Terahertz Spectrum of Energetic Mixed Crystals, Phase-Transition Crystals and Co-Crystals

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Abstract. Terahertz spectroscopy has been shown to be an attractive means to characterize molecular vibration in energetic materials, which may shed light on the fine structures of mixed crystals, phase-transition crystals and co-crystals, and may contribute to the molecular design of novel explosives and their applications. In this contribution, various energetic single crystals, polymorphisms and co-crystal were examined with terahertz time-domain spectrometer (THz-TDS) operating in a spectral range from 0.1 THz to 2.2 THz. The results reveal that each single explosive exhibits a characteristic terahertz absorption spectrum. The absorption spectrum of a mixed crystal is nearly a mixture of those of its components, while the terahertz spectrum of co-crystals is evidently different from those of the co-formers. An obvious α-β phase transition in FOX-7 was observed at 384K. Density functional theory (DFT) calculations of various energetic materials were also performed, a comparison of which with the experimental terahertz spectrum confirmed a strong correlation between the formation of absorption peaks in the terahertz range and molecular vibration or rotation behaviors.

Introduction

The use of spectroscopic techniques for material characterization is an important technique to research material structure, depending on the difference of frequency spectrum that leads to the characterization of such molecular behavior as electron transition from the nucleus to the molecules, and rotation and vibration of macromolecules. Spectroscopy research on energetic materials can effectively characterize the vibration, rotation and twisting of particular perssads and molecular bonds, providing empirical technological means for researching the change rule of the molecular structure under the conditions of the establishment of a molecular model of energetic materials and external stimulations, which has been the important technical means to the energetic materials characterization.

As is known to us that the macromolecules generally rotate and vibrate in THz (Terahertz, THz) since the atomic nucleus operate relative motion, lattice of molecules perform vibration, and the molecules twirl around its three axes of inertia etc, the terahertz spectrum technology can be adopted to effectively characterize the rotation and vibration of the macromolecular of energetic materials, and low frequency oscillation of the lattice by the intensity and frequency of absorption, which provide theoretical basics for researching the
interaction between the molecular structure of energetic materials and the environment (temperature, pressure and so on).

In recent years, the terahertz spectral characterization of energetic materials has developed rapidly in the establishment of the characteristic fingerprint peaks and the description of molecular motion. A number of research institutions at home and abroad have received dozens of common single-compound explosive such as a C4 explosive, PETN, Semetx A, TNT, RDX, HMX as well as the absorption characterization peaks of terahertz spectroscopy of such composite explosive as R852, R791, PW30, 8701, 8702[3-30]. Meanwhile, based on the quantum chemistry theory and first-principles of calculation, a number of research institutions also carried out analysis on terahertz spectroscopy and description of the fine structure of energetic materials. The software such as Gaussian, Dmol3 was applied to calculate the vibration frequency of energetic materials such as 2, 4-DNT, 4-DNT, 2, 6-DNT, β-RDX, α-RDX, β-HMX, TNT, PETN, TNPG. Comparison between the theoretical results and the experimental spectrum contributes to the confirmation of the formation mechanism of absorption peaks and its corresponding molecular motion mode[6, 10, 17, 19, 20, and 25].

In terms of mixed crystal, phase-transition crystal and co-crystal, the research group conducted the terahertz spectroscopic characterization of several energetic materials under the three crystalline states and obtained their terahertz spectrum charts. In addition, based on the first principles, they made a comparison between the experimental spectra and theoretical spectra by analyzing their differences of the energetic materials under several crystalline states.

1. Experimental Methods and Sample Preparation

1.1 Test Methods of THz Time-domain Spectroscopy

Based on the terahertz time-domain spectroscopy, with the terahertz source of radiation as the photoconductive antenna, the ZnTe crystal as the detector crystal, the central wavelength of light pulse produced by femtosecond lasers for 800nm, half-width for 8.9nm, the optical system is shown in Figure 1. In order to reduce the impact of water molecules in the air on the experimental results, part of terahertz optical path remains closed, filled with dry air or, ambient temperature is controlled at 23.5 °C, with the relative humidity less than 1%.

