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Analysis of Spectral Properties of Photosynthetic Pigments and Water Molecule with a Method of Quantum Chemistry and its Application to Remote Sensing

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ABSTRACT

In remote sensing, many spectral indices such as NDVI (Normalized Difference Vegetation Index) or NDWI (Normalized Difference Water Index) have been developed for plant management in agriculture. However an essential problem exists that the remote sensing indices are not based theoretically on the spectral properties of the molecules of photosynthetic pigment, nutrient or water in plant. This article presents that spectral properties of the pigments and water were analyzed with a molecular orbital method derived from quantum chemistry and related to remote sensing indices. The electromagnetic wave absorption spectrum calculations for a single molecule of chlorophyll *a*, lutein and water were carried out with semi-empirical molecular orbital method software. The chlorophyll *a* is main photosynthetic pigments in plants and lutein is one of carotenoids served as sub material of the pigments. Water molecule is the solvent in pant cells. Chlorophyll *a* showed two main absorption bands in 360 nm and 600 nm, and lutein in 410 nm. The molecules showed their main absorption bands moved low in a region of 50 nm to 100 nm approximately in comparison with the actual bands *in vitro* measured by a spectrometer. This difference was thought due to a solvent effect. Both molecules are actually surrounded with water, protein and other molecules. The NDVI uses reflectance from a red absorption band around 660 nm and a near-infrared around 860 nm, suggesting that the NDVI dependents strongly on the spectral properties of chlorophyll *a*. Water molecule showed the three main absorption bands in k_1=3,850 cm^{-1} (2,600 nm), k_2=1,750 cm^{-1} (5,700 nm), k_3=4,000 cm^{-1} (2,500 nm), ranging in infrared and caused from the oscillations among the three atoms of H_2O. Those fundamental absorption bands created two characteristic compound absorption bands at red color region around 600 nm and at infrared around 900 nm. For examples, k_1+3k_3 =15,850 cm^{-1} (630 nm) and $2k_1+k_3$=11,700 cm^{-1} (850 nm). The NDWI is defined as the reflectance ratio of (860 nm - 1,240 nm) / (860 nm + 1,240 nm), implying a relationship with the characteristic compound absorption band in 850 nm of water molecule.

Keywords: Chlorophyll *a*, Lutein, Molecular orbital method, Remote sensing index, Spectral property, Water, Japan

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1. INTRODUCTION

Satellite or aircraft remote sensing has been widely explored as a tool for detection and mapping of geological or biological resources in the earth (Tucker and Sellers, 1986; Omasa *et al.*, 2000). In agricultural area, a close range remote sensing based on the plat station such as an unmanned helicopter or a tractor is advancing apace for management of water, nutrients, yield and diseases in crops (Sugiura *et al.*, 2005; Suzuki *et al.*, 2008). Many spectral indices such as NDVI (Normalized Difference Vegetation Index) or NDWI (Normalized Difference Water Index) in remote sensing have been used for crop management.

However an essential problem exists that the remote sensing index is not based theoretically on the spectral properties of the molecules of photosynthetic pigments, nutrients or water in plant. We can be aware of many colors in daylight, which are electromagnetic waves emitted, scattered or transmitted from the molecules of surrounding materials. If we know the exact spectral properties of the molecules of the pigments, nutrients or water in plant cells, the existing remote sensing indices will be revaluated and new indices can be expected.

In plant physiology or biochemistry, more than 50 kinds of chlorophylls and bacteriochlorophylls have been founded and their spectral properties were analyzed by experimental or theoretical methods (e.g. Sheer, 2006; Mimuro *et al.*, 2011). In quantum chemistry, the spectral property of chlorophyll *a* was analyzed by Sundoholm (2000) and Suendo and Viridi (2012). However those articles did not mentioned on the subject of remote sensing index. In addition, an immediate progress in processing power of a personal computer can allow us to analyze the structure and function of chlorophylls or other molecules in life science (Hirayama, 2002).

This article presents that spectral properties of the pigments and water molecule with a molecular orbital method derived from quantum chemistry were analyzed and related to remote sensing indices.

