氏　　名	PONSECA Carlito Jr.
学位（専攻分野）	博士（理学）
学 位 記 番 号	総研大甲第1120号
学位授与の日付	平成２０年３月１９日
学位授与の要件	物理科学研究科　機能分子科学専攻 学位規則第６条第１項該当
学位論文題目	Development of Integrated Optics for the first Principle Analysis of the terahertz Spectrum of Some Biomolecules
論文審査委員	主　査　教授　大森　賢治 准教授　繁政　英治 准教授　米満　賢治 准教授　中村　敏和 教授　横谷　篤至(宮崎大学) 教授　猿倉　信彦(大阪大学)

論文内容の要旨

In this thesis the development of an integrated optics for the first principle analysis of terahertz (THz) spectrum of selected biomolecules is presented. Two designs of THz waveguides were characterized and two biomolecules were studied. In each of the works, THz spectra were obtained both experimentally and by using theoretical calculation models in order to complement each other's veracity.

Planar photonic crystal waveguide (PPCW), a sheet-like polymer-based material with high transparency from the deep ultraviolet to the far infrared regime, was investigated in the THz region. Frequency-selective characteristic of the PPCW was revealed and found to have center frequency about 0.45 THz. At a length of 30 mm, single mode propagation was achieved. The calculation using finite difference time domain (FDTD) method was also implemented and used to compare to the experimental results. Relative agreement between the experimental data and theoretical calculation was attained. The coupling loss was estimated to be 1.2 dB while the broadband propagation loss value of 3.6 dB/cm.

The transmission of THz radiation using microstructured polymer optical fiber was also analyzed. The time domain reference signal showed a single pulse while that of the fibers manifested two pulses, with the second pulse delayed by about 20 ps with respect to the first pulse. The first pulse is attributed to the THz wave that propagated through the hollow core while the second signal is surmised as the component of the THz wave that propagated in the microstructured. The snapshots of the FDTD simulation show that such delay is present as the THz wave is propagating through the fiber. When the frequency spectra of the fibers were plotted, a shift in the central frequency was observed. The experimental transmission band is 0.8 – 1.4 THz for fiber 1 and 1.0 – 1.6 THz for fiber 2; its width is approximately 50% of the centre frequency. FDTD calculation also showed this shift in the frequency bands but its center frequency is different to that of the experiment, which was surmised to be due to the elliptical microstructured cladding of the fibers while circular cladding were used in the calculation. These fibres were also reported to guide in the visible and infrared by the photonic bandgap mechanism, and a theoretical investigation of the photonic bandgaps of such fibres were reported for visible and telecommunications wavelengths. Propagation losses were estimated to be as low as 0.9 dB/cm using the same method in obtaining the losses of PPCW.

Far infrared spectra of naphthalene and 1,4-dihydroxynaphthalene (1,4-naphthol), which exhibits estrogenic like activity and potentially mimic natural hormones, were measured in the region from 0.5 to 6.3 THz at 4 K and room temperature using a GaP THz wave generator. Quantum chemical calculations were also performed to obtain normal mode coordinates and frequencies for an isolated molecule and unit cell case using density functional theory (DFT). A shift in the absorption peaks in the 4 K spectra of naphthalene and 1,4-naphthol with respect its

room temperature spectra were observed. This is related to the temperature dependence of sample density and average hydrogen-bond strength, as well as anharmonic distribution of vibrational states. Correlation field splitting was also observed in the low temperature spectra that originated from the dipole-dipole coupling between the molecules that split the intramolecular vibrational modes in the crystal. Another origin of the splitting is deduced to be due to changing of vibrational motions of between two pairs of 1,4-naphthol brought about by their orientation in the unit cell. Density functional theory (DFT) calculations for both the isolated molecule and unit cell models predicted the shift in the absorption peaks of the experimental spectra brought about by the presence of the hydroxyl group. Normal modes were also assigned which are both the intra- and intermolecular interaction.

Retinal isomers, 9-*cis*, 13-*cis*, and all-*trans*, which are chromophores found in vertebrates, are investigated from 0.5-6.5 THz in the low temperature environment. Shift in absorption peaks were observed. Such changes were attributed to changes in the intramolecular interaction of each retinal isomer near the ground state condition. DFT calculations showed that the modes are dominated by intramolecular interaction and supported the assertion that shifts in the absorption peaks are due to the changes in the intramolecular interaction of each retinal isomer.