Fig. 1. Optical graph of THz-TDS system

In the experiment, firstly the researchers collected the time-domain waveform of THz pulse in free space (reference signal) and that of the transmitted samples (sample signal), on which they conducted the Fast Fourier Transform, finally achieving the corresponding frequency domain signal. With absorption spectroscopy of the samples’ terahertz obtained on the base of Beer-Lambert Law [31], the mathematical formula is as follows:

$$A = -\ln\left(\frac{I_{\text{Sample}}}{I_{\text{Reference}}}\right)$$  \hspace{1cm} (1)
Where, A is the relative absorption coefficient of the sample, $I_{\text{sample}}$ is the intensity of terahertz wave of the sample signal, and $I_{\text{reference}}$ is the intensity of the terahertz waves of the reference signal. In this paper, the mean values of test results of the same sample are processed and analyzed for three times in order to reduce experimental errors.

### 1.2 Sample Preparation

Samples were prepared by direct compression method. Since the polyethylene (PE) and polytetrafluoroethylene (PTFE) have no characteristic absorption in the range of 0.1 THz ~ 2.2 THz, the PE or PTFE powder is added to the explosive sample in the sample preparation in order to reduce the impact of excess samples on the absorption. The mixed powder samples were fully polished until its surface had no reflected light. The explosive crystal of the sample had content of about 20%, with its diameter for φ13mm, the pressure for about 70kN, a sample dimension for about φ13mm × 1mm, and its weight for about 0.2g.

To verify the permeability of terahertz to PE / PTFE, the test was conducted to compare the terahertz signal of PE / PTFE and dry air / nitrogen. It can be seen from the Figure 2 that when the terahertz waves penetrates PE / PTFE material, there is almost neither absorption nor unique absorption peaks.

![Figure 2. THz signal of PE / PTFE and dry air / nitrogen.](image)

### 2 Experimental Results and Analysis

#### 2.1 Terahertz Spectroscopy of Mixed Crystal and Co-crystal Explosives

The mixed crystal explosive refers to the compound of two or more single-compound explosives, which is common in the application of explosives. A large number of PBX explosives and cast explosives are made of mixed crystal explosives; the co-crystal explosive: two or more kinds of explosive molecules interact through non covalent bond combined in the same microscopic lattice to form multi-component explosives molecular crystals with specific structure and properties. For example, the co-crystal explosive featured with high energy can be obtained by combining the explosive molecules with high energy and low energy in molecules. Mixed crystal and co-crystal explosive are obtained by mixing two or two more single-compound explosives which are greatly different in molecules.

In order to research the CL-20 (hexanitrohexaazaisowurtzitane) and NTO (3- nitro-1, 2, 4-triazol-5-ketone) which are common explosives, the research group implemented the terahertz spectroscopy experiments on mixed crystal explosive and co-crystal explosive. With the experimental data collection and operation of Fast Fourier Transform, the terahertz absorption spectrum of the single-compound explosives CL-20 and NTO is shown in 3 (a), the terahertz absorption spectrum of the mixed explosive and co-crystal sample is shown in 3 (b), and the table 1 is the statistics about the THz absorption characteristic peak positions of four different samples in the range of 0.1 THz ~ 2.2 THz.
Figure 3. The terahertz absorption spectroscopy of CL-20 and NTO mixed sample and co-crystal samples.

Table 1. THz absorption characteristic peak positions of the four samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Terahertz absorption peaks (0.1 THz ~ 2.2 THz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL-20</td>
<td>0.98, 1.31, 1.43, 1.58, 1.66, 2.07</td>
</tr>
<tr>
<td>NTO</td>
<td>1.58, 1.87</td>
</tr>
<tr>
<td>mixture of CL-20 and NTO</td>
<td>0.98, 1.31, 1.43, 1.58, 1.87, 2.10</td>
</tr>
<tr>
<td>CL-20/NTO co-crystal</td>
<td>0.67, 1.14, 1.62, 1.80, 2.15</td>
</tr>
</tbody>
</table>

The experimental results show that sample CL-20 has 6 absorption characteristic peaks in total within the range of 0.1 THz-2.2 THz. The absorption at 0.98THz, 1.31THz and 2.07THz is relatively strong; sample NTO has 2 absorption characteristic peaks within the range of 0.1 THz-2.2 THz with the absorption at 1.58THz as the strongest.

