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研究課題名(和文) Exploration of the anharmonicity of phonons modes in molecular crystals with temperature-dependent and high-field terahertz spectroscopy and ab initio simulation

研究課題名(英文) Exploration of the anharmonicity of phonons modes in molecular crystals with temperature-dependent and high-field terahertz spectroscopy and ab initio simulation

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研究成果の概要(和文)：The PI has performed temperature-dependent THz measurements. Quasi-harmonic calculations have been performed to qualitatively explain the temperature-dependent frequency shifts for a few THz peaks. The correlation between the quasi-harmonicity and the nature of the THz modes has been discussed.

研究成果の学術的意義や社会的意義

This research work gives an insight into the anharmonicity of THz modes, which may help to understand many related macroscopic properties such as thermal (or negative) expansion and heat conduction.

研究成果の概要(英文)：The PI has performed temperature-dependent THz measurements for alpha-lactose monohydrate, theophylline, and alpha-L-xylose. Interesting temperature dependencies have been observed in these systems. Quasi-harmonic calculations, which introduce an explicit dependence on unit-cell volume of THz modes and retain the harmonic expression for the Helmholtz free energy, have been performed to all three systems. The Quasi-harmonic results have been qualitatively explained the temperature-dependent frequency shifts for a few THz peaks. The correlation between the quasi-harmonicity and the nature of THz modes has been discussed. Due to the COVID-19 pandemic, the proposed high-field THz spectroscopic experiments have not been carried out. The PI expects to be able to complete this part of work after the pandemic. An interplay between the temperature-dependent and high-field terahertz spectroscopic measurements will lead to a more complete understanding of the anharmonicities of THz modes.

研究分野：physical chemistry

キーワード：THz spectroscopy pure anharmonicity quasi-harmonicity temperature dependency crystal disorder THz intensity

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様式 C-19、F-19-1、Z-19 (共通)

1. 研究開始当初の背景

Terahertz (THz) spectroscopy has shown a promising potential to be applied in analytical chemistry. It has been proved a sensitive probe of the structural variations induced by various external stimuli such as temperature and pressure. THz peaks of a molecular crystal usually display complicated temperature and pressure dependencies, challenging the theoretical interpretation of THz spectroscopy.

By taking α -Lactose monohydrate as an example, we have observed various temperature-dependent behaviors in its THz spectra. As shown in Figure 1b, Peak *a* has temperature dependency barely in terms of both frequency and line shape; Peaks *b* and *c* undergo weak blue shifts and line-shape sharpening with the decrease of temperature; while Peak *d* experiences the most significant peak shift and line-sharpening with the decrease of temperature. In another example of theophylline, although both the two THz peaks *a* and *b* undergo blue shift at a lower temperature, their line shapes show different temperature dependencies, as shown in Figure 2b. The line shape of Peak *a* is sharpened significantly, while that of Peak *b* varies to a small extent. In a more complicated case represented by L-xylose, Peaks *a* and *b* undergo red shifts with the decrease of temperature, while Peaks *c* and *d* experience blue shifts, as shown in Figure 3b.

For molecular crystals, the interpretation of the temperature dependencies of THz modes is, in fact, mode-nature specified. To be precise, molecules have three forms of vibrations in the THz frequency range: intermolecular translation, intermolecular libration, and intramolecular vibration. The temperature dependency of an intermolecular translational mode is prominently affected by the pure anharmonicity (PAH) of its potential surface. PAH induces both the frequency shift and line shape variation. When the intermolecular translational mode approaches the anharmonic region of the potential surface, it produces an expansion or shrinking of the unit cell. The temperature dependencies of intermolecular librations and intramolecular vibrations are, however, affected by two major components. One is, obviously, the PAHs of their potential surfaces, similar to the case of intermolecular translations. The other is the size effect of the unit-cell expansion or shrinking, induced by the anharmonicity of the intermolecular translations. The latter one is termed quasi-harmonic (QH). QH refers to merely the change of intermolecular distance and thus the variation of the strengths of intermolecular interactions. As a result, QH induces only the frequency change but the line-shape variation.

Based on the above analysis, one crucial problem in the theoretical interpretation of the temperature dependence of THz peaks is how to distinguish the contributions of PAH and QH. To give an answer to this question, the PI proposed this research plan.

2. 研究の目的

This research plan has a two-fold purpose.

