TERAHERTZ SPECTROSCOPY OF FREON SUBSTITUTE REFRIGERANT AND MOLECULAR VIBRATION ANALYSIS

Yukinari Hirai*, Ryo Saito, Tatsuya Ishizuka**, Satoshi Matsumoto***
***Graduate School of Engineering and Science, Shibaura Institute of Technology**
****Department of Electrical Engineering, Shibaura Institute of Technology**
Email Address: ma14090@shibaura-it.ac.jp

ABSTRACT

Terahertz spectroscopy has recently been applied in many research fields. The terahertz band is located between light and radio waves and it combines the characteristics of both. It allows an easy observation both of interactions between molecules and vibrations of large molecules. Research purpose of this study is to contribute the expansion of terahertz database and development of terahertz technology, by measuring the refrigerant by the terahertz light. In this study, we tried measuring spectrum about fluorine-based hydrofluoroether using a terahertz spectrometer. In addition, we analyzed the vibration of the molecule by molecular orbital analysis software (Winmostar™ or MOPAC). We tried to observe the interaction between the vibration of the molecule by the combination of the molecular orbital analysis software technology and spectrum measured in terahertz beam. From the experiment are that we succeeded in observing the new spectrum which was not possible to detect by infrared spectroscopy and detecting the natural vibration modes of the molecules in the terahertz band. Therefore, terahertz spectroscopy was found to be effective to material discrimination and diagnosis for fluorine-based refrigerants.

1. INTRODUCTION

"CFC emissions Law" was amended in April 2015. Accordingly, comprehensive measures of the entire life cycle leading to the disposal from the production of CFCs were built [1]. Since then, the importance of the simple inspection and periodic inspection is increasing. As a new diagnostic technique of refrigerant, terahertz light is expected. Furthermore observing the state of the refrigerant in the terahertz light has been found to be effective [2-4].

In this study, we have measured the terahertz transmittance spectrum of Novec™ 7100 and 7200 [5]. This samples has a much lower global warming potential (GWP) compared to other HFC or PFC. In addition; there is no possibility of the ozone layer destruction [5]. Therefore, it is possible to suppress the burden on the environment. Terahertz light is located on the lower energy bands than infrared; this light can be observed electromagnetic wave absorption spectrum by vibration and intermolecular interactions of large molecules [5-7]. In order to help the development of a new refrigerant diagnostic technology and terahertz technology, we measured the hydrofluoroether. Besides, we tried to capture a group vibration of molecules in the terahertz band using molecular orbital method [8] in order to expansion of terahertz database and to get the basic physical data.

2. EXPERIMENAL METHOD

2.1 Spectrophotometer

Figure 1 shows THz Spectrophotometer. Fourier Transform Terahertz Spectroscopy was used to measure the transmittance spectrum of samples in the range between 100 cm^{-1} and 600 cm^{-1}. Measurements were repeated 64 times with a resolution of 2.0 cm^{-1}. (1THz = 33.3 cm^{-1})

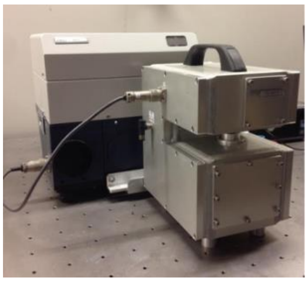


Fig. 1 THz Spectrophotometer (JASCO type VIR-F)

2.2 Measuring Cell

Figure 2 shows Measuring Cell. The samples were placed in a polyethylene (PE) cell. The thickness of the PE plate was 1mm and the sample thickness was 0.6mm.

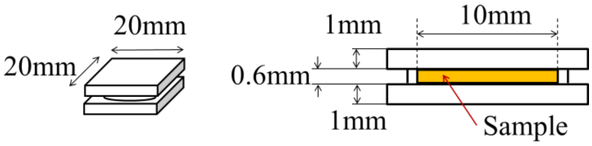


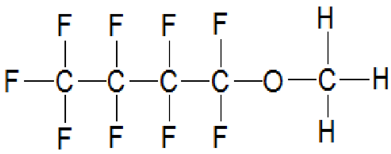
Fig. 2 Measuring Cell

2.3 Molecular vibration analysis

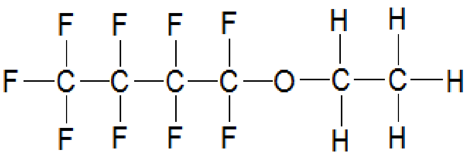
Molecular vibrations were analyzed using the molecular orbital analysis software (Winmostar™) and Semi-empirical molecular orbital method calculation software (MOPAC).