It can be seen from the mixed samples and co-crystal samples that both samples have obviously different absorption characteristics, showing that it is feasible to use terahertz time-domain spectroscopy for researches on explosive co-crystal process. The absorption characteristic peaks of mixed samples are respectively at 0.98THz, 1.31 THz, 1.43 THz, 1.58 THz, 1.87 THz and 2.10 THz, which is consistent with the superposition of two kinds of single-compound explosive absorption characteristic peaks. Due to the reducing high-frequency signal quality, samples at 2.10THz have deviation. In addition, the 1.66THz characteristic peak of explosive CL-20 is not fully represented in mixed samples because explosive NTO has an extremely strong absorption peak at 1.58THz with its full width at half-maximum reaching to 0.22THz. Relatively weaker absorption peak (shown as Figure 4) of explosive CL-20 at 1.66THz has been covered up in mixed samples. The absorption peak positions of co-crystal samples are respectively at 0.67 THz, 1.14 THz, 1.62 THz, 1.80 THz and 2.15 THz, which is quite different from single-compound and mixed samples. It shows clearly that in co-crystal process the intermolecular interaction force of two single-compound explosives has been changed and caused the integrated movement behavior change of co-crystal explosive molecules. Compared with single-compound mixture, it has different molecular structure and movement mode.

2.2 THz spectroscopy of polymorphism and phase-transition explosives

Polymorphism and crystal form transformation serve as a distinct characteristic of explosive. Most explosive has more than one crystal structure and can generate crystal form transformation under various external incentive conditions. Due to the change of molecular structure, the same single-compound explosive of different crystal forms will represent different physicochemical characteristics. Furthermore, their crystal lattice size, density and detonation performance are all quite different from each other\[^{[35, 36]}\]. It is of great importance for explosive synthesis, armament design and practical application to carry out single-compound explosive polymorphism representation and crystal transformation process representation. Research group takes HMX and FOX-7 as research targets, and conducts
researches on terahertz spectroscopy of polymorphism explosive \( \alpha \)-HMX and \( \beta \)-HMX as well as FOX-7 material’s crystal form transformation process terahertz spectroscopy in temperature experiment.

2.2.1 Study on Terahertz Absorption Spectrum of Polymorphism HMX

Absorption spectrum of \( \beta \)-HMX and \( \alpha \)-HMX is shown as Figure 4. It can be seen from Figure 4 that HMX of two crystal forms has varying degrees of absorption with the absorption characteristic peak position of \( \beta \)-HMX at 1.79THz and the absorption characteristic peak position of \( \alpha \)-HMX at 0.82THz, 1.51THz and 1.93THz are obvious. Even though the molecular formula of all experimental subjects is \( \text{C}_4\text{H}_8\text{N}_8\text{O}_8 \), the terahertz absorption spectrum of two crystal forms is obviously different from each other.

In order to further analyze the characteristic peak of explosive crystal terahertz absorption spectrum and carry out the absorption frequency calculation of HMX of two crystal forms, the calculation is accomplished by Gaussian09 software and Dmol\(^3\) module of Materials Studio software on basis of Density Functional Theory, acquiring the absorption frequency of HMX of two crystal forms. The calculation of single molecule model is accomplished by Gaussian09 software with its function set as B3LYP/B-31G (d, p); the calculation of molecular model which has varying degrees of symmetry in a same unit cell is accomplished by Dmol\(^3\) software with its settings as PWC and VWN function in Local Density Approximate (LDA) as well as PW91, BP, BLYP, BOP, VWN-BP, RPBE and HCTH function in General Gradient Approximate (GGA). Its basis set is DNP (double numerical with d and p polarization) which is corresponding to B-31G (d, p) setting in Gaussian09. In this paper, the molecular structure parameters used for modeling are all from Cambridge Crystallographic Data Centre (CCDC)\(^{[37]}\). The molecular structure is shown as Figure 5. All the calculation results have no imaginary frequency, showing the stability of final results. The frequency of terahertz wave band in calculation results is shown as Table 2 and Table 3.

