Spectral Calculation of Cucurbituril[n] Molecule Based on Density Functional Theory

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Abstract. The cucurbituril[n] (CB[n]) is a class of chemical supramolecular substances. In order to calculate the spectrum of the cucurbituril[n] molecules, the density functional theory (DFT) and the time-dependent density functional theory (TD-DFT) are used to optimize the geometrical structure of CB[n](n=5-10) at the level of 6-311g(d) in the gas phase environment. Then, the infrared (IR) spectrum and ultraviolet (UV) spectrum of CB[n] (n=5-10) are calculated respectively. The results show that: (1) The absorption peaks of two vibration modes of ν(β-H) and ν(γ-H) of CB[n](n =7,8) are degenerated. (2) The absorption frequency of the stretching vibration ν(α=O) is red shifted. (3) The increase of the absorption peak intensity in the vibration mode near the 1200 cm⁻¹ wavenumber is especially noticeable. (4) The ring tension of CB[n](n=5~10) gradually decreases with n increasing. (5) The UV absorption wavelength of the maximum absorption peak of CB[n](n=5-10) increases from 198.8317nm to 202.2633nm with n from 5 to 10. The methylene CH2 has isolating action in the formation process of the UV spectrum of CB[n] (n=5-10). The distribution of electron and hole is symmetric and locally excitated (LE) for CB[n] (n=5-10).

1. Introduction
In recent years, with the development of supramolecular chemistry, cucurbituril[n] (CB [n]) has become an emerging one in supramolecular chemistry after crown ether [1], cyclodextrin (Cyclodextrin) [2] and calixarenes [3]. It has extensive and attractive applications in many fields such as supramolecular catalysis, supramolecular assembly, molecular molecular probes, chiral recognition, wastewater treatment, drug release and so on. The cucurbituril was firstly synthesized by Behrend et al. in 1905 [4]. In 1981, Freeman et al. [5] used single crystal X-ray diffraction technique to analyze the number of methylene, the number of glycolic cells and the spatial structure of cucurbituril [6]. After that, scientists have conducted extensive research on the synthesis methods, properties and applications of CB[n] [7-12]. CB[n] is a white crystal, which has a poor solubility in neutral aqueous solutions and is insoluble in organic solvents but soluble in a strong solvent. CB[n] has a unique space structure that can form stable complex compound with many substances. CB[n] has hydrophobic cavity. It can combine with other substances to form complex supramolecular entities by the interaction such as ion-dipole and hydrogen bonding between molecules through the carbonyl O atom on both sides of the port. There are identification methods of CB[n] such as nuclear magnetic resonance, mass spectrometry, infrared spectrum, ultraviolet-visible spectrum and so on [13, 14]. The cucurbituril[n] modification, as well as the interaction with CB[n], gas molecules, metal ions and organic molecules can be seen in many
references [15-22]. Less theoretical studies of the molecular spectra of CB[n] have been conducted so far [23-25]. Because the infrared spectrum and UV-visible spectral can play an important role in the study of the structure, dynamics and electron transitions of compounds, the spectral characteristics of CB[n] (n=5-10) are calculated and analyzed in this paper by the density functional theory (DFT) in the modern quantum chemistry. It provides a theoretical reference for studying the chemical activity site as well as the chemical stability and derivatives of CB[n].

2. Model and Computational method
In the gas phase environment, the geometrical structures of CB[n] (n=5-10) are optimized by the density functional theory (DFT) in the Gaussian 09 software package at the level of 6-311g(d). The frequency analysis has no imaginary frequency, which indicates that the optimized structure is stable. On the basis of structural optimization, the frequency data are calculated by DFT in Gaussian99 software at the level of B3LYP/6-311-g(d). The frequency data are corrected by calibration factor (0.966) [26] in the Multiwfn package [27] to obtained the infrared spectrum of CB[n] (n=5-10) in gas phase environment. Similarly, on the basis of structural optimization, the 15 excited states of CB[n] (n=5-10) are calculated by using the time-dependent density functional theory (TD-DFT) [28, 29] at the same basic group level, which can get the ultraviolet spectrum of CB[n] (n=5-10).