2. MATERIALS AND METHODS

2.1 Experimental Molecules

As experimental molecules in plants, chlorophyll *a*, lutein and water were selected and analyzed, shown in Figure 1. The chlorophyll *a* is main photosynthetic pigments in plants as well as in phototrophic bacteria, and the lutein is one of carotenoids served as sub material of the pigments in plants. Water molecule is the solvent. The 3-D geometric coordinates of them were obtained from a database (Honma and Kawabata, 1999).

Chlorophyll *a* ($C_{55}H_{72}O_5N_4Mg$) has a molar mass of 893.5 g mol^{-1} and 137 in atoms, which is composed of two parts, porphyrin and phytol. Porphyrin is composed of tetra pyrrols,

including nitrogen (N) and ringing in double bond. At the center of the porphyrin, a magnesium ion (Mg^{2+}) is located. Phytol is a long chain, connected with the porphyrin. Lutein ($C_{40}H_{56}O_2$) has a molar mass of 568.9 g mol^{-1} and a polyene chain, containing double bonds. To human eyes, chlorophyll *a* shows green and lutein yellow. Water molecule (H_2O) contains one oxygen (O) and two hydrogen (H) atoms connected by covalent bonds.

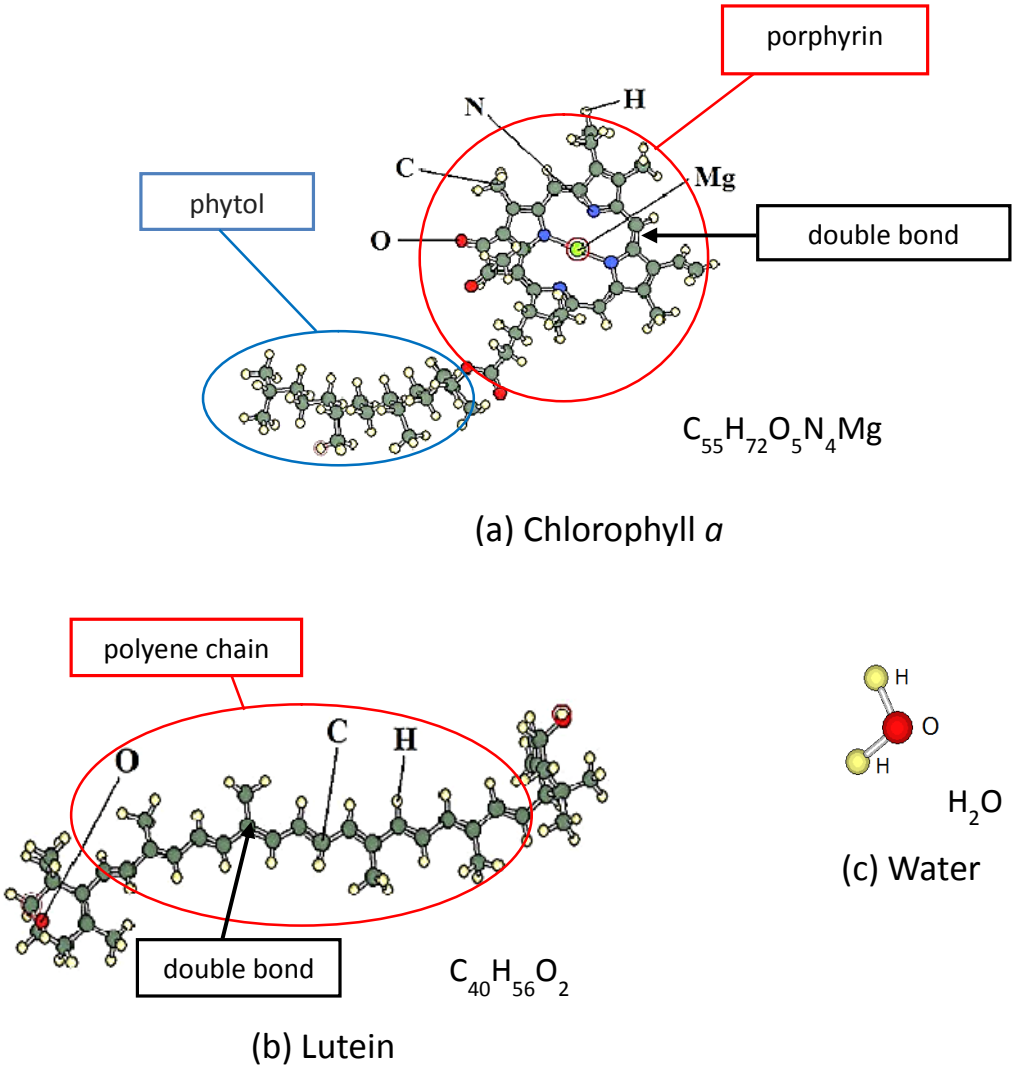

Figure 1. Three experimental molecules, (a) chlorophyll *a*, (b) lutein, (c) water.

2.2 Computation Methods

1) Fundamental Equation

For analyzing the spectral property of a molecule, the time-independent Schrödinger equation was applied as bellows. This equation is an eigenvalue equation.

$$H\Psi=E\Psi$$

Where, H is Hamiltonian operator, means the total energy of kinetic and potential for the atoms and electrons of a molecule. Ψ is a wave function, and E an eigenvalue. Since the equation is very complex, it can be dissolved with an approximation method such as MO (Molecular Orbital) method combined with a computer (Yonezawa et al., 1983). Thus the vibration of the atoms and electrons of the molecule determines the spectral properties and their energy.

2) Software and Computer

In molecular computation, we applied a software of MOPAC2012 (Stewart, 2012) combined with a support software of Winmostar (ver. 4.0; Senda, 2006). MOPAC2012 is one of semi-empirical quantum chemistry methods, easy handling and quick calculating. Winmostar is an input and output data support system of molecular computation and it serves for the calculation of the exited state of a molecule with methods of COND/S (Complete Neglect of Differential Overlap/Spectroscopic) and CI (Configuration Interaction). As hardware, we used a PC server (TX100 S3, Fujitsu, Japan). The server is operated by Windows Server 2008 R2 and installed of 64-bit CPU (Xeon E3-1220, Intel, USA; 4 Cores, 3.10 GHz), 500 GB HDD and 20 GB RAM.