- (1) Establish an experimental approach to identify the prominent elements—PAH or QH—in determining the temperature dependency of a THz peak.
- (2) Calculate the contributions of PAH and QH to the temperature dependency of a THz peak in theory.
- (3) Discuss PAH and QH of different THz peaks regarding the nature of motions, precisely, intermolecular vibrations, intramolecular vibrations, and mixing of these two.

3. 研究の方法

First, the PI proposed using high-field THz pulse excitation to directly access the PAH of a THz peak. A THz pulse lasts only tens femtosecond; in such a short interaction time, the molecular crystal does not have time to expand or shrink and thus, produces a QH effect to the THz mode. Alternatively, the temperature-dependent measurement gives access to both PAH and QH of the THz mode. By comparing the results between the high-field THz excitation and the temperature-dependent measurement, we can qualitatively distinguish the contributions of PAH and QH to the THz peak.

Second, the PI will then perform QH calculations under the periodic boundary conditions for each molecular crystal. In this step, he will manually induce the unit-cell shrinking at low temperature for each system. He will then perform frequency calculations by retaining the harmonic expression for the Helmholtz free energy under the periodic boundary conditions. In such a manner, he examines the contributions of QH to the frequency shift of a THz peak in theory.

Lastly, the PI will examine the correlation between the frequency shift induced by QH and the nature of the THz mode. He is, in particular, interested in the differences between intermolecular translation, intermolecular libration, and intramolecular vibration, regarding their QH behaviors.

4. 研究成果

The high-field THz experiments were initially planned to be performed in the laboratory of our collaborators in 2019. This plan was, however, postponed to 2020 due to a laser failure in that year. The outbreak of the COVID-19 pandemic at the beginning of 2020 eventually made long-distance travel and the long-term guest-stay impossible. So, the PI expects to be able to perform the high-field THz experiments

after the pandemic. In the current situation, he has been focusing on collecting and interpreting the temperature-dependent THz spectra.

Table 1. Crystal structure information of the three molecules at room temperature

	Space group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Volume (Å ³)
α -Lactose monohydrate	$P2_1$	4.801	21.637	7.727	90	105.5	90	773.368
Theophylline	$Pna2_1$	24.012	3.918	8.500	90	90	90	799.577
L-xylose	$P2_12_12_1$	9.128	12.262	5.771	90	90	90	645.937

The temperature-dependent THz spectra of α -Lactose monohydrate, theophylline, and α -L-xylose are shown in the top panels of Figures 1, 2, and 3, respectively. The QH calculations were performed using crystal structures with the unit-cell parameters displayed in Table 1 as the starting points. Shrinking is manually induced to the crystal structures to produce unit cells with varied volumes. The frequency calculations were then performed by retaining the harmonic expression for the Helmholtz free energy in CRYSTAL17 software package. The calculation results are shown beneath the experimental data for each system. The PI also quantifies the nature of the THz modes in terms of the contributions of intermolecular translations, librations, and intramolecular vibrations. And the results are shown in Panels (c) in Figures 1, 2, and 3. By combining Panels (b) and (c) in each figure, one can clearly examine the QH effect on the frequency of any THz peak, associating with its vibrational nature. By taking Peak *a* of α -Lactose monohydrate as an example, this peak exhibits bare temperature dependence, and the calculation shows that the QH does not induce a frequency shift to the peak. These two results imply that the PAH of Peak *a* is marginal. In another example of Peak *b* of theophylline, it undergoes a remarkable blue shift with the decrease of temperature, yet QH does not change its frequency notably. This fact indicates that the frequency shift is mainly induced by PAH of this mode.