3. SAMPLES

Figure3 shows the molecule structures of samples. Samples are Novec™7100 and Novec™7200 manufactured by 3M Japan LTD. These samples have a feature excellent thermal and chemical stability. Table 1 shows the samples specification.



(a) Novec™ 7100



(b) Novec™ 7200

Fig. 3 Molecule structures of samples [5]

Table 1 Samples Specification

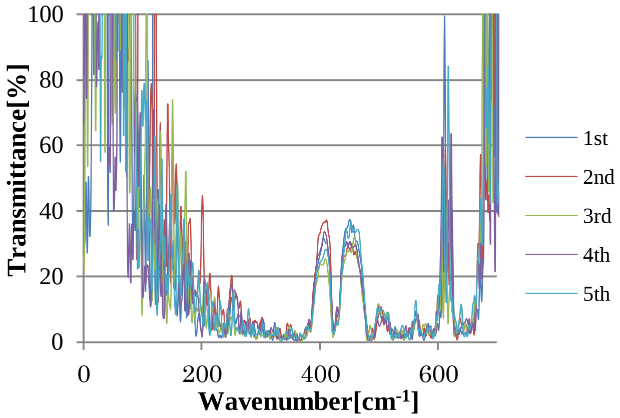
Sample name	Novec™ 7100	Novec™ 7200
Boiling point [℃]	61	76
Density [kg/m^3]	1,520	1,430
Absolute viscosity [Pa・s]	5.8×10^{-4}	5.8×10^{-4}
Flash point	-	-
Surface tension [mN/m]	13.6	13.6
Permittivity [1kHz]	7.52	7.35
Solubility of water [ppm(Wt.)]	95	92
Ozone Depletion Potential (ODP)	0	0
Global Warming Potential (GWP)	297	59

4. RESULTS

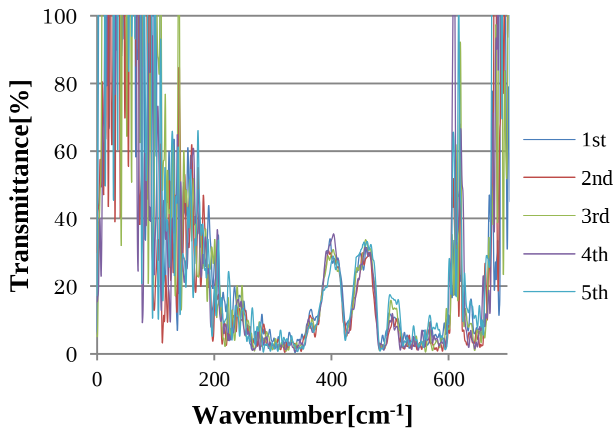
4.1 Transmittance Spectrum

Figure 4 shows transmittance spectrum of samples. Samples were measured five times. Novec™ 7100 and Novec™ 7200 have been observed a specific spectrum. Transmittance of Novec™ 7100 decreased characteristically at the wavenumber of 427 cm^{-1} and 479 cm^{-1} respectively. It indicates that terahertz light was absorbed by molecular vibration at the wavenumber of 427 cm^{-1} and 479 cm^{-1}. In the same way, transmittance of Novec™ 7200 decreased characteristically at the wavenumber of 428 cm^{-1} and 491 cm^{-1}.

From these results, it was found that samples has inherent vibration peak.



