THz Optical Properties of Graphene Quantum Dot with Transition Metal Adatom - Time Dependent DFT Study

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Mono-layer graphene quantum dots with an attached transition metal adatom were considered for the next generation optical devices [1]. Due to their intriguing tunabilities due depending on their size and the type of adatoms, the graphene quantum dot(GQD) can have wide range of photo luminescence spectra. Their emission frequencies which cover from mid to far infrared, and the device utilizing them can provide a fundamental solution in this spectral region. However, understanding the electron transition behavior between the excitation states from first principles, which is essential to understand the optical responses of the GQD, is a challenging topic since density functional theory is basically aimed to find the ground state solutions. In order to describe energy gap between excited states, the time dependant density functional theory(TD-DFT) has been developed and widely adopted.

In this study, we present a systematically approach to obtain the transition rates between excited state from the TD-DFT study. By carefully investigating to the transition metal graphene quantum dot system in THz region, we examine the applicability of the developed approach to the general optical response problems. We considered three size of GQDs(GQD-4, GQD-12 and GQD-16) and five heavy transition metals (Cr, Mo, W, Pd and Pt). As illustrated in Fig. 1, all of the adhesion metal were optimized with the most stable position (hollow or bridge depending on the elements), at first. As the next step, frontier orbital states including HOMO and LUMO that were mixed into SOC excited states [3],[4] were obtained. Then, Fermi's Golden rule was applied to calculate the transition dipole matrix in order to obtain the life time of triplet sub-levels. The results indicate that structures named GQD-12 are predicted to absorb dominant THz spectra due to the relatively small energy gap between frontier orbitals (Fig. 2). In Fig. 3, absorption peak analysis clearly shows that heavier transition metals interact more strongly. Zero-field spiltting(ZFS) originated from these heavy atoms is considered to lift the degeneracy among triplet-sublevels [5]. Therefore, GQD-12 with both Pt and W have largest peak spectrum.

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[1] X. Hai et al., J. Mater. Chem. B, **vol. 6**, no. 20, pp. 3219–3234 (2018)

[2] P. Adrien Maurice Driac, Proc. R. Soc. A, **vol. 114**, no. 767, pp. 243–265 (1927)

[3] B. De Souza et al., J. Chem. Theory Comput., **vol. 15**, no. 3, pp. 1896–1904 (2019)

[4] F. Neese et al., Wiley Interdiscip. Rev. Comput. Mol. Sci., **vol. 8**, no. 1, pp. 4–9 (2018)

[5] K. Mori et al., Phys. Chem. Chem. Phys., **vol. 16**, no. 28, pp. 14523–14530 (2014)

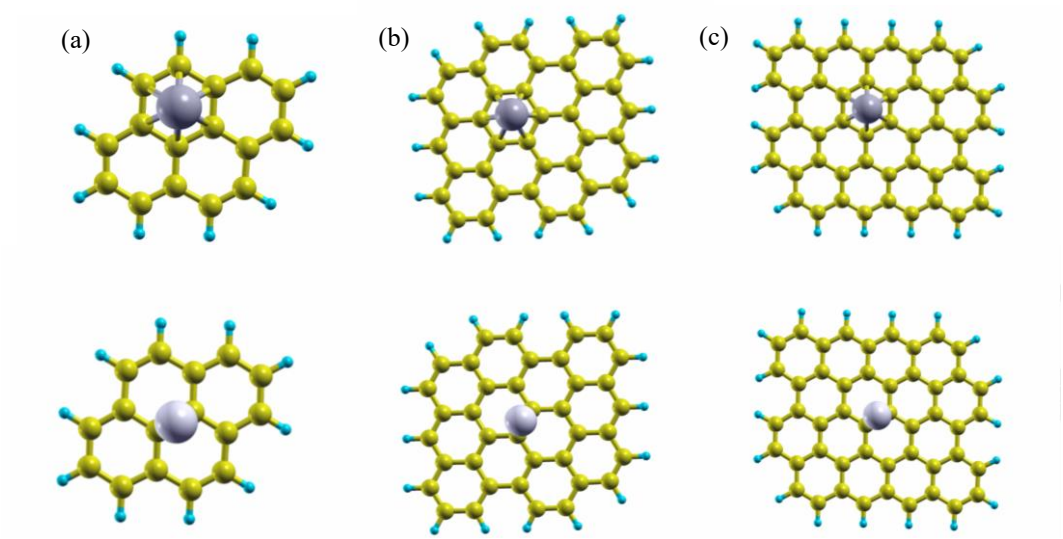

Fig. 1: Hollow and bridge transition metal absorption stie for various GQDs: (a) GQD-4, (b) GQD-12, and (c) GQD-16. All of graphene quantum dots are terminated by hydrogen.