3. Results and Discussions
3.1. The calculation of infrared spectrum
On the basis of structural optimization, the vibration spectrum of CB[n] (n=5-10) are calculated in the gas phase environment. Comparing the calculated results with the references [27, 29, 30], the calculation results are in good agreement with that in the references. However, they are larger than the reference value, which is mainly caused by different frequency correction factors because the base group B3LYP/6-311g(d) used in this paper is larger than the base group B3LYP/6-31g(d) used in the reference. Because the structure of CB[n] (n=5-10) is similar, its infrared spectrogram is similar. But the infrared spectrum displays frequency shift as n increases due to the structural difference. After the frequency correction, the infrared spectra of CB[n] (n=5-10), as shown in figure 1, have been obtained after the processing of Origin software. For easy description, the carbonyl C atom in CB[n] is named α atom, the methylene C atom named β atom and the submethyl C atom named γ atom.

As shown in figure 1, the vibration of CB[7] and CB[8] in the vicinity of the wave number of 2800cm⁻¹ is the stretching vibration of ν(β-H) and ν(γ-H). The absorption peak is enhanced in turn and is stronger than that of CB[n] (n=5, 6, 9, 10). This is because the wave number of the two absorption peaks of CB[7] is 2996.61 cm⁻¹ and 2996.80 cm⁻¹ respectively, and the interval is 0.19 cm⁻¹. But the wave number of the two superimposed absorption peaks of CB[8] is 2989.75 cm⁻¹, and the interval is 0. So the coupling effect of CB[8] is more obvious, and the absorption peak is more intense. The absorption peak near 1800cm⁻¹ is caused by the stretching vibration of ν(α=O) with a slight bending vibration of δ(β-H). With the increase of the glycosides urea unit n, the absorption frequency is red shifted. The main reasons are as follows.

1) Because the structure of CB[n] (n=5-10) has a high degree of symmetry, the conjugate effect of CB[n] (n=5-10) is increasing and π electrons are going to go up with the increase of the glycosides urea unit n. It reduces the bond energy of carbonyl C=O. This causes the absorption frequency to move to the low wave number.
2) Because the left and right sides of carbonyl C=O are linked together with N atom and the electron absorbability of the O atom in C=O functional groups is greater than that of the N atom, the N atom in CB[n] (n=5-10) is belong to the group of losing electron. It makes that the double bond of carbonyl C=O has a tendency to change to a single bond and that the force constant of double bond goes down. This causes the absorption frequency to move to the low wave number.
3) The hydrogen bonding formed in CB[n] (n=5-10) molecule or among them reduce the bonding force constant of C=O bond. The infrared absorption frequency is reduced. But the formation of
hydrogen bonds can lead to the change of dipole moment and the increase of absorption peak intensity, as shown in Figure 1.

![Infrared spectra of CB[n] (n=5-10)](image_url)

**Figure 1.** The infrared spectra of CB[n] (n=5-10)

As the number n of glycosides urea unit increases, the infrared absorption frequency of carbonyl C=O decreases. This indicates that the ring tension of CB[n](n=5-10) decreases with the increase of n.

The bending vibrations of δ(γ-H) and δ(β-H) near the wave number 1200 cm⁻¹ are often accompanied by the stretching vibration of ν(β-N-β). The intensity of absorption peak of CB [n] (n=5-10) increases gradually obvious. It is because the wavenumber and absorption peak strength of the two absorption peaks corresponding to this vibration mode are similar or identical, along with the coupling of the two absorption peaks.

The main vibration modes of the infrared absorption peaks of CB[n] (n=5-10) are detailed in table 1, where ν represents the telescopic vibration and δ represents the bending vibration. From the table 1, the absorption peak interval of the two vibration modes of ν(β-H) and ν(γ-H) reduces from 32 cm⁻¹ for CB[5] to 0 for CB[8], then gradually increases to 20 cm⁻¹ for the CB[10]. The two vibration modes of ν(β-H) and ν(γ-H) of CB[7] and CB[8] have obvious coupling effect.

As n increases, the absorption peaks of ν(β-H) move towards the lower wave number. This is because the methylene CH₂ of CB[n](n=5-10) is associated with N atoms that have stronger absorption of electrons than C. Because of the induced effect of electrons, the C-H single bond enhancement of methylene CH₂ and submethyl CH is increased.