(a) Novec™ 7100

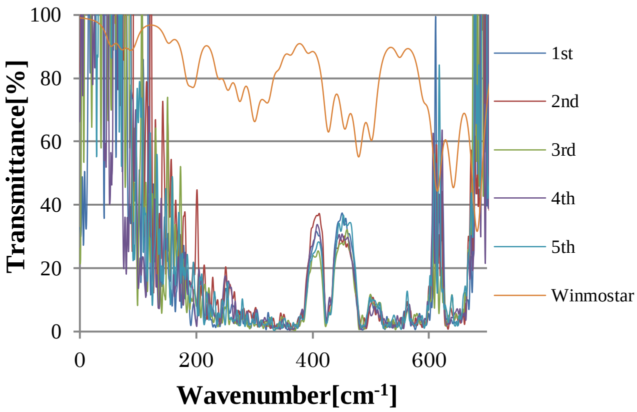


(b) Novec™ 7200

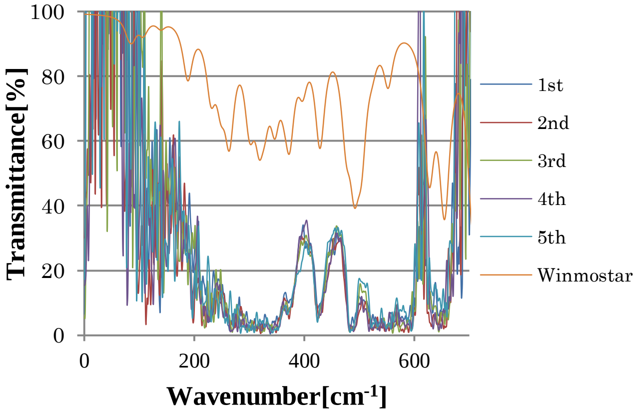
Fig. 4 Transmittance spectrum of samples

4.2 Comparison of the measurement value and analysis value

Analysis values were calculated by using the molecular orbital analysis software (Winmostar™). Figure 5 shows comparison of the measurement value and analysis value. Transmittance of Novec™ 7100 is difference, but the inherent vibration peak at the wavenumber of 427 cm^{-1} and 479 cm^{-1} are consistent. Similarly, the inherent vibration peak of Novec™ 7200 is consistent at the wavenumber of 428 cm^{-1} and 491 cm^{-1}.



(a) Novec™ 7100



(b) Novec™ 7200

Fig.5 Comparison of the measurement value and analysis value

4.3 Molecular orbital analysis

Figure 6 shows molecule structures of Novec™ 7100. Vibration mode was simulated based on this structure. Table 2 and 3 show vibration analysis results by MOPAC. When the value of RADIAL is low, it represents the bending vibration. By contrast, if the value of RADIAL is high, it represents the stretching vibration. Table 2 shows vibration analysis result of wavenumber of 427 cm^{-1}. It is revealed that bending vibration of F4 and F5 occurred at the wavenumber of 427 cm^{-1}. In the same way, Table 3 shows vibration analysis result of wavenumber of 479 cm^{-1}. It is revealed that bending vibration of C3 and C8 occurred at the wavenumber of 479 cm^{-1}.

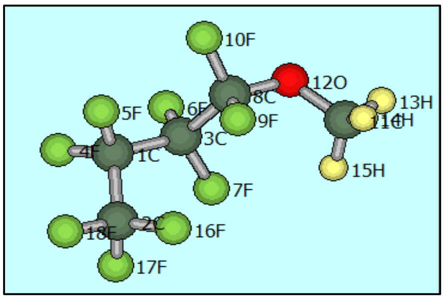


Fig. 6 Molecule structures of Novec™ 7100

Table 2 Vibration analysis result of 427cm^{-1}

		ATOM PAIR	ENERGY CONTRIBUTION	RADIAL
VIBRATION	18			
FREQ.	426.90	F 4 -- F 5	18.3% (102.2%)	2.5%
T-DIPOLE	.9918	C 1 -- C 2	16.0%	.3%
TRAVEL	.0914	C 1 -- C 3	15.1%	8.7%
RED. MASS	9.4435	C 1 -- F 5	11.7%	5.7%
		C 1 -- F 4	11.3%	12.4%

