

Terahertz vibrational spectra of metallocene

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Abstract

The terahertz transmission spectra of crystalline metallocenes and decamethyl metallocene were clearly measured in the range of 0.7–6.2 THz by a recently developed GaP Raman terahertz spectrometer. The low-frequency mode of ring–metal–ring bending and CH₃ out-of-plane oscillation were observed, and the force constants of bending were estimated from the absorption frequencies based on a three-body model.

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1. Introduction

Structural investigations have been conducted since Wilkinson et al. first suggested the sandwich-like structure of ferrocene [bis(cyclopentadienyl)iron, Cp₂Fe] over 50 years ago [1]. X-ray analyses using projection methods by Fischer and Pfab [2], Eiland and Pepinsky [3], and Dunitz and Orgel [4] corroborated the validity of the suggestion, and a 3-D X-ray structure analysis by Dunitz et al. [5] provided a more precise description of the unusual structure.

The vibrational spectra of Cp₂Fe have also been widely studied using FT-IR and Raman spectroscopy. The first systematic study of Cp₂Fe was published by Lippincott and Nelson [6], who measured the infrared spectra of Cp₂Fe in solution and the vapor phase in the range of 400–3500 cm⁻¹ (12–106 THz). It is easy to calculate the frequencies of vibrational modes such as symmetric and anti-symmetric stretching and bending of linear X–Y–X molecules, which can be solved as three-body problems. In the same way, the frequencies of the vibrational mode of a metallocene Cp–M–Cp molecule (where Cp is a ring ligand and M is a metal atom) can be approximately calculated. It was noted that the bending vibration ω_{22} in CO₂

and CS₂ had a frequency that was roughly half the frequency for symmetric X–Y stretching ω_4 . On that basis, Lippincott and Nelson estimated that the bending mode of Cp₂Fe was in the neighborhood of 150 cm⁻¹. They assigned the 170 cm⁻¹ absorption band (cited as a private communication without a spectrum) to ω_{22} . Further, they calculated ω_{22} for ruthenocene [bis(cyclopentadienyl)ruthenium, Cp₂Ru] and nickelocene [bis(cyclopentadienyl)nickel, Cp₂Ni] with the aid of the ratio ω_4/ω_{22} observed in Cp₂Fe. This yielded values of 185 and 125 cm⁻¹ for ruthenocene and nickelocene, respectively.

Winter et al. [7] were the first to investigate the infrared spectrum of crystalline Cp₂Fe in the range of 450–6000 cm⁻¹ (14–180 THz). Adams and Fernando [8] reported Raman and infrared spectra of crystalline ruthenocene at ambient and liquid-nitrogen temperatures and assigned 165 and 172 cm⁻¹ to ω_{22} . Bodenheimer and Low [9] published a comparative study, which substantiated the previous spectral studies of Raman and infrared spectra of Cp₂Fe and ruthenocene. They assigned the 179 and 170 cm⁻¹ band to ω_{22} in the solid-state Cp₂Fe and Cp₂Ru, respectively. However, clear absorption spectra have never been shown in these reports because it is difficult to observe low-frequency modes using conventional spectrometers.

The structure and kinetics of metallocene is of interest to quantum chemists. The force constants of the bonds

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between metal atoms and ligands, which are estimated using three-body models from the vibrational frequencies of the low-frequency fundamental modes, such as Cp–M–Cp stretching and bending, provide the basic parameters for computer calculations. Thus, more precise values of frequencies and assignments are needed. In this report, we present the transmission spectra of Cp₂Fe, Cp₂Ni, Cp₂Ru, deuterated Cp₂Fe (Cp₂Fe-d₁₀), and bis(pentamethylcyclopentadienyl)iron (Cp₂^{*}Fe) in the range of 0.7–6.2 THz as measured by the recently developed GaP Raman terahertz spectrometer.