The gradual decrease of absorption peak frequency of the vibrational mode ν(β-H) indicates that the ring tension of CB[n] (n=5-10) decreases with the increase of n. The absorption peak frequencies of the vibrational mode ν(β-H), ν(α-O)+δ(β-H), ν(N-β) and δ(γ-H)+ δ(β-H)+ ν(β-N-β) gradually decrease in turn with the increase of n. This shows that the molecular system is closer to the plane and that the
conjugate increase with the increase of n. It results that the infrared absorption moves to the end of low wavenumber. It can be predicted that CB[n] is not the standard bucket structure when n is greater than a certain value. For example, the twisted CB[14] (tCB[14]) was obtained by Tao Zhu group of Guizhou University in 2013 when they separated CB[5] and CB[7] by using ion exchange resin [12].

### Table 1. The attribution of CB[n](n=5-10) vibration mode / cm⁻¹

| The attribution of vibration mode | CB[5]  | CB[6]  | CB[7]  | CB[8]  | CB[9]  | CB[10] |
|----------------------------------|--------|--------|--------|--------|--------|--------|
| ν(β-H)                           | 2930   | 2908   | 2894   | 2888   | 2885   | 2884   |
| ν(γ-H)                           | 2898   | 2890   |        |        | 2869   | 2864   |
| ν(α=O)+δ(β-H)                    | 1798   | 1790   | 1786   | 1782   | 1781   | 1778   |
| δ(β-H)+δ(γ-H)                    | 1424   | 1424   | 1424   | 1423   | 1422   | 1422   |
| δ(γ-H)+ν(γ-γ)                    | 1359   | 1360   | 1359   | 1358   | 1356   | 1356   |
| ν(N-β)                           | 1306   | 1303   | 1300   | 1298   | 1295   | 1294   |
| δ(N-α-N)+ν(γ-N)                  | 1272   | 1276   | 1275   | 1274   | 1272   | 1170   |
| δ(γ-H)+δ(β-H)+ν(β-N-β)           | 1206   | 1203   | 1199   | 1195   | 1191   | 1188   |
| δ(γ-H)+ν(N-β)                    | 1167   | 1168   | 1168   | 1167   | 1167   | 1166   |
| Twisting vibration in ring plane of eight heterocyclic | 947    | 954    | 958    | 962    | 964    | 967    |
| Bending vibration inside the frame ring of eight heterocyclic | 771    | 779    | 783    | 784    | 787    | 787    |

#### 3.2. The calculation of UV-Visible spectrum

In the gas phase environment, the 15 excited states of CB[n] (n=5-10) are calculated by the time-dependent density functional theory (TD-DFT) on the basis of structural optimization. The UV spectra of CB[n] (n=5-10) are shown in figure 2. Compared with the reference [31, 32], the calculation value of this paper is smaller than the reference value. It is because the ultraviolet spectrum, in the reference, is the supramolecular spectrum, formed by cucurbituril[n] and object, which shifts to long wavelength direction. In figure 2, the black curve (Total) is obtained by adding the Y value of all the transition curves on the normalized absorption curve of the electronic transition of CB[n] (n=5-10). The red curve and blue curve are the transition expansion curves of the Gaussian function which the oscillator strength is greater than 0.01. The S0 represents ground state, and S5, S6, S7, S8, S11, S12, and S13 respectively represent fifth, sixth, seventh, eighth, eleventh, twelfth and thirteenth excited states in figure 2.

From the figure 2, the electron transition with larger contribution to the UV spectra of CB[n] (n=5, 6) are mainly S0→S5 and S0→S6 transition. The electron transition with larger contribution to the UV spectra of CB[n] (n=7, 8) are mainly S0→S7 and S0→S8 transition. The electron transition with larger contribution to the UV spectra of CB[9] includes S0→S11 and S0→S12 transition. The electron transition with larger contribution to the UV spectra of CB[10] includes S0→S12 and S0→S13 transition.

The absorption wavelength and the vibrator strength of the two transition modes with the maximum contribution of UV spectrum in CB[n] (n=5-7, 9, 10) are slightly different. But the absorption wavelength and vibrator strength of the two transition modes with the maximum contribution of UV spectrum in CB[8] are completely coincident and cannot be separated, as shown in the upper right corner of figure 2.
Figure 2. The UV spectra of CB[n] (n=5-10)

Corresponding to figure 2, the wavelength of the UV spectrum and the weight of contribution of the main transition absorption peak to the UV spectrum of CB[n] (n=5-10) are listed in table 2. It shows that the absorption wavelength of UV spectrum CB[n] (n=5-10) increases from 198.8317nm to 202.2633nm with the increase of n. This is because:

1) The conjugation degree of CB[n] (n=5-10) increases gradually with the increase of the nucleoside n. The conjugation effect makes the conjugate atoms form π bond. The electrons of π bond are more likely to be excited to transit to π antibonding orbit, so the ultraviolet absorption wavelength red shifts to long wavelength direction.