![Figure 4. Terahertz absorption spectrum of HMX of two crystal forms.](image)

![Figure 5. Molecular structure diagram of \( \beta \)-HMX (left) and \( \alpha \)-HMX (right).](image)
Table 2. Low-frequency calculated value of \( \beta \)-HMX vibrational frequency (\( \text{cm}^{-1} \))

<table>
<thead>
<tr>
<th>Method</th>
<th>PW</th>
<th>VWN</th>
<th>PW91</th>
<th>BP</th>
<th>BLYP</th>
<th>BOP</th>
<th>VWN-BP</th>
<th>RPBE</th>
<th>HCT</th>
</tr>
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<tbody>
<tr>
<td>B3LYP/6-31G(d,p)</td>
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<td>27.03</td>
<td>26.5</td>
<td>23.53</td>
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<td>22.18</td>
<td>13.85</td>
<td>9.89</td>
<td>13.72</td>
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<tr>
<td>PWC</td>
<td>52.33</td>
<td>54.08</td>
<td>54</td>
<td>30.85</td>
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<td>27.46</td>
<td>33.96</td>
<td>34.74</td>
<td>27.62</td>
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<tr>
<td>VWN</td>
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<td>56.77</td>
<td>56.72</td>
<td>49.73</td>
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<td>48.59</td>
<td>49.5</td>
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<td>PW91</td>
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<td>69.32</td>
<td>69.26</td>
<td>57.02</td>
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<td>58.37</td>
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<tr>
<td>BP</td>
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<td>69.03</td>
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<td>60.62</td>
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<tr>
<td>PBE</td>
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<td>92.21</td>
<td>92.1</td>
<td>83.41</td>
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<tr>
<td>BLYP</td>
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<td>111.72</td>
<td>111.78</td>
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<td>89.25</td>
<td>88.1</td>
<td>83.45</td>
<td>89.2</td>
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</tbody>
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Table 3. Low-frequency calculated value of \( \alpha \)-HMX vibrational frequency (\( \text{cm}^{-1} \))

<table>
<thead>
<tr>
<th>Method</th>
<th>PW</th>
<th>VWN</th>
<th>PW91</th>
<th>BP</th>
<th>BLYP</th>
<th>BOP</th>
<th>VWN-BP</th>
<th>RPBE</th>
<th>HCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/6-31G(d,p)</td>
<td>28.65</td>
<td>27.58</td>
<td>27.47</td>
<td>17.96</td>
<td>4.47</td>
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<td>18.98</td>
<td>7.64</td>
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<tr>
<td>PWC</td>
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<td>29.16</td>
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<td>33.76</td>
<td>37.91</td>
<td>16.26</td>
<td>15.06</td>
</tr>
<tr>
<td>VWN</td>
<td>53.91</td>
<td>65.76</td>
<td>65.6</td>
<td>61.69</td>
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<td>61.29</td>
<td>46.69</td>
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<tr>
<td>PW91</td>
<td>55.07</td>
<td>74.5</td>
<td>74.54</td>
<td>63.51</td>
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<td>62.74</td>
<td>52.95</td>
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<td>47.71</td>
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<td>BP</td>
<td>72.53</td>
<td>83.51</td>
<td>83.52</td>
<td>67.44</td>
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<td>54.28</td>
<td>48.51</td>
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<tr>
<td>BLYP</td>
<td>97.97</td>
<td>95.36</td>
<td>95.45</td>
<td>87.29</td>
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<td>79.94</td>
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<tr>
<td>BOP</td>
<td>105.66</td>
<td>122.2</td>
<td>122.24</td>
<td>95.38</td>
<td>75.47</td>
<td>96.67</td>
<td>93.03</td>
<td>76.89</td>
<td>75.62</td>
</tr>
</tbody>
</table>

Figure 6. Comparison of terahertz absorption spectrum experimental result (line graph) and calculated result (bar graph) of HMX of two crystal forms.