There are three primary means of generating terahertz electromagnetic waves: a free electron laser, a femtosecond laser, and difference-frequency generation. Time domain spectroscopy (TDS) using the terahertz pulses generated by femtosecond laser pulses is the most widely used by researchers. However, the frequency range of the spectra obtained by TDS is limited below 3 THz.

The GaP Raman terahertz spectrometer used in this study is principally based on the difference-frequency generation in a GaP crystal based on the Raman effect of phonon-polariton mode. This spectrometer can sweep frequencies from 0.5 to 6.2 THz. In the time since the first generation of terahertz waves at a frequency of 12 THz were produced by a GaP Raman laser [10,11], we have developed two types of tunable terahertz wave generators and spectrometers. A schematic diagram is displayed in Fig. 1. A high resolution is available for the one device pumped by a 1064-nm Nd:YAG laser with an optical parametric oscillator (OPO) [12–15]. The other system is a simpler and more compact device pumped by two Cr:Forsterite lasers that are operated in the 1.2-μm band. The resolution of the former system is 1.5 GHz, which enables detection of fine spectral structure at low temperature, and the latter is 30 GHz. The Cr:Forsterite system is suitable for conventional measurement. In this study, we used the Cr:Forsterite system with pyroelectric detectors for the detection of reference and transmission beams. The details of the GaP terahertz generator and spectrometer are described elsewhere [16].

2. Materials and methods

Sample pellets for the measurement of transmittance spectra were prepared by mixing milled metallocene and

polyethylene powder (300 mg) followed by pressing the mixture into a disk. The pellets were 20 mm in diameter and approximately 1 mm thick. The concentration of substance in the pellet was 0.3 mol/L. For only Cp₂Fe, we investigated pellets with concentrations of 0.3 and 1.0 mol/L. All the substances were commercial products (Cp₂Fe: TCI, >95%; Cp₂Ru: Acros, >99%; Cp₂Ni: TCI, >90%; Cp₂^{*}Fe: Aldrich, >97%; Cp₂Fe-d₁₀: C/D/N isotopes, 99%), and further purification was not performed. In the Cp₂Fe-d₁₀, 99.1% of the hydrogen was deuterated. As a reference, we made and measured a pure polyethylene pellet.

3. Results and discussion

3.1. Cp₂M compounds

The terahertz transmission spectra of Cp₂Fe, Cp₂Ru, and Cp₂Ni at room temperature are shown in Fig. 2. For all the compounds, single or split absorption peaks appear over 4 THz. It should be noted that the ring–metal–ring bending frequency of a metallocene is half of the symmetry stretching frequency, so it is expected to be located at 3–6 THz. Therefore, absorption peaks at 4–6 THz were assigned to the bending mode.

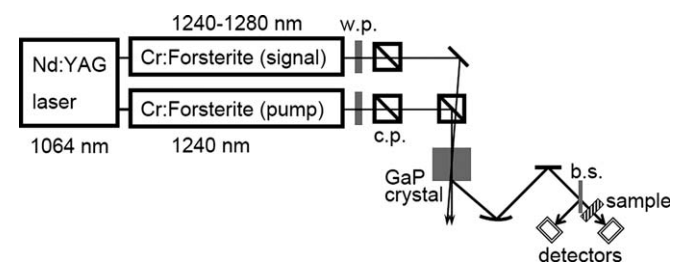


Fig. 1. Schematic diagram of GaP Raman terahertz spectrometer. w.p., waveplate; c.p., cubic polarizer; and b.s., beam splitter.

