculations. Effect of metal doping on vibrational spectra of pristine as well as B/N substituted benzene is also studied.

2 Computational Details

Second order Møller-Plesset\textsuperscript{12} (MP2) method along with 6-311++G** basis set is used to optimize the geometries of C\textsubscript{6}H\textsubscript{6}, C\textsubscript{6}H\textsubscript{6}M, C\textsubscript{4}B\textsubscript{2}H\textsubscript{6}, C\textsubscript{4}B\textsubscript{2}H\textsubscript{6}M, C\textsubscript{4}N\textsubscript{2}H\textsubscript{6} and C\textsubscript{4}N\textsubscript{2}H\textsubscript{6}M (where M= Li, Be and Ti) complexes. The vibrational spectra of all these complexes were obtained at the same level of theory. We have used 0.95 scaling factor for the vibrational frequencies obtained at MP2/6-311++g** level of theory\textsuperscript{13}. Gaussian 09 suits of program is used to perform all the calculations\textsuperscript{14}.

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3 Results and Discussion

Figure 1(a) shows the optimized geometry of pristine benzene (C₆H₆). Two exactly opposite carbon atoms of the benzene ring are replaced by two B/N atoms. The optimized geometries of boron substituted (C₄B₂H₆) and nitrogen substituted benzene (C₄N₂H₆) complexes are shown in Figs 1(b,c), respectively. Pristine as well as B/N substituted benzene rings are further modified by doping of alkali metal (Li), alkaline earth metal (Be) and transition metal (Ti) and corresponding optimized structures are shown in Figs 2, 3 and 4, respectively. Structural parameters of pristine and B/N substituted benzene complexes before and after metal doping are given in Table 1. The B/N substituted benzene complexes are isoelectronic to the benzene and have a nearly equal C-C bond length. Doping of the metal atoms alters the C-C bond length of pristine as well as B/N substituted
benzene complexes. The C-B bond is little longer than the C-N and C-C bonds. All metal atoms are bonded at a longer distance from the N substituted benzene molecule than the pristine and B substituted benzene molecules. Among all the metal doped complexes, Be atom gets bonded at smaller distances from all the substrates, whereas the Li atom is bonded at longer distances. It indicates that the Be atom gets strongly bonded to all the substrates than Ti and Li atoms.

The vibrational spectra of benzene (pristine, B/N substituted benzene), Li, Be and Ti doped complexes are shown in Figs 5, 6, 7 and 8, respectively, and selected vibrational modes for these complexes are summarized in Table 2. All these complexes have intense and high IR absorption in the 3500-250 cm\(^{-1}\) region. Most intense peak for the benzene is the C-H wagging mode appeared at 642 cm\(^{-1}\). The B-H stretching and N-H wagging modes are the most intense modes observed for the C\(_4\)B\(_2\)H\(_6\) and C\(_4\)N\(_2\)H\(_6\) complexes, respectively. The vibrational frequency for the respective mode is found to be 2504 and 588 cm\(^{-1}\). The CCC bending, C-H wagging and C-H stretching modes for benzene are observed at 958, 642 and 3069 cm\(^{-1}\), respectively, and are in good agreement with the corresponding experimental modes observed at 1010, 674 and 3057 cm\(^{-1}\). The CCC bending and C-H wagging modes are red shifted in C\(_4\)B\(_2\)H\(_6\) as well as C\(_4\)N\(_2\)H\(_6\) complexes than that for the C\(_6\)H\(_6\) complex, whereas the C-H stretching mode is red and blue shifted for C\(_4\)B\(_2\)H\(_6\) and C\(_4\)N\(_2\)H\(_6\) complex, respectively, than that for the benzene. The red shift of 169(161) and 109(165) is found for the CCC bending and C-H wagging mode respectively for the C\(_4\)B\(_2\)H\(_6\) (C\(_4\)N\(_2\)H\(_6\)) than that for the benzene. The C-H stretching mode is red(blue) shifted by 57(39) cm\(^{-1}\) for the C\(_4\)B\(_2\)H\(_6\) (C\(_4\)N\(_2\)H\(_6\)) than that for the benzene.
The most intense peak for $\text{C}_6\text{H}_6\text{Li}$, $\text{C}_4\text{B}_2\text{H}_6\text{Li}$ and $\text{C}_4\text{N}_2\text{H}_6\text{Li}$ complexes represents the CCC stretching, CCB bending and N-H wagging mode respectively with respective vibrational frequency of 1048, 862 and 620 cm$^{-1}$. The CCB bending mode for the $\text{C}_6\text{H}_6\text{Li}$ complex is observed at 901 cm$^{-1}$ and it is red shifted by 104 cm$^{-1}$ for $\text{C}_4\text{B}_2\text{H}_6\text{Li}$ and blue shifted by 25 cm$^{-1}$ for $\text{C}_4\text{N}_2\text{H}_6\text{Li}$ complex. In $\text{C}_4\text{B}_2\text{H}_6\text{Li}$ complex, the C-H and B-H stretching modes are observed at 2994 and 2500 cm$^{-1}$, respectively. The C-H and N-H stretching modes for the $\text{C}_4\text{N}_2\text{H}_6\text{Li}$ complex are blue shifted by 7 and 280 cm$^{-1}$, respectively. The C-H and N-H stretching modes are the most intense modes in $\text{C}_4\text{Li}$ complex and red shifted in $\text{C}_4\text{N}_2\text{H}_6\text{Be}$ complexes by 7 and 280 cm$^{-1}$, respectively. For the $\text{C}_6\text{H}_6\text{Be}$, $\text{C}_4\text{B}_2\text{H}_6\text{Be}$ and $\text{C}_4\text{N}_2\text{H}_6\text{Be}$ complexes the most intense peak represents the C-H wagging, B-H stretching and N-H wagging modes, respectively, with respective vibrational frequency of 745, 2535 and 495 cm$^{-1}$. The CCC bending, C-H stretching and C-Be stretching mode of $\text{C}_6\text{H}_6\text{Be}$ complex are observed at 916, 3074 and 584 cm$^{-1}$ and all the three modes are red shifted in $\text{C}_4\text{B}_2\text{H}_6\text{Be}$ complex and blue shifted in $\text{C}_4\text{N}_2\text{H}_6\text{Be}$ complex. The C-H wagging, B-H stretching and C-H wagging modes are the most intense modes in $\text{C}_6\text{H}_6\text{Ti}$, $\text{C}_4\text{B}_2\text{H}_6\text{Ti}$ and $\text{C}_4\text{N}_2\text{H}_6\text{Ti}$ complexes and observed at 645, 2473 and 709 cm$^{-1}$. The CCC bending, C-H stretching and C-M stretching modes for the $\text{C}_6\text{H}_6\text{Ti}$ complex are observed at 898, 3073 and 417 cm$^{-1}$ and these modes are red shifted in $\text{C}_4\text{B}_2\text{H}_6\text{Ti}$ and $\text{C}_4\text{N}_2\text{H}_6\text{Ti}$ complexes. The C-H wagging mode for $\text{C}_6\text{H}_6\text{Ti}$ complex is observed at 645 cm$^{-1}$ and it is blue