Figure 6 shows the comparison of absorption frequency calculated result and terahertz absorption spectrum achieved in experiment of HMX of two crystal forms. As for \( \beta \)-HMX, the results on basis of HCTH, VWN-BP, BOP and BP function of GGA are quite consistent with the achieved terahertz absorption spectrum characteristic peak at 1.79THz in experiment with little deviation; as for \( \alpha \)-HMX, the achieved characteristic peaks at 0.82THz and 1.51THz in experiment accord with the B3LYP/6-31G(d,p) calculated results in Gaussian09, but achieved characteristic peak at 1.93THz is quite close to the frequency calculated by HCTH, VWN and PWC function.

The comparison also shows that theoretical calculation results can not be fully consistent with the experimental results for many reasons. Firstly, density functional calculation is based on ab initio theory, so all the results are structure parameters of molecular model under absolute zero condition. The calculated absorption frequency is actually different from the real experimental environment; secondly, for the reason that the corresponding absorption frequency of intermolecular weak interaction, macromolecular skeletal vibration and lattice low-frequency vibration in crystal is generally located at terahertz wave band, the terahertz absorption spectrum achieved in experiment should be the
synthetic action results of intermolecular vibration, intermolecular interaction, lattice vibration and phonon mode. However, the theoretical modeling in this paper mainly bases on unimolecular mode and polymolecular mode with varying symmetry in unit cell, taking no full consideration of intermolecular interaction and lattice movement; in addition, the function calculation deviation of multiple density functional theory also shows that choosing different functions and adopting different estimation ways will acquire different calculation results.

By using software visualization module, research group also identifies the terahertz absorption spectrum characteristic peak forming reason of β-HMX and α-HMX crystal. The results show that the characteristic absorption peak of β-HMX crystal at 1.79THz originates from the movement of two nitro in molecular structure; of three terahertz spectrum absorption peaks of α-HMX crystal, 0.82THz absorption frequency is formed by the symmetry swing of two nitro, 1.51THz absorption frequency is formed by the symmetry swing of another two nitro, but 1.93THz absorption frequency is formed by nitro swing, twist, and swing of C-H keys. Identified situations of each characteristic peak are shown as Figure 7.

![Terahertz Spectrum Absorption Characteristic Peak of HMX Molecules of Two Crystal Forms](image)

Figure. 7. Identified Terahertz Spectrum Absorption Characteristic Peak of HMX Molecules of Two Crystal Forms.

2.2.2 Study on terahertz absorption spectrum of FOX-7 with temperature load in phase-transition process

The temperature load range in experiment is between 298K and 393K. In sustained heating process, the terahertz absorption spectrum of FOX-7 within the THz frequency of 0.2~2.2 is shown as Figure 8. When the temperature is 298K, FOX-7 presents two terahertz absorption characteristic peaks which are respectively at 1.59 THz and 2.13THz. When the temperature is 384K, the absorption spectrum is changed and a new absorption characteristic peak appears at 1.12 THz, showing the crystal transfer. That is to say FOX-7 has been changed from α crystal form to β crystal form. As sample temperature increases, the peak intensity of 1.12 THz characteristic peak is gradually increasing and the peak width also tends to be wider. In the absorption spectrum detected at different temperature spots, no frequency shift happens at 2.13THz peak position, but the original 1.59 THz peak position is confronted with certain frequency shift because of temperature influences. Here are many reasons. Firstly, as the sample temperature increases, samples’ crystal structure will be changed. Figure 9-a and 9-b are the calculated dihedral angles of the same face after sample crystal geometry
optimization when the temperature is respectively 298K and 393K. The dihedral angles of α and β crystal form are respectively -6.212° and 22.564°. It is obvious that the change of crystal form will cause different absorption spectrum represented by sample molecular vibration. Secondly, in the process of crystal type transform from α to β, perssad component (-NO₂ or -NH₂) change will possibly cause the reducing molecular structure symmetry and further influence the absorption strength of absorption peak. In addition, in molecular vibration process, dipole moment change will bring about the change of absorption band. When the sample temperature falls to 298 K, the terahertz absorption spectrum reversible situation of FOX-7 is not quite different from that before temperature rise as Figure 10, showing that the samples’ crystal transfer process from α to β is reversible.

Figure 8. Absorption spectrum of FOX-7 under different temperatures.

