Monitoring the reaction between $AlCl_3$ and o-xylene by using terahertz spectroscopy*

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(Received 25 July 2013; revised manuscript received 16 August 2013)

Terahertz time-domain spectroscopy (THz-TDS) is used to study the interaction between $AlCl_3$ and o-xylene in a temperature range from 300 K to 368 K. For comparison, the three isomers of o-, m-, and p-xylene are measured by using THz-TDS. The o-xylene carries out isomerization reaction in the presence of catalyst $AlCl_3$. The absorption coefficient of the mixed reaction solution is extracted and analyzed in the frequency range from 0.2 THz to 1.4 THz. The temperature dependence of the absorption coefficient, which is influenced by both the dissolution of $AlCl_3$ and the production of the two other isomer resultants, is obtained, and it can indicate the process of the isomerization reaction. The results suggest that THz spectroscopy can be used to monitor the isomerization reaction and other reactions in chemical synthesis, petrochemical and biomedical fields.

Keywords: terahertz, ultrafast spectroscopy, absorption coefficient

PACS: 87.50.ux, 78.47.jh, 78.20.Ci **DOI:** 10.1088/1674-1056/22/11/118701

1. Introduction

Tracing a reaction process is a difficult task. As is well known, terahertz time-domain spectroscopy (THz-TDS) has been widely used to study the properties of various petrochemical products, such as gasoline, kerosene, diesel, and lubricants.[1–4] As the resultants of reaction can be detected by the terahertz spectroscopy, some processes can be studied with the terahertz time-domain spectroscopy. The research on DNA and oxaliplatin showed a clear and distinct reaction time dependence through evaluating the reaction dynamics.[5] The process and the mechanism of the solid-state reaction between solid L-tartaric acid and sodium carbonate monohydrate were tentatively elucidated by THz-TDS.[6] By using THz spectroscopy, the study on heating copper sulfate hydrates revealed more information about the lattice vibration and the hydrogen bond of the hydrates.[7] Those researches demonstrate promising applications of THz-TDS for detecting chemical interaction processes.

As is well known, $AlCl_3$ is a Lewis acid that can catalyze the isomerization reaction.[8–12] The methyl groups on o-xylene can be transferred and the o-xylene can be isomerized into m-xylene and p-xylene with the catalysis of $AlCl_3$. THz spectroscopy is highly sensitive to isomers,[13–17] therefore, it is an effective method to study the interaction process of organic molecule isomerism. Thus, we can investigate the isomerization reaction of o-xylene by THz measurements. In this paper, we use THz-TDS to monitor the interaction between $AlCl_3$ and o-xylene. With the catalysis of $AlCl_3$, o-xylene isomerizes at different temperatures, meanwhile $AlCl_3$ dissolves in the mixed solution. The absorption coefficient of the mixed solution is obtained in the THz spectrum, which is used to analyze the isomerization reaction process and the dissolution process of $AlCl_3$ with the temperature increasing.

2. Experiment

The THz spectra of the samples were obtained using a standard THz-TDS setup with the transmission method.[18] The reaction was carried out in a glass reactor which did not interact with the reactant and catalyst. To achieve a good precision, the quantities of o-xylene and $AlCl_3$ were weighed by an electronic balance each time. The weights of o-xylene and $AlCl_3$ were 15 g ($\pm$0.5 g) and 0.6 g ($\pm$0.03 g), respectively. The reactor containing o-xylene and $AlCl_3$ was placed into a super constant temperature water bath to heat them and let them react. In the process of reaction, the mouth of the reactor was covered with a polyethylene membrane to prevent volatilization. The temperature of the super constant temperature water bath was adjustable and the temperature accuracy was 1 K. The reactor was heated in the super constant temperature water bath for 1 h for the isomerization reaction. Each reaction was separately carried out from 300 K to 368 K. One hour later, the mixed solution was moved out and cooled down to room temperature for terahertz measurements. A mixed solution without heating was prepared as comparison. Thus a series of 15 samples of mixed reaction solution was obtained. The pure o-, m-, and p-xylene were prepared for measurement,

*Project supported by the National Basic Research Program of China (Grant No. 2013CB328706), the Specially Funded Program on National Key Scientific Instruments and Equipment Development, China (Grant No. 2012YQ14005), the Beijing National Science Foundation, China (Grant No. 4122064), and the Science Foundation of the China University of Petroleum (Beijing) (Grant Nos. QZDX-2010-01 and KYJJ2012-06-27).