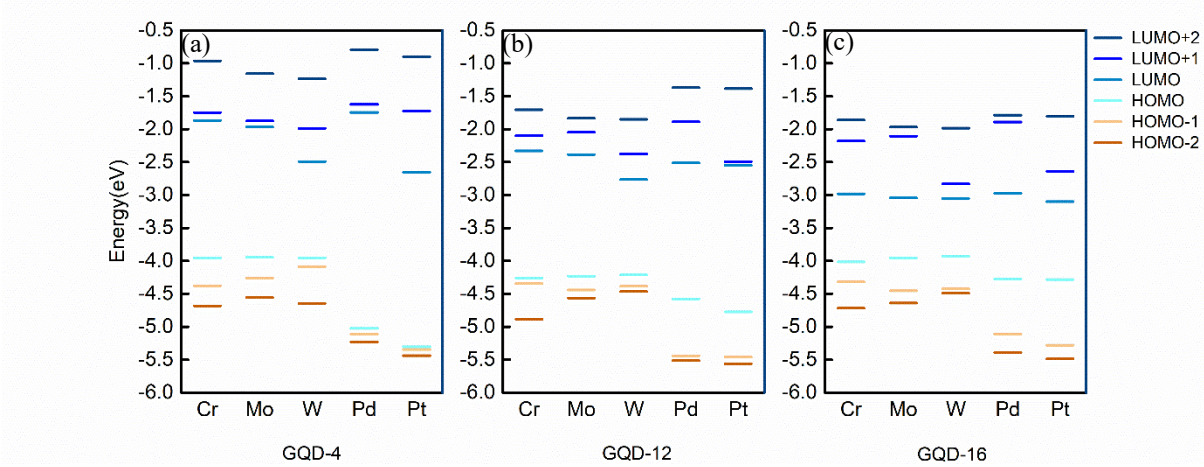

Fig. 2: Frontier molecular orbital analysis for (a) GQD-4, (b) GQD-12 and (c) GQD-16 with five different transition metal. Note that x-axis has no scale but indicate type of metal.

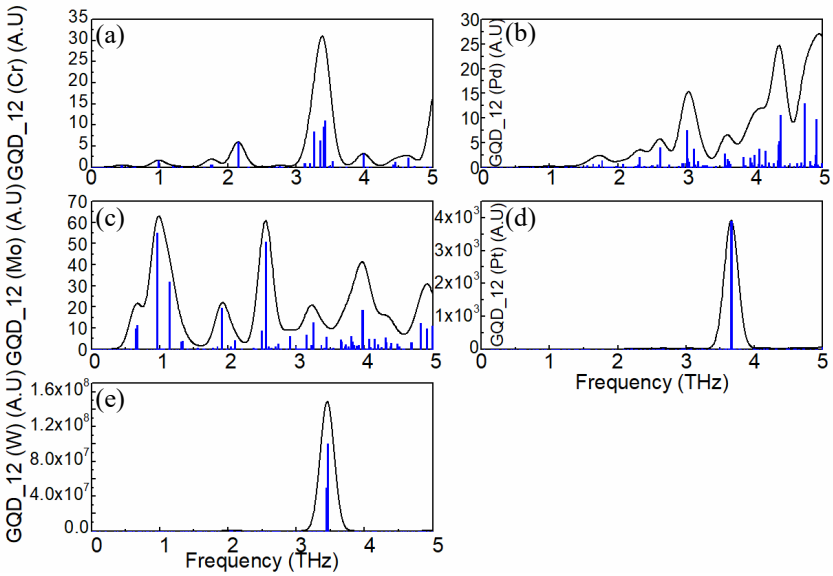

Fig. 3:Optical absorption spectra analysis on (a) Cr-GQD-12, (b) Pd-GQD-12, (c) Mo-GQD-12, (d) Pt-GQD-12 and (e) W-GQD-12 obtained from Fermi's Golden Rule transition rate calculation. The results of five different transition metal are corrected for comparision.