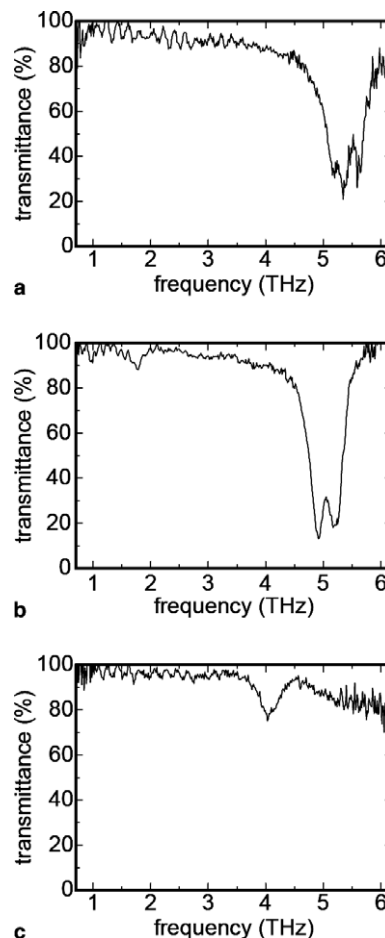


Fig. 2. Transmittance spectra of: (a) Cp₂Fe, (b) Cp₂Ru, and (c) Cp₂Ni.

Cp₂Fe had three split peaks at 5.2, 5.4, and 5.6 THz (173, 178, and 187 cm⁻¹) as seen in Fig. 2a. Splitting was also seen in Cp₂Ru, but two peaks were present at 4.9 and 5.2 THz (164 and 174 cm⁻¹; Fig. 2b). In contrast, Cp₂Ni had a single peak at 4.0 THz (134 cm⁻¹; Fig. 2c). The vibrational frequencies of the bending mode obtained in this study and past reports, including calculations, are indicated in Table 1.

The origin of splitting and the number of split peak is not clear. Lokshin et al. [17] mentioned that it is because of crystal effect. However, crystal structure of Cp₂Fe is monoclinic at room temperature which is identical to Cp₂Ni, while the peak of Cp₂Ni does not split. Beside, split number of Cp₂Fe at low temperature is identical to the number at room temperature while Cp₂Fe has transition point at 163.9 K from monoclinic to triclinic crystal structure (unpublished data). Further experimental and theoretical studies are needed.

The force constant of ring–metal–ring bending H , which can be estimated from Eq. (1) with the frequencies of the bending mode based on a three-body model, are summarized in Table 1

$$\omega_{22} = \frac{1}{2\pi} \sqrt{2H/\mu} \quad \left(\mu = \frac{m_m \cdot m_r}{m_m + 2m_r} \right), \quad (1)$$

where m_m and m_r represent the mass of the metal atom and ligand, respectively. In accordance with the order of the H -value, they increased in the series Cp₂Ni < Cp₂Fe < Cp₂Ru. The H -value indicates the rigidity of the linear shape of the Cp–M–Cp molecule.

The 1.8-THz band of Cp₂Ru is not a fundamental mode because other fundamental modes have higher frequencies than the bending mode in linear X–Y–X molecules [6]. It is likely due to intermolecular interaction or the lattice mode [9].

3.2. Deuteration

The terahertz transmission spectrum of Cp₂Fe-d₁₀ is displayed in Fig. 3. Three peaks shifted to 4.8, 5.0, and 5.2 THz (159, 165, and 173 cm⁻¹), respectively. Treating

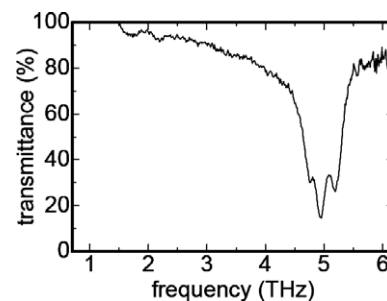


Fig. 3. Transmittance spectra of Cp₂Fe-d₁₀.

the molecule as a linear X–Y–X molecule, the peak shift is expected to be about 50 GHz from the absorption frequencies of Cp₂Fe using Eq. (1) or

$$\omega_{22} \propto \sqrt{1/\mu}. \quad (2)$$

The experiment showed a much larger value of 400 GHz, approximately 8 times larger than the calculated value. One possible explanation is that deuteration influences the hybridization of the carbon atoms in the ligand, which is slightly modified and adds to the binding force between the iron atom and the ligand [18]. In a solid state, the effects from the surroundings must also be considered as potential causes of the disagreement in the value.