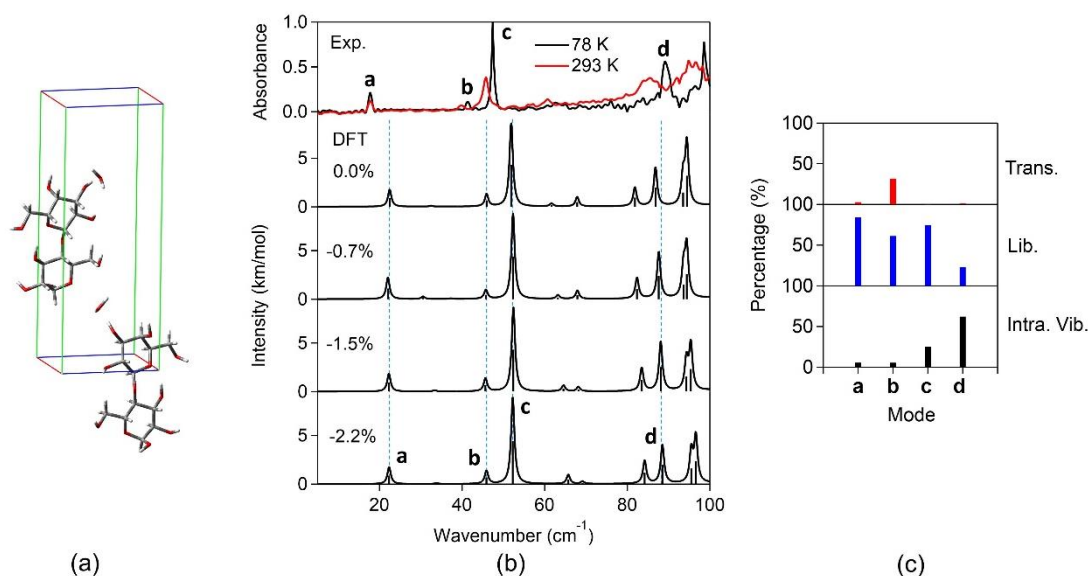


Figure 1. Crystal structure and THz modes of α -lactose monohydrate. Panel (a) shows the crystal's structure. Panel (b) compares the experimental temperature-dependent THz spectra (top panel) and the calculated THz peaks with varied unit cell volumes. The shrink ratios of the unit cell volumes are evaluated with respect to the value at room temperature. Lorentzian line shapes with arbitrary full-width-at-half-maximum (FWHM) are evolved into all peaks to provide a visual guide. Panel (c) displays the energy contributions of intermolecular translations (Trans.), intermolecular librations (Lib.), and intramolecular vibration to the vibrational energy of each mode.

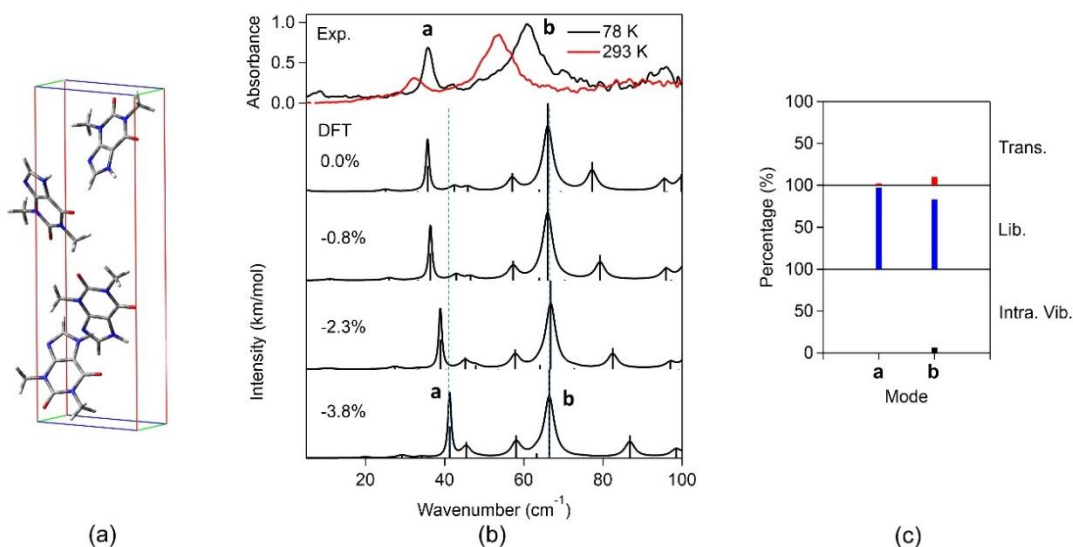


Figure 2. Crystal structure and THz modes of theophylline. Panels (a) shows the crystal's structure. Panel (b) compares the experimental temperature-dependent THz spectra (top panel) and the calculated THz peaks with varied unit cell volumes. The shrink ratios of the unit cell volumes are evaluated with respect to the value at room temperature. Lorentzian line shapes with arbitrary full-width-at-half-maximum (FWHM) are evolved into all peaks to provide a visual guide. Panel (c) displays the energy contributions of intermolecular translations (Trans.), intermolecular librations (Lib.), and intramolecular vibration to the vibrational energy of each mode.

