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A Theoretical Investigation of Photo Absorption in Boronoxide NanoCluster

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Abstract : The Photoabsorption in B₆O₂ isomers were investigated using time-dependent density functional theory (TD-DFT). The first resonant peak for B₆O₂-I is found to occur at around 2.13 eV corresponding to the molecular transitions mostly of HOMO to LUMO (98 percent) whereas the first peak for B₆O₂-II is found at around 1.69 eV contributed from completely HOMO to LUMO transition. Though first few resonant peaks of all the isomers are observed to fall in visible region, the absorption spectrum of B₆O₂-II is red-shifted as compared to the other isomers. The nature of these excitations were investigated by analyzing the frontier molecular orbitals involved with these optical transitions. In the case of B₆O₂-I the LUMO is found to be a hybrid orbital contributed from both *s* (12 percent) and *p* (86 percent), whereas the LUMOs of other isomer is purely *p* type orbitals.

Keywords: TDDFT; Photo absorption; oscillator strength; Boron oxide

Introduction

The possibility of exploiting unique size dependent properties has invoked great interest in semiconducting and metal cluster in nano-meter size range. Among them boron clusters have attracted much attention of both theoretical and experimental physicists due to its multi-fold structural variety similar to carbon. In addition to the study of different properties, optical and dielectric properties of boron nanoclusters have also been investigated by various authors. For example, optical absorption spectrum of B₆ and B₆⁺ isomers were theoretically studied by Shinde and the coworkers^{1,2}. Similarly, structural and electronic properties of hetero-atom doped boron nanoclusters, especially boron oxides have been investigated by many authors. Few examples include the investigations of the re-activities and electronic structures of boron oxides by Anderson *et al*³ and Tai *et al.*⁴ respectively. However, study of the optical properties of boron oxides are yet to be performed comprehensively. Realizing the fact that study of optical properties might provide an insight of the structural and electronic properties of boron oxide cluster, we in this paper investigated the optical absorption of B₆O₂ isomers using time dependent density functional theory (TDDFT) employing adiabatic approximation in real time⁵.

Computational analysis

Boron isomers were optimized using B3LYP/6-311+G(d) methodology within the framework of density functional theory (DFT). Optical absorption spectra of the B₆O₂ isomers were computed using time-

dependent density functional theory (TD-DFT) employing adiabatic approximation in real time³. The oscillator strength is calculated using the following formulation,

$$f = \frac{2m_e}{3\hbar^2} E_{ij} |\mu_{ij}|^2$$

Where, E_{ij} is the energy difference between i^{th} and j^{th} levels and μ_{ij} is the associated dipole moment. All the calculations were performed using the computational chemistry program Gaussian 09 and the graphical user interface Gauss view and Chemcraft software⁶.

Results and discussion

The computed excitation energies and the corresponding oscillator strengths (f) of both the B_6O_2 isomers are presented in Fig. 1, and Fig.2, and the spectroscopic data are provided in Table 1. It is found that between the two isomers the planer ring with C_s point-group symmetry is more stable than the rest. For B_6O_2 -I, the first spectacular optical absorption occurs to singlet state at around 2.13 eV with oscillator strength $f=0.005$. and dipole-moment (μ) 0.0922 a.u. This peak in the visible region (wavelength=582.3nm) corresponds to the optical transition of $|HOMO \rightarrow LUMO\rangle$. The highest peak of this isomer occurs at around 3.56 eV with $f=0.0242$ and $\mu=0.2779$ a.u. And corresponds to mostly $|HOMO-2 \rightarrow LUMO+0\rangle$ (67%) transition. Another contribution is $|HOMO-1 \rightarrow LUMO+1\rangle$ (25%) transition state. For B_6O_2 -II the first peak occurs at around 1.6945 eV with $f=0.006$ and $\mu=0.1454$ a.u which corresponds to totally $|HOMO-1 \rightarrow LUMO\rangle$ (100%) transition. The highest resonant peak for B_6O_2 -II occurs at around 4.28 eV with $f=0.3590$ a.u. and $\mu=3.4263$ a.u. , and the maximum (60%) contribution for this peak arises due to the transition state of $|HOMO-1 \rightarrow LUMO\rangle$ and the rest from $|HOMO \rightarrow LUMO+1\rangle$. The next peak is found to occur at 4.97 eV with oscillator strength 0.2048.

The above spectral analysis shows that, the first transition peaks for both the isomers falls mostly in the visible region. The possible reason of red-shifting the TDDFT peaks from B_6O_2 -II to B_6O_2 -I isomer may be that the LUMO of B_6O_2 -I is a combination of s (12%)+ p (86%) hybrid orbitals whereas the LUMO of another isomer is purely p -types.