3) Computation Procedures

We computed the spectral property of a molecule to accord with following procedures.

(1) An optimal structure of the molecule, where keeps the minimal energy state or the ground state.
(2) Ultraviolet-Visible (UV-VIS) spectra, where the electrons of the molecule are excited when receive light energy or photons.
(3) Infrared (IR) spectra, where the atoms of the molecule keep harmonic vibrations due to thermal motion.

3. RESULTS AND DISCUSSION

3.1 UV-VIS Spectra of Chlorophyll *a* and Lutein

After computation of optimal structures of the molecules of chlorophyll *a*, lutein and chlorophyll *a* (non-Mg) with MOPAC2012, Ultraviolet-Visible (UV-VIS) spectra of them were given in Figure 2. At the computation of UV-VIS spectra of them, methods of COND/S and CI (Yonezawa *et al.*, 1983) were applied with Winmostar. In addition, we examined a case of the absence of Mg in chlorophyll *a* with Winmostar.

Chlorophyll *a* showed two peaks of spectrum at 360 nm and 605 nm, those were equivalent to UV and Yellow-Red color regions, respectively. Lutein, sub pigment in plants, showed a large peak of spectrum at 410 nm (Blue color region). The actual

absorption peaks of the molecules that the chlorophyll *a in vitro* at from 400 nm to 450 nm in Violet-Blue color region and from 610 nm to 660 nm in Red color region, and that of lutein at 440 nm to 470 nm, Violet-Blue color region (Nobel, 2009). Despite the actual data shows a broad range of absorption peaks, the simulated peaks for the chlorophyll *a* and lutein showed their peaks shifted to short wave side in approximately 50 nm to 100 nm. The simulations were done in two assumptions that the molecules were located in vacuum and their nuclei were fixed in a certain configuration, the later called the Born–Oppenheimer approximation (Yonezawa et al., 1983). The molecules are actually surrounded with water, protein and other molecules at an ambient temperature. The differences were thought due to a solvent effect as well as a nucleic vibration effect. The NDVI uses the reflectance from a red absorption band around 660 nm and a near-infrared around 860 nm, suggesting that the NDVI dependents strongly on the spectral properties of chlorophyll *a*.