Figure 9. Dihedral angles of FOX-7 of different crystal forms a: α-FOX-7, b: β-FOX-7

Gaussian software is also used for the vibrational frequency calculation of FOX-7 of two crystal forms. The value, which is lower than 2.2 THz in frequency calculation results, is shown as Table 4. Through comparison, it is found that the calculated rate of FOX-7’s two crystal forms is consistent with detected data in experiment very well. The 1.123THz, 1.762THz, and 2.134THz positions of β crystal form in calculation frequency are respectively corresponding to the 1.12 THz, 1.64 THz, and 2.13 THz in experimental results. The 1.584 THz and 2.090 THz positions of α crystal form in calculation frequency are consistent with the absorption peaks at 1.59 THz and 2.13 THz in experimental data very well.

Table 4. Vibrational frequency calculation value of FOX-7 (THz)

<table>
<thead>
<tr>
<th>Crystal Form</th>
<th>Basis Set</th>
<th>Calculation Frequency (THz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-FOX-7</td>
<td>BP/DNP</td>
<td>1.016, 1.123, 1.203, 1.261, 1.762, 2.014, 2.046, 2.134, 2.315, 2.448, 2.496</td>
</tr>
<tr>
<td>α-FOX-7</td>
<td>VWN/DND</td>
<td>1.153, 1.524, 1.556, 1.584, 1.917, 2.090, 2.200, 2.223, 2.388, 2.494</td>
</tr>
</tbody>
</table>

With help of Materials Studio 6.0 visual module, the terahertz absorption characteristic peak forming mechanism of FOX-7 of two crystal forms is indentified. The identified absorption peak is shown as Table 5. Figure 11 is the visual mode of absorption peak with the
size of green arrow representing the strength of perssad vibration. Compared with experimental value at 1.64 THz, frequency calculation value at 1.762 THz has relatively big deviation, so the analysis of vibrational mode remains to be further discussed.

<table>
<thead>
<tr>
<th>Temperature (Crystal Form)</th>
<th>Calculation Frequency(THz)</th>
<th>Vibration Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>298K (α-FOX-7)</td>
<td>1.59</td>
<td>swing of -NO₂ and -NH₂</td>
</tr>
<tr>
<td></td>
<td>2.09</td>
<td>swing and twist of -NO₂ and -NH₂</td>
</tr>
<tr>
<td>393K (β-FOX-7)</td>
<td>1.123</td>
<td>swing of -NO₂ and -NH₂</td>
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<tr>
<td></td>
<td></td>
<td>twist of -NO₂ and N-H</td>
</tr>
<tr>
<td></td>
<td>1.762</td>
<td>-NH₂ swings around C atom</td>
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<tr>
<td></td>
<td></td>
<td>twist of -NO₂ and -NH₂</td>
</tr>
<tr>
<td></td>
<td>2.134</td>
<td>swing of -NO₂</td>
</tr>
</tbody>
</table>

Figure. 11. Identified terahertz characteristic peak of FOX-7 before and after crystal form change under Temperature of 384K

3. Conclusion

Terahertz wave with unique penetration performance and structural characterization of material structure has vital application prospect in fields like fine structural characterization of energetic material, dangerous substance detection, nondestructive testing, etc. In explosive mixed crystal, phase-transition crystals and co-crystal, terahertz spectrum can effectively represent explosive molecular vibration and its behavior, and provide fine structural model for explosive molecular designing and actual application. Time-domain spectroscopy system with effective range as 0.1 THz ~ 2.2 THz has been used for terahertz spectrum researches of multiple single-compound explosive, polymorphism explosive and co-crystal explosive. The results show that each elemental crystal has different terahertz absorption peak but mixed crystal explosive absorption peak is the superposition of various single-compound explosive absorption peaks. However, co-crystal explosive represents its absorption characteristics different from single-compound explosive. Under temperature of 384K, FOX-7 explosive crystal has an obvious crystal phase transformation from α to β. The theoretical calculation of multiple single crystals, polymorphism and crystal transformation explosive has been carried out on basis of density functional theory. In addition, the molecular vibration spectrum under theoretical calculation mode is compared with experimental spectrum, and the terahertz spectrum of explosive is also analyzed. Results indicate that the unique absorption peak forming reason of explosive at terahertz wave band is closely linked with molecular vibration and rotary movement.
References