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too. Polyethylene cells, which had a low refractive index and THz absorption, were used in the terahertz measurement. The thicknesses of all solutions and samples were kept at 10 mm. The polyethylene cells containing samples were tested to obtain time-domain signals, and the empty polyethylene cell signal was used as a reference. The corresponding frequency domain spectrum was obtained through fast Fourier transform.

3. Results and discussion

In order to investigate the isomerization reaction and resultants, we have measured the THz spectra of three xylene isomers. Figure 1 shows the THz absorption spectra of o-, m-, and p-xylene in the frequency range from 0.2 THz to 1.5 THz. As the polarity of o-xylene is stronger than that of the other two isomers, its absorption coefficient is larger than that of m- and p-xylene. It can be seen that the three xylenes exhibit four characteristic absorption peaks at about 0.32 THz, 0.651 THz, 0.938 THz, and 1.20 THz. The peaks of m- and p-xylene shift toward lower frequency slightly compared with those of o-xylene. The relative height of the absorption curve corresponds to the arrangement of the methyl groups sequencing ortho-, meta-, and para-position on the benzene, which is consistent with the result reported in Ref. [16]. The Beer–Lambert law is used to calculate the absorption coefficients of the mixed components, we can use $\alpha(\omega) = \sum_{i=1}^{n} b_i \alpha_i(\omega)$,[14] where $\alpha(\omega)$ is the absorption coefficient of the mixture, b_i is the ratio of pure compounds, and $\alpha_i(\omega)$ is the absorption coefficient of the pure compound. The absorption coefficient of o-xylene is the largest among the three xylene isomers in the frequency range from 0.2 THz to 1.4 THz, so the absorption coefficient of the o-xylene solution mixed with the two other xylene isomers decreases under the same sample thickness. In the process of isomerization reaction, the absorption coefficient of the mixed solution will be reduced if the m- and p-xylene are produced.

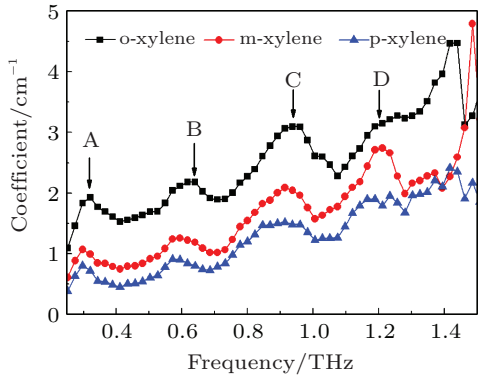


Fig. 1. (color online) Absorption spectra of o-, m-, and p-xylene in the THz region. Four main absorption peaks are indicated with A, B, C, and D, respectively.

THz-TDS measurements are performed for a series of reaction solutions, where the interaction takes place between o-xylene and $AlCl_3$ for one hour at different temperatures (300 K to 368 K), as shown in Fig. 2. Because the reaction temperature interval is small, the amplitude changes are slight and the phase delays are subtle. In fact, the THz waveforms of the solutions at different temperatures are different from each other. Figure 3 displays the absorption coefficients of the o-xylene reaction solutions, where the isomerization occurs in the presence of catalyst $AlCl_3$ at different temperatures. The absorption coefficients of the reaction solutions with different reaction temperatures ranging from 300 K to 368 K can be distinguished. It can be seen that there are four feature peaks at about 0.32 THz, 0.651 THz, 0.938 THz, and 1.20 THz, which are corresponding to the absorption peaks of pure o-, m-, and p-xylene in Fig. 1.

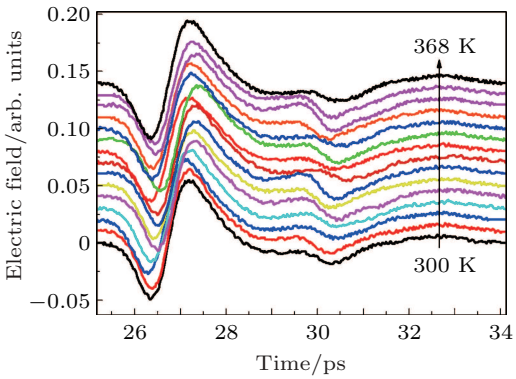


Fig. 2. (color online) THz time-domain waveforms of the mixed reaction solution of o-xylene and $AlCl_3$ at different temperatures (waveforms are shifted vertically for clarity).