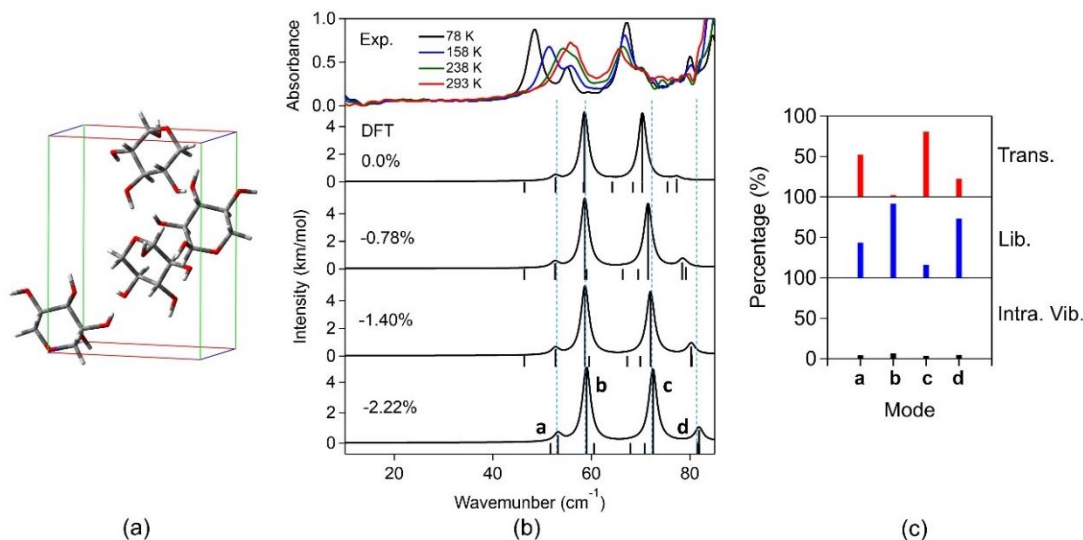
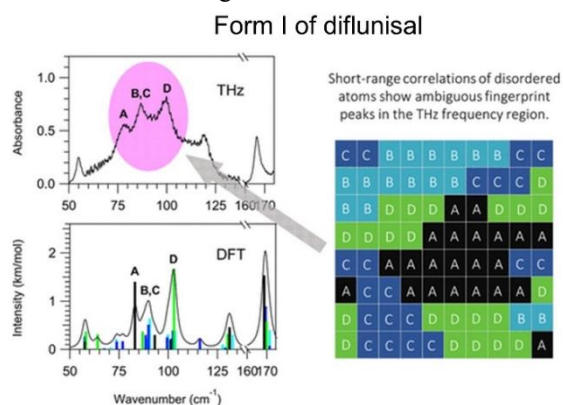


Figure 3. Crystal structure and THz modes of α -L-xylose. Panels (a) shows the crystal's structure. Panel (b) compares the experimental temperature-dependent THz spectra (top panel) and the calculated THz peaks with varied unit cell volumes. The shrink ratios of the unit cell volumes are evaluated with respect to the value at room temperature. Lorentzian line shapes with arbitrary full-width-at-half-maximum (FWHM) are evolved into all peaks to provide a visual guide. Panel (c) displays the energy contributions of intermolecular translations (Trans.), intermolecular librations (Lib.), and intramolecular vibration to the vibrational energy of each mode.

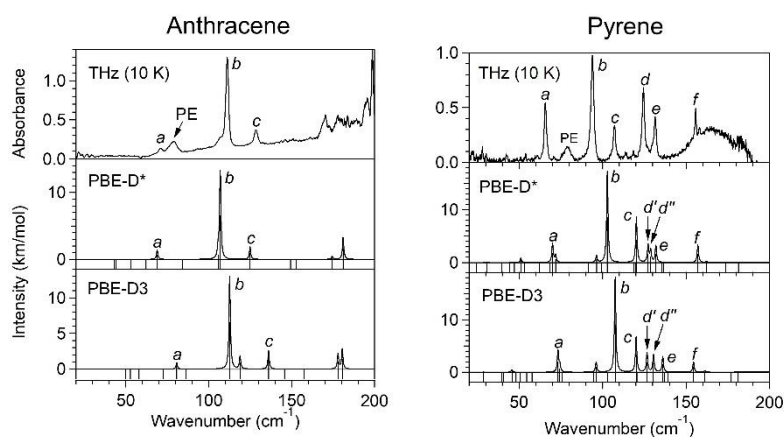
At last, besides the proposed works in this research plan, the PI has also performed a series of fundamental studies for achieving a more complete interpretation of the experimental THz spectra under the support of this grant. He will list out some major ones in the following.