2) The change of molecular structure leads to change its UV spectrum. The coplanarity between groups in the CB[n] (n=5-10) is getting better and better with the increase of n. The energy of electronic transition from the ground state to the excited state is getting lower and lower, so the ultraviolet absorption wavelength red shifts to long wavelength direction.

3) The chromophore C=O links the auxochrome N atom containing a lone pair electrons in CB[n] (n=5-10) that can cause the conjugation effect of the lone pair electrons transition to π electron. This makes not only the absorption wavelength of π - π* electron transition red shift to the direction of long wavelength but also increase the absorption intensity.
Table 2. The contribution of major transition absorption peak to the UV spectrum of CB[n] (n=5-10)

| CB[n] | Wavelength(nm) | Total peak | Major transition | Transition peak | Weight of contribution (%) |
|-------|----------------|------------|------------------|----------------|---------------------------|
| CB[5] | 198.8317       | 7006.7950  | S0→S5           | 3453.17144     | 49.2832                   |
|       |                |            | S0→S6           | 3429.19521     | 48.9410                   |
| CB[6] | 200.7355       | 11906.3422 | S0→S5           | 5965.30873     | 50.1019                   |
|       |                |            | S0→S6           | 5941.0335      | 49.8981                   |
| CB[7] | 201.2535       | 17689.6530 | S0→S7           | 8865.05526     | 50.1144                   |
|       |                |            | S0→S8           | 8824.59778     | 49.8856                   |
| CB[8] | 201.6397       | 23982.5341 | S0→S7           | 11991.26703    | 50                        |
|       |                |            | S0→S8           | 11991.26703    | 50                        |
| CB[9] | 201.9942       | 30647.5292 | S0→S11          | 15307.59014    | 49.9472                   |
|       |                |            | S0→S12          | 15339.93909    | 50.0528                   |
| CB[10]| 202.2633       | 37543.0217 | S0→S12          | 18781.62373    | 50.0269                   |
|       |                |            | S0→S13          | 18761.39799    | 49.9731                   |

The wavelength growth of ultraviolet absorption peak of CB[n] (n=5-10) gradually decreases with the increase of n. This may be because the methylene CH$_2$ between two nucleoside urea units suppresses the conjugation effect of group in CB[n] (n=5-10). It indicates that the methylene CH$_2$ has isolating action in the formation process of the ultraviolet spectrum of CB[n] (n=5-10).

4. Conclusion

On the basis of structural optimization, the vibration spectrum of CB[n] (n=5-10) are calculated by using the B3LYP method in the density functional theory (DFT) at the level of 6-311g(d) in the gas phase environment. The 15 excited states and ultraviolet spectra of CB[n] (n=5-10) are calculated by using the time dependence density functional theory (TD-DFT) at the same base level. The conclusions are as follows:

1. The vibration of CB[7] and CB[8] near the wave number of 2800cm$^{-1}$ is the stretching vibration of $\nu$(β-H) and $\nu$(γ-H). Due to the obvious coupling effect, the absorption peak is stronger than that of CB[n] (n = 5, 6, 9, 10). The vibration of CB[n] (n=5-10) near the wave number of 1800cm$^{-1}$ is the stretching vibration of $\nu$(α=O), which is accompanied by a slight bending vibration of $\delta$(β-H). The absorption frequency shifts to lower wave number with the increase of n. The vibration of CB[n] (n=5-10) near the wave number of 1200cm$^{-1}$ is the bending vibration of $\delta$(γ-H) and $\delta$(β-H), which is accompanied by a slight stretching vibration of $\nu$(β-N-β). The absorption peak intensity obviously increases gradually with the increase of n. The absorption peak frequency of the vibrational mode $\nu$(β-H) gradually decreases, which indicates that the ring tension of CB[n] (n=5-10) decreases with the increase of n.

2. In the 15 excited states, only two electronic transition modes contribute the most to the UV spectrum of CB[n] (n=5-10). The absorption wavelength of UV spectrum CB[n] (n=5-10) increases from 198.8317nm to 202.2633nm with the increase of glycosides urea number n. The gradual decrease of wavelength growth indicates that the methylene CH$_2$ has isolating action in the formation process of the UV spectrum of CB[n] (n=5-10).

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