3.3. Cp₂*Fe

As seen in Fig. 4 Cp₂*Fe has a strong absorption peak at 6.0 THz (200 cm⁻¹) and weak peaks at 1.6 and 4.2 THz (54 and 140 cm⁻¹). In previous studies by several groups [19,20], the 6.0-THz band was assigned to out-of-plane CH₃ oscillations. There are some opinions about the assignments of low-frequency fundamental modes. Based on Raman spectra, Duggan and Hendrickson [21] concluded that symmetric stretching ω_4 , antisymmetric stretching ω_{11} , and antisymmetric ring tilt ω_{21} , correspond to 169, 451, and 515 cm⁻¹ (5.07, 13.5, and 15.5 THz), respectively. In contrast, Phillips et al. [19] reported that the 511- and 454-cm⁻¹ bands correspond to ω_{11} and ω_{21} . Recently, Stanghellini et al. [20] published a report that agreed with

Table 1
Absorption frequency (wavenumber), its assignment, and calculated force constant of bending H of ring–metal–ring

Compound	Frequency (THz)	Wavenumber (cm ⁻¹)	Assignment	Other reports (cm ⁻¹)	H (N/m)
Cp ₂ Fe	5.2, 5.4, 5.6	173, 178, 187	ω_{22}	(170 ^a) 179 ^c	18.7 ± 1.5
Cp ₂ Ru	1.8	60	Intermolecular?		
	4.9, 5.2	164, 174	ω_{22}	185 (calc.) ^a , 165 and 172, ^b 170 ^c	24.0 ± 1.4
Cp ₂ Ni	4.0	134	ω_{22}	125 (calc.) ^a	10.8
Cp ₂ Fe-d ₁₀	4.8, 5.0, 5.2	159, 165, 173	ω_{22}		16.4 ± 1.3
Cp ₂ *Fe	1.6	54	Intermolecular?		
	4.2	140	ω_{22}		13.4
	6.0	200	Out-of-plane CH ₃ oscillation	200 ^d	

^a Ref. [6].

^b Ref. [8].

^c Ref. [9].

^d Refs. [19,20].

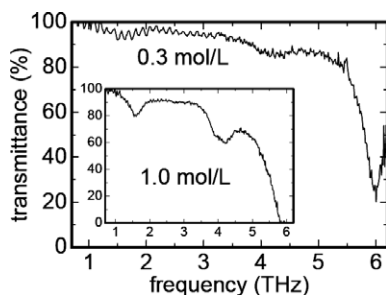


Fig. 4. Transmittance spectra of Cp_2^*Fe of 0.3 mol/L and 1.0 mol/L (inset).

the assignments by Duggan et al. Anyway, the bending mode has not been found. If the assignment of 6.0-THz band to CH_3 oscillation is correct, one possibility is that the weak 4.2-THz (140 cm^{-1}) band observed in this study was the bending mode because, as mentioned before, the bending mode has the lowest frequency among the fundamental vibrational modes of a linear X–Y–X molecule. Assuming that the 4.2-THz band corresponds to the ring–metal–ring bending mode, the force constant of ring–metal–ring bending of Cp_2^*Fe is estimated to be 13.4 N/m in the same way as with metallocenes. This value is not far from the value of Cp_2Fe . Assignment of the 1.6-THz band is difficult with the present results, but we suggest a possibility that it is related to intermolecular interaction like the 1.8 THz-band of Cp_2Ru .

4. Conclusions

The transmission spectra of crystalline metallocene and decamethyl metallocene were obtained using a GaP Raman terahertz spectrometer. Low-frequency modes were clearly observed and force constants were estimated. The results demonstrate the ability of the spectrometer to measure the fundamental vibrational mode in organometallic compounds and other large-scale molecules.

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