(1) The PI has illustrated a THz spectroscopy approach to investigating one of the outstanding problems in crystallography—the structure analysis of a crystal with disorder. Form I of diflunisal, in which the two ortho sites on one phenyl ring of diflunisal show occupational disorder, was used for an illustration. THz radiation interacts with the collective vibrations of correlated disorder, thus providing a promising tool to examine the symmetry of short-range correlations of disordered atoms. Through a thorough examination of the selection rule of THz



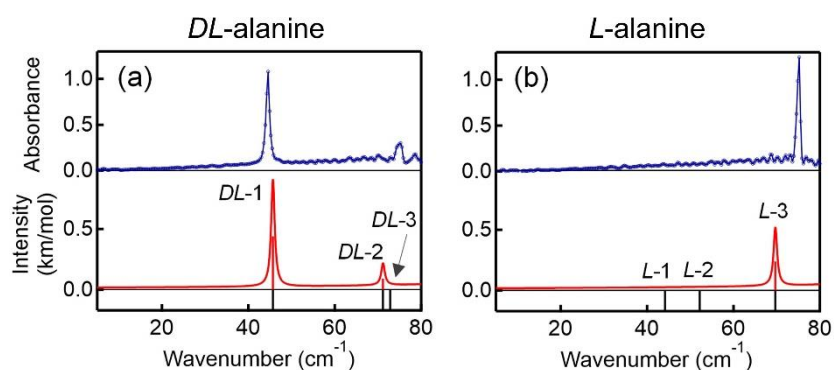
vibrations in which the disordered atoms are involved to different extents, we deduced that only four short-range correlation possibilities of disorder exist and all of them display unambiguous fingerprint peaks in the 50–170 cm^{-1} frequency region. We finally proposed an alternating packing model in which the correlation lengths of disorder are on the nanometer scale. Based on this work, some projects aiming to reveal the microscopic structures of other disordered systems, such as organic perovskites and configurational disordered molecules, have been going on.

(2) The PI has examined the reliability of an empirical-corrected DFT approach for THz mode assignment by using the anthracene and pyrene crystals as examples. The performance of the PBE functional augmented by Grimme's two dispersion correction terms, D^* and D3, respectively, are rigorously evaluated against the experimental criteria of frequency and isotope shift (IS). The D^* and D3 terms use



empirical and semi-classical approach for correcting the London-type dispersion interactions, respectively. The nature of each THz mode simulated by PBE- D^* and that by PBE-D3 is quantitatively compared in terms of the percentage contributions of the intermolecular and the intramolecular vibrations to the vibrational energy. We find that the two methods have equivalent performance in reproducing the frequencies, ISs, and nature of THz modes of both the anthracene and pyrene crystals.

(3) The PI has quantitatively discussed the nature of the IR intensities of THz modes. Although significant efforts have been made to establish THz spectroscopy, IR intensities have not been sufficiently studied. We have elucidated the interpretation of the selection rule and origins



of intensities of THz modes through a comparison discussion of the THz spectra of DL- and L-alanine crystals. The two systems give rise to almost identical distributions of normal modes in the 5–80 cm^{-1} THz frequency range; however, their THz absorption features are different. By calculating the Born Charges induced by the motions of individual molecules, we have visualized their vector sum and thus, explained the selection rule of the low-frequency normal modes in DL- and L-alanine crystals. Based on the experience acquired in mid-IR spectroscopies, it has been self-evident that the dominant motion in a normal mode makes the maximum contribution to IR intensity. In the application to terahertz spectroscopy of molecular crystals, whether this presumption holds or not has not yet been examined. Our analysis suggests that this presumption requires reconsideration. All the THz modes in the investigated frequency range feature predominantly intermolecular translations in both systems, contributing to $\geq 97\%$ of the vibrational energies. The intermolecular librations and intramolecular vibrations, in spite of their marginal presence in these THz modes, play a nontrivial role in determining IR intensities.

5. 主な発表論文等

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オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

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〔産業財産権〕

〔その他〕

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6. 研究組織

氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
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7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

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