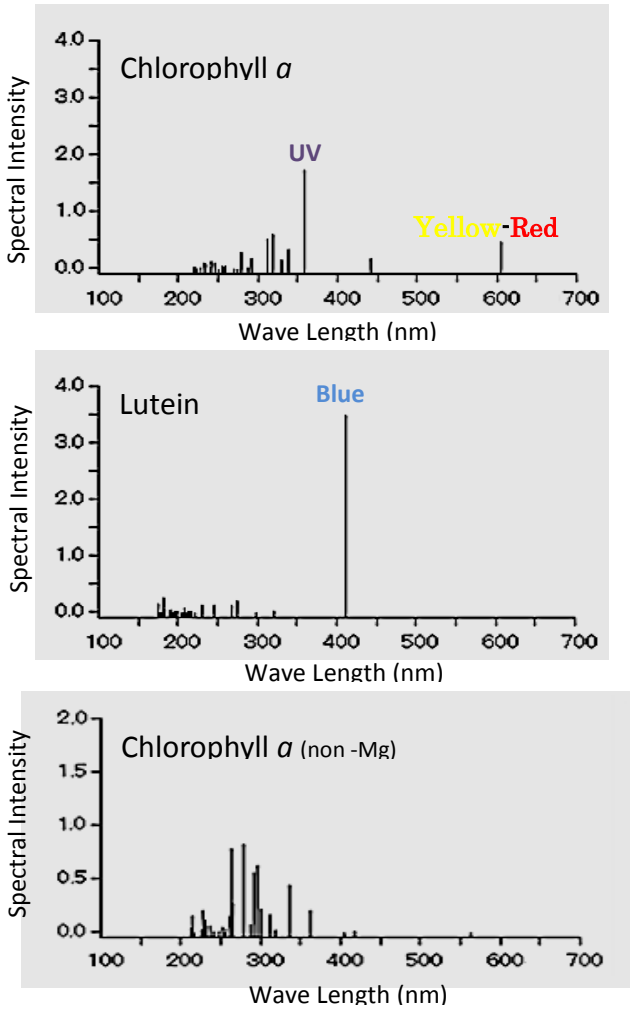

Figure 2. UV-VIS spectra of chlorophyll *a*, lutein and chlorophyll *a* (non-Mg).

In the absence of magnesium ion (Mg^{2+}) in chlorophyll *a*, the absorption peak at Red color region was disappeared and the UV peak intensity at 360 nm was decreased. This implies that Mg^{2+} play an important role in absorption of the light energy at a Red color region.

3.2 IR Spectra of Water Molecule

After computation of optical structures of water molecule with MOPACK2012, infrared (IR) absorption bands were computed and shown in Figure 3.Water molecule showed the three main absorption bands in k_1=3,850 cm^{-1} (2,600 nm), k_2=1,750 cm^{-1} (5,700 nm), k_3=4,000 cm^{-1} (2,500 nm), ranging at an infrared region and caused from the oscillations among the three atoms of H_2O, as shown with three illustrations of water molecule with arrows. The arrow depicts a direction of oscillations.