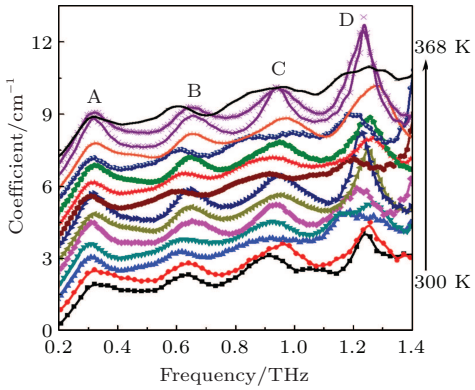


Fig. 3. (color online) Temperature dependent absorption spectra of the mixed reaction solution of $AlCl_3$ and o-xylene. Peaks A, B, C, and D are at frequencies 0.32 THz, 0.651 THz, 0.938 THz, and 1.26 THz, respectively. All of the curves are shifted vertically by +0.5 cm^{-1} for clarity.

In order to further explore the relation between the absorption coefficient and the reaction temperature, we extract the absorption coefficients at the peaks (in Fig. 3) and depict these data in Fig. 4. The curve marked with empty circles indicates the reaction temperature dependence of the absorption coefficient at 0.32 THz, and the other curve marked

with black solid circles indicates the dependence at 0.651 THz. The similar tendencies of the two curves show the similar vibrating modes of these solutions in the terahertz frequency range. With increasing temperature, the clastic $AlCl_3$ dissolves in the xylene solution and the isomerization reaction occurs. Both the dissolution of $AlCl_3$ and the production of chemical reaction resultants will influence the absorption intensity. The $AlCl_3$ dissolved in xylene demonstrates the molecular states, showing that these molecules are polar ones like H_2O molecules and have a strong absorption in the THz wave band.[19,20] In the initial stage (300 K to 328 K), the temperature is low and the o-xylene reacts weakly, and the terahertz absorption is mainly influenced by catalyst $AlCl_3$ which is dissolved in the solution. So the curve rises sketchily. For the intermediate stage (328 K to 358 K), the curve displays oscillations because the dissolving $AlCl_3$ increases the absorption and the reaction resultants reduce the absorption. The oscillations derive from the combination of the two effects. The curve drops down monotonically at the final stage (358 K to 368 K). In this stage, the solubility of $AlCl_3$ increases to a maximum, and it does not dissolve even if the temperature increases. The decline of the absorption curve at this stage is due to the production of a large quantity of m- and p-xylene. We can see that the absorption coefficient of the reaction solution at 368 K is smaller than that at room temperature.

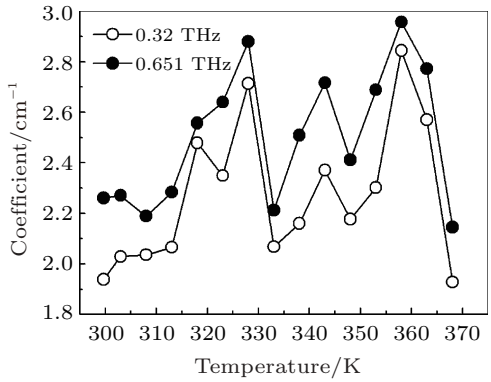


Fig. 4. Reaction temperature dependences of the absorption coefficient of $AlCl_3$ and o-xylene at 0.32 THz and 0.651 THz, respectively.

Based on the aforementioned results, we can find that the THz wave is sensitive to isomer molecules and can be used to investigate the interaction between $AlCl_3$ and o-xylene. Extracting the absorption coefficient, we obtain detailed information about the isomerization reaction at different temperatures. This verifies that it is a new effective way to study the isomerization reaction. Furthermore, we have demonstrated the feasibility and validity of the terahertz method for realizing real time monitoring of chemical reactions. Combining with other methods, such as theoretical modeling, molecular dynamics simulation, and Raman spectroscopy, the specific process and microscopic mechanism of isomerization reaction may be clarified clearly.

4. Conclusion

In this work, we utilize THz-TDS to study the reactions between $AlCl_3$ and o-xylene. The refractive indices and the absorption coefficients for the isomerization reaction solution of o-xylene in the presence of catalyst $AlCl_3$ are obtained at different temperatures. We extract the absorption coefficients at the peaks and obtain the temperature dependences of the absorption coefficients for the o-xylene reaction solution. Three reaction stages corresponding to three different temperature ranges are identified based on the temperature dependences of the absorption coefficients for the reaction solution. It is found that the absorption coefficient is influenced by two factors, the $AlCl_3$ dissolution and the production of m- and p-xylene. The results indicate that the THz detection could be an effective method to investigate the isomer reaction. From this work, we find that monitoring and characterizing a reaction process by using THz spectroscopy is conductive to obtaining information about the reaction rate and quantities of resultants, and this will help to control and optimize the reaction processes in chemical synthesis, petrochemical and biomedical fields.

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