Table 2 — Selected vibrational modes (cm$^{-1}$) of $\text{C}_6\text{H}_6$, $\text{C}_6\text{H}_6\text{M}$, $\text{C}_4\text{B}_2\text{H}_6\text{M}$, $\text{C}_4\text{N}_2\text{H}_6\text{M}$ (where M=Li, Be and Ti) complexes at MP2/6-311++G** level of theory.

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<th>Complex</th>
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<tr>
<td>$\text{C}_6\text{H}_6$</td>
<td></td>
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<td>674</td>
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<td>3057</td>
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<td>(Experimental)</td>
<td></td>
<td>958</td>
<td>642</td>
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<td>3069</td>
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<tr>
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<td>477</td>
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<td>3108</td>
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<tr>
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<td>627</td>
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<td>3049</td>
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<tr>
<td>$\text{C}_4\text{B}_2\text{H}_6\text{Li}$</td>
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<td>598</td>
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<tr>
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<td>703</td>
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<td>3109</td>
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<tr>
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<td>745</td>
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<tr>
<td>$\text{C}_4\text{B}_2\text{H}_6\text{Be}$</td>
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<td>667</td>
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<td>$\text{C}_4\text{N}_2\text{H}_6\text{Be}$</td>
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<tr>
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<td>675</td>
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<tr>
<td>$\text{C}_4\text{N}_2\text{H}_6\text{Ti}$</td>
<td></td>
<td>868</td>
<td>709</td>
<td>533</td>
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shifted by 30 and 64 cm\(^{-1}\) in \(\text{C}_6\text{B}_2\text{H}_6\text{Ti}\) and \(\text{C}_6\text{N}_2\text{H}_6\text{Ti}\) complexes, respectively.

The gap between highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) is calculated for all the complexes. A larger HOMO-LUMO gap implies the good stability of a complex. The HOMO-LUMO gap for the benzene is found to be 8 eV and it is increased by 1.51 eV after boron substitution whereas it is decreased by 2.03 eV after N substitution. The HOMO-LUMO gap for \(\text{C}_6\text{H}_6\text{Li}, \text{C}_4\text{B}_2\text{H}_6\text{Li}, \text{C}_6\text{N}_2\text{H}_6\text{Li}, \text{C}_6\text{H}_6\text{Be}, \text{C}_4\text{B}_2\text{H}_6\text{Be}, \text{C}_6\text{H}_6\text{Ti}, \text{C}_4\text{B}_2\text{H}_6\text{Ti}\) and \(\text{C}_6\text{N}_2\text{H}_6\text{Ti}\) complexes is found to be 4.44, 7.21, 3.92, 6.47, 7.77, 6.25, 6.42 and 4.99 eV, respectively. Li doped complexes are less stable among all the metal doped complexes. The \(\text{C}_4\text{B}_2\text{H}_6\text{Li}\) complex is found to be the most stable, whereas the \(\text{C}_6\text{N}_2\text{H}_6\text{Li}\) complex is the least stable complex among all the complexes.

4 Conclusions
The vibrational spectra of pristine as well as B/N substituted benzene complexes are obtained at MP2/6-311++G** level of theory. Theoretical vibrational modes of benzene are in good agreement with the experimental determinations. Effect of Li, Be and Ti doping on vibrational spectra of benzene is studied. The vibrational frequencies of pristine and B/N substituted benzene complexes are significantly altered after metal doping. The CCC bending and C-H wagging mode of benzene are enormously shifted after B/N substitution as well as metal doping for all the complexes. The C-H stretching mode of all complexes lies in the range of 3149-3273 cm\(^{-1}\). A large HOMO-LUMO gap of 9.51 eV for the \(\text{C}_6\text{B}_2\text{H}_6\) complex indicates that it is the most stable complex among all complexes.

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References