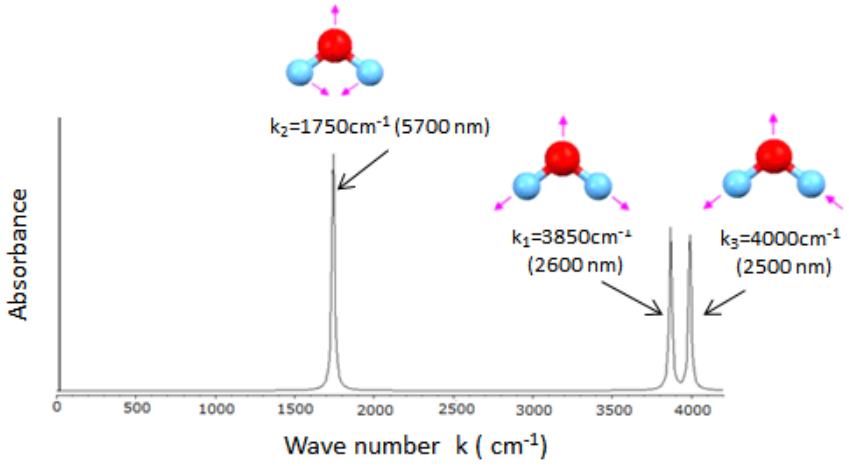

Figure 3. IR absorption bands of water molecule.

The three fundamental absorption bands created two characteristic compound absorption bands at red color region around 600 nm and at infrared around 900 nm as shown in Table 1. For examples, k_1+3k_3 =15,850 cm^{-1} (630 nm), shown in the red square, and $2k_1+k_3$=11,700 cm^{-1} (850 nm), shown in the blue square. The compound absorption bands are called as “overtone”, similar to sound phenomena (Ozaki *et al.*, 1996).

The NDWI is defined as the reflectance ratio of (860 nm - 1,240 nm) / (860 nm + 1,240 nm), implying a relationship with the characteristic compound absorption band in 850 nm of water molecule. Figure 4 showed the changes of the reflectance of solar radiation on orchard grass cut and laid on a table, where moisture content of the grass was varied at 83%, 72% and 65%. At a range of 800 nm to 900 nm, the change of reflectance between the grasses 1 to 3 was great, as shown in the blue circle. At a range of 500 nm to 600 nm, a small change was observed, as shown in the red circle. These changes were thought due to an overtone effect.

Table 1. Overtone of water molecule

Fundamental (k_1,k_2,k_3) & Overtone	Wave number k (cm^{-1}) (Wave length, nm)
k_1	3850 (2600)
k_2	1750 (5700)
k_3	4000 (2500)
$3k_1+k_3$	15550 (640)
k_1+3k_3	15850 (630)
$3k_1+k_2+k_3$	17300 (580)
$k_1+k_2+3k_3$	17600 (570)
$3k_3+2k_2+k_1$	19350 (520)
$2k_1+k_3$	11700 (850)

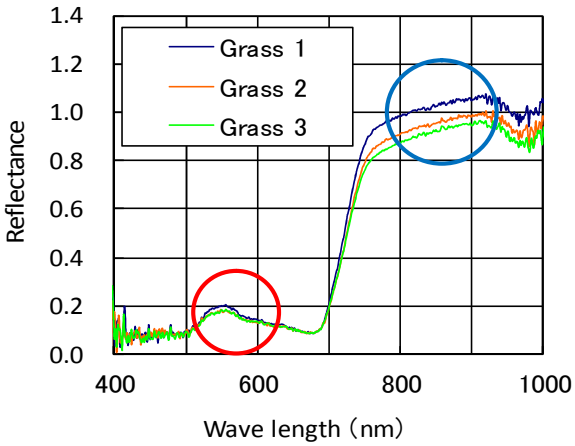

Figure 4. Changes of the reflectance of solar radiation on grass cut, where moisture content was varied at 1=83%, 2=72% and 3=65%.

4. CONCLUSION

This article presents that spectral properties of the pigments and water molecule with a molecular orbital method derived from quantum chemistry were analyzed and related to remote sensing indices. The results are as follows.

- Chlorophyll *a* showed two main absorption bands in 360 nm and 600 nm, and lutein in 410 nm.
- Their main absorption bands moved to shortwave side in a region of 50 nm to 100 nm approximately in comparison with the actual bands *in vitro*.
- Water molecule showed the three fundamental absorption bands.
- The fundamental absorption bands created two characteristic compound absorption bands at red around 600 nm and at infrared around 900 nm.

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