Table 3 Vibration analysis result of 479cm^{-1}

		ATOM PAIR	ENERGY CONTRIBUTION	RADIAL
VIBRATION	20			
FREQ.	479.07	C 3 -- C 8	14.0% (92.9%)	1.5%
T-DIPOLE	1.1800	C 8 -- F10	11.7%	.0%
TRAVEL	.0881	F10 -- O12	11.1%	30.9%
RED. MASS	9.0577	C11 -- O12	10.6%	.7%

Figure 7 shows molecule structures of Novec™ 7200. Table 4 shows vibration analysis result of wavenumber of 428 cm^{-1}. Bending vibration of F4 and F5 occurred at the wavenumber of 428 cm^{-1}. Vibration mode is very similar to the case of 427 cm^{-1}; therefore, in this frequency band, it was found that the group vibration centered on F4 and F5 is occurred. Table 5 shows vibration analysis result of wavenumber of 491 cm^{-1}. It is revealed that bending vibration of C8 and C10 occurred at the wavenumber of 491 cm^{-1}.

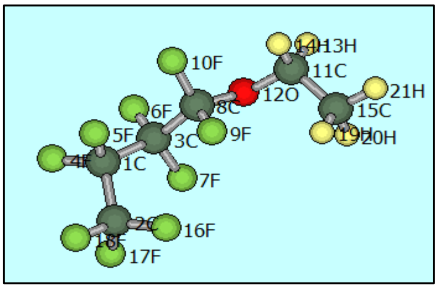


Fig. 7 molecule structures of Novec™ 7200

Table 4 Vibration analysis result of 428cm^{-1}

		ATOM PAIR	ENERGY CONTRIBUTION	RADIAL
VIBRATION	20			
FREQ.	428.18	F 4 -- F 5	17.8% (102.4%)	1.8%
T-DIPOLE	.8401	C 1 -- C 2	15.6%	.9%
TRAVEL	.0912	C 1 -- C 3	14.6%	7.4%
RED. MASS	9.4760	C 1 -- F 5	11.2%	6.1%
		C 1 -- F 4	11.1%	11.4%

Table 5 Vibration analysis result of 491cm^{-1}

		ATOM PAIR	ENERGY CONTRIBUTION	RADIAL
VIBRATION	22			
FREQ.	491.07	C 8 -- F10	11.6% (77.1%)	.0%
T-DIPOLE	1.0919	C 3 -- C 8	11.2%	9.5%
TRAVEL	.0876	F 9 -- F10	11.0%	96.1%
RED. MASS	8.9359	C 8 -- O12	9.8%	51.0%

5. CONCLUSION

This paper represents the results of terahertz spectrum measurements of hydrofluoroether (Novec$^{\mathrm{TM}}$ 7100, and Novec$^{\mathrm{TM}}$ 7200). Additionally, group vibration was analyzed by molecular orbital method based on the results of terahertz spectrum measurement. As a result of the measurement and analysis, the properties of the spectra are as follows;

(i) By this measurements, it was possible to obtain a spectrum of the terahertz band of the hydrofluoroether.

(ii) By using the measurement results and molecular vibrations analysis, it found to detect the group vibration of hydrofluoroether at the wavenumber of 427 cm^{-1} and 479~491 cm^{-1}.

(iii) It was possible to know the validity of the terahertz spectrometry by comparing the measurement results and analysis results.

Those measurement results will contribute to a better understanding of THz research.

6. REFERENCES

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Yukinari Hirai received the B. Eng. in the Department of Electrical Engineering from Shibaura Institute of Technology. He is currently pursuing his M. Eng. degree in the same institute.

Ryo Saito is currently pursuing his B. Eng. Degree in Shibaura Institute of Technology.

Tatsuya Ishizuka is currently pursuing his B. Eng. Degree in Shibaura Institute of Technology.

Satoshi Matsumoto received the M. Eng. and Dr. degrees in electrical engineering from the University of Tokyo in 1981 and 1984, respectively. In 1984, he joined Toshiba Corporation. He has been a Professor in the Department of Electrical Engineering of Shibaura Institute of Technology since 2007. He is a Senior Member of IEEE and IEEJ.