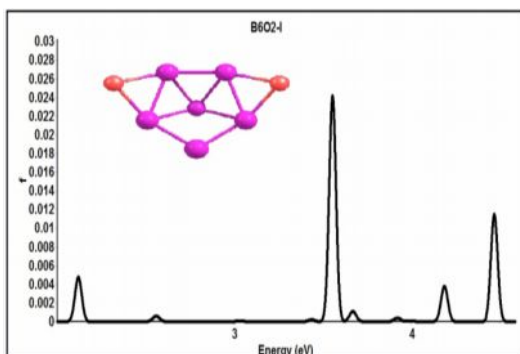


Figure 1 : Photo Absorption Spectrum of B_6O_2 -I Cluster.

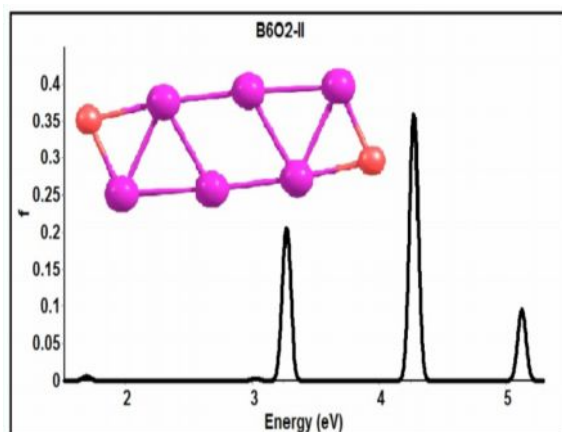


Figure 2 : Photo Absorption Spectrum of B_6O_2 -II Cluster.

In order to have a better insight towards the interaction of O₂ with B₆O₂ cluster we have examined energy difference between the bare-cluster HOMOs and isolated O₂ LUMOs which are shown in fig 3 and fig 4 respectively. It is found that the energy of the bare-cluster HOMOs ($E=-6.488$ eV and -6.680 eV) is lower than the energy of O₂ LUMOs ($E=0.0787$ eV). Since O₂ is highly electronegative, most of the electron density donated to O₂ comes from the HOMO of the bare-cluster, therefore decreasing the HOMO energy of boron cluster.

Table 1: Total energy, Excitation Energy, Oscillator strength (*f*), Transition states, C.I. Coefficient, Dipole-moment (μ), $E(\text{HOMO}_{\text{host cluster}})-E(\text{LUMO}_{\text{O}_2})(\Delta)$

Boron Isomer	Total energy (Ha)	Excitation Energy (ev)	Oscillator strength (<i>f</i>)	Transition states (% contribution)	C.I.coefficient	Dipole-moment (μ)	Δ (HOMO-LUMO) eV
B6O2-I	-299.5160	3.56	0.0242	H-2→L+0> (67%)	0.57721	0.2779	-6.680
		4.47	0.0115	H-1→L+4> (22%)	0.67857	0.1048	
B6O2-II	-299.5700	4.27	0.3590	H-1→L+0> (60%)	0.54725	3.4263	-6.488
		4.97	0.2048	H-0→L+1> (70%)	-0.38517	2.5566	

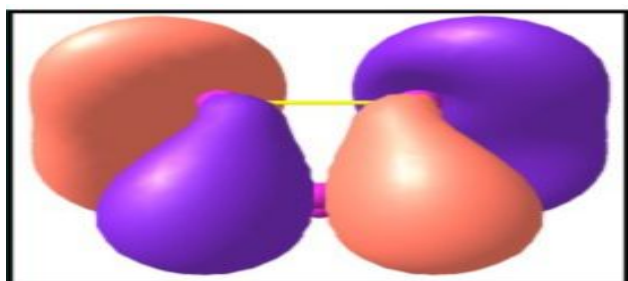


Figure 3: HOMO of B₆O₂-I Cluster

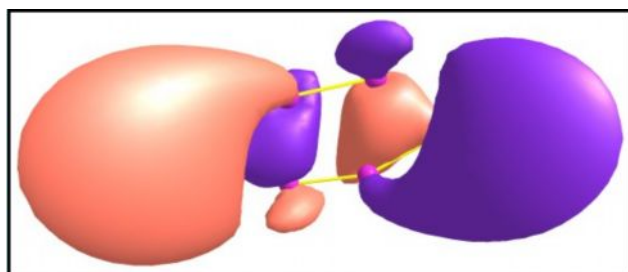


Figure 4: HOMO of B₆O₂-II Cluster

Conclusion

In conclusion, we presented the optical-absorption spectra based on TD-DFT methodology of B₆O₂ isomers to investigate the interaction of O₂. It was found that for both the B₆O₂-I and B₆O₂-II isomers the first resonant peaks occurred corresponding to the molecular transition of |HOMO→LUMO>, with maximum *p* orbital contribution. However, all the spectacular transitions of the spectra occurred in the visible region of

electromagnetic spectrum. In addition to this the HOMO-LUMO gap and excitation energy for the first cluster is found to be greater which signifies it as a more stable candidate for optical transition than the rest one.

References:

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