This work showed first principles analysis of selected biomolecules and the development of integrated optics with low losses in the THz. However, there are still challenges that are needed to be address before fully functional THz optic devices are realized for biomolecular applications. First, though the presented THz waveguides here are so far has the lowest reported loss in their class, its design and flexibility is yet to be optimized. Second, since vibrations in this region correspond to collective motions of large portions of the molecules with considerably large moving masses and weak potential forces, its spectra is rather complicated and its vibrational mode is difficult to assign. Single molecule or unit cell model are not sufficient to accurately predict these parameters and periodic boundary condition is therefore needed.

論文の審査結果の要旨

本論文は、”Development of Integrated Optics for the first Principle Analysis of the terahertz Spectrum of Some Biomolecules”と題し、7章から構成されている。

第1章『Introduction』では、研究の背景について述べた後に、本論文では生物分子のTHzスペクトル解析のための新たなオプティクスを開発し、そこで用いた導波管の特性を調べるとともに、いくつかの重要な生物分子のTHzスペクトルを測定すること、およびその意義について述べている。また、得られたTHzスペクトルの正確さを検証するため理論との比較を行うと述べている。

第2章『Experimental Techniques used for THz spectroscopy』では、本研究で用いたTHz time domain transmission spectroscopy (TDTS)というTHz分光法について述べている。

第3章『CYTOP planar THz waveguide: A highly transparent plastic for hybrid optics applications』では、本論文で用いたPlanar photonic crystal waveguide (PPCW)について述べている。導波管を薄いシート状にした場合に低伝搬損失および低結合損失を達成したと述べている。また、PPCW透過スペクトルから周波数選択性があることを明らかにし、その理由にも言及している。さらに、finite-difference time-domain (FDTD)シミュレーションによってPPCWがシングルモードで十分長い伝搬距離を持つことを示し、このことは実験的にも確かめられたと述べている。一方、CYTOPは幅広い周波数領域で高い透過性を示すので、光学系の設計において潜在的な利用性を有していると述べている。以上から、本論文がCYTOPから製造されたPPCWの実用可能性を示したと述べている。

第4章『Transmission of THz radiation using microstructured polymer optical fiber』では、本論文で用いたもう一つの導波管であるmicrostructured polymer optical fiber (mPOF)について述べている。このmPOFにTHz波を通しその伝搬を調べた結果、THzスペクトルに透過帯が観測されたが、これはバンドギャップの存在から予想される結果と一致すると述べている。また、FDTDシミュレーションの結果、透過帯に一部シフトが見られるものの実験結果が再現されたと述べている。

第5章『Experimental and calculated THz spectra of naphthalene and 1,4-dihydroxynaphthalene in the 0.5 - 6.0 THz region』では、0.5から6.3 THzにおけるナフタレンと1、4-ナフトールの吸収スペクトルを室温と4 Kで測定した結果について述べている。4Kでは室温と比較して吸収ピークが高端数側へ移動し、線幅にも変化が見られ、さらにダブレットピークが観測されたと述べている。単一分子と単位セルについて行ったDensity Functional Theory (DFT)計算によるスペクトルと実測されたスペクトルを比較することによって、分子内・分子間相互作用の識別を行い、分子内相互作用については、OH結合の存在による分子内相互作用の強度の違いが吸収のピークシフトとして表れることを実験結果とDFT計算の結果の両方から示したと述べている。一方、分子間相互作用については、DFT計算と実験ではピークの周波数がシフトしており、これは、シミュレーションに用いたモデルが十分な精度ではないためであると述べている。

第6章『Vibrational analysis of all-trans, 13-cis, and 9-cis retinal isomers in the 0.45 to 5.50 THz region』ではレチナールの異性体が固有の吸収スペクトルを示すことを述べている。吸収のピークシフトは分子内相互作用で説明でき、DFT計算からも同様の異性

体間のピークシフトが得られたと述べている。

第7章『Conclusion and Recommendation』では、本研究で得られた結果をまとめ、今後の課題について述べている。

以上を要するに、本研究は初めて生体分子のテラヘルツスペクトルの第一原理解析を示し、そのスペクトルを測定するためのTHzオプティクスを開発したものであり、理学上貢献するところが大である。よって、本論文は博士(理学)の学位論文として十分に価値のあるものと認める。