Investigation of the Phase Transitions of FOX-7 by Temperature-dependent FTIR Spectroscopy

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Abstract：Two kinds of phase transitions ($\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$) of the insensitive high explosive, 1,1-diamino-2,2-dinitroethylene(FOX-7), have been investigated by temperature-dependent Fourier transform infrared(FTIR) spectroscopy, and the effects of intermolecular H-bonding interactions and molecular structure in the phase transitions of FOX-7 were discussed. The frequency of ν_{11}[$NH_2(\nu_{as})$] and ν_{10}[$NO_2(\nu_s)$] shifts about 20 cm^{-1}, together with the loss of ν_{18}[$C-NO_2(\nu)$] in the range of 55 ℃ to 122 ℃, while ν_{12}[$C-NH_2(\nu)$] disappears and ν_{20}[$NO_2(\omega)$] transforms to another broad peaks in the range of 122 ℃ to 190 ℃. The analytical results of the IR spectra indicate that intermolecular hydrogen bonding interactions change in the phase transitions of the FOX-7, which cause the changes of the molecular structure. Moreover, in the process of $\alpha \rightarrow \beta$ transition, the changes of H-bonding length with increasing temperature are not consistent with the linear thermal expansion formula, and ν_{11},ν_4[Fermi resonance between the $NH_2(\nu_{as})$ and the overtone mode of the NH_2 scissor ($2\nu_5$)],ν_7 and ν_{10}[$NO_2(\nu_{as})$] show special frequencies, which are different from those of α and β-FOX-7. The results confirm the transition state in the $\alpha \rightarrow \beta$ transition.

Key words：phase transition；1,1-diamino-2,2-dinitroethylene(FOX-7)；temperature-dependent Fourier transform infrared (FTIR)；molecular structure；H-bonding

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1　Introduction

In the field of high explosives, many efforts have been focused on exploring more powerful, safer and environmentally friendly explosives. 1,1-diamino-2,2-dinitroethylene ($C_2H_4N_4O_4$), commonly referred to FOX-7, is a novel high explosive[1]. Compared with the most widely used and powerful explosive 1,3,5-trinitro-1,2,4-triazacyclohexane(RDX), FOX-7 combines two important aspects, i.e., high performance and low sensitivity[2]. However, FOX-7 possesses several polymorphs[3], which suppresses its application. It is well known that phase transitions of energetic materials commonly observed under high temperature directly affect the stability and performance[4]. Indeed, the most stable polymorph at ambient conditions is always sought owning to its highest detonation veloci-

ty[5]. Moreover, phase transitions induced by high temperature frequently result in crystal defects which can sensitize the explosive by forming hot spots and super-rate burning[5]. Therefore, developing a deeper understanding of phase behaviors can lead to valuable insight into the complex interplay of intra- and inter-molecular interactions which are responsible for shock-initiated chemical reactions.

Crystalline FOX-7 has three polymorphs, i.e., α, β and γ. The most stable phase at room temperature is α-FOX-7, and it can be converted to other polymorphs at higher temperatures, and upon cooling the explosive directly but incompletely restores to the α phase[6]. The phase transition behaviors of FOX-7 have been explored by X-ray diffraction methods, Raman, and thermal techniques[6−10]. However, the phase transition mechanism is still confusion. The effects of H-bonding and molecular structure might be the key for understanding the polymorphism. But the information on the behavior of the related H-bonding vibrations is not observed in FOX-7[11]. Indeed, the stability of FOX-7 mainly depends on the strong H-bonds between nitro oxygen atoms and amino hydrogen atoms. Furthermore, detailed analysis of the changes of H-bonding properties of the FOX-7 crystals under extreme conditions could provide important insight for understanding the detonation behavior of FOX-7 at molecular level[12]. Evers[7] and

Crawford[8] have investigated the molecular structure and the effects of H-bonding of FOX-7 by X-ray single crystal methods. But few tools and techniques including X-ray single crystal diffraction could visually present the changes of H-bonding and molecular structure with increasing temperature in a single figure.

Recently, temperature-dependent Fourier transform infrared (FTIR) spectroscopy is recognized as a powerful technique for *in-situ* characterization of phase transitions of energetic material. Temperature-dependent FTIR spectroscopy could give information about intermolecular vibrational modes mediated by the H-bonding and access knowledge about the structure and vibrational dynamics of solids[13-15]. Pressure-induced changes of FOX-7 were observed by using FTIR spectroscopy[9], and the effects of H-bonding and molecular structure with pressures were discussed. Temperature-induced changes were investigated by Bishop[16] using IR. The H-bonding effects of FOX-7 with temperatures were investigated but the changes of molecular structure were ignored. Thus, we sought to conduct a FTIR study of FOX-7 to observe and compare the effects of H-bonding and molecular structure on molecular vibrations with temperatures and to investigate the phase transitions of FOX-7. This study would also offer the valuable insight into the interesting secondary explosive behaviors under high temperature conditions.

2 Experimental

The FOX-7 samples were provided by Institute of Chemical Materials, Chinese Academy of Engineering Physics. FTIR spectra were taken with KBr pellets in Model Nicolet 6700 spectrograph. The resolution was 1 cm^{-1}, and the scan range was 400 – 4000 cm^{-1}. Spectra were recorded during heating from 55 ℃ to 190 ℃ at a constant heating rate of 5 ℃·min^{-1}. Then, the spectra were obtained during the cooling process.

Powder X-ray diffraction(XRD) patterns were recorded on a Bruker D8 Advance with a CuK_α radiation ($\lambda = 1.5406$ Å), the voltage and current applied are 40 kV and 40 mA, respectively. Samples of FOX-7 were heated from 55 ℃ to 190 ℃,

and data were collected from 5° to 60° (2θ) with an increment of 0.02° and a continuing time of 0.1 s for each increment.

3 Results and Discussion

3.1 $\alpha \rightarrow \beta$ Phase Transition

3.1.1 Bands Assignments for Vibrational Modes

The temperature-dependent FTIR spectra of FOX-7 heating from 55 ℃ to 122 ℃ in the region of 3500 – 3150, 1670 – 970 cm^{-1} and 900 – 400 cm^{-1} are displayed in Fig. 1. As shown in Fig.1a, ν_1, ν_2 and ν_3 have the tendency to shift toward higher wavenumber when the temperature increases. As shown in Fig. 1b, ν_5(1632 cm^{-1}) shifts toward lower wavenumber with increasing temperature. Subsequently, ν_6 overlaps or incorporates with ν_5. The frequencies of bands appearing at 1526 (ν_7), 1470 (ν_8) and 1394 (ν_9), 1350 (ν_{10}) cm^{-1} remain nearly constant during heating (see in Fig.1b). Generally speaking, the frequencies of FOX-7 in most vibrational bands show little changes during heating in the range of 55 ℃ to 105 ℃. The FOX-7 molecules show strong intermolecular H-bonds within the wave-shaped layers. When the H-bonding is reduced or grows weaker, the stretching vibrational band usually shifts to higher frequency, whereas the deformation vibrational band usually moves to lower frequency[17]. According to the frequency shifts of H-bonding interaction, vibrational modes are clearly assigned[18-24], listed in Table 1. Besides, ν_4 can be assigned to Fermi resonance between the NH_2 (ν_{as}) and the overtone mode of the NH_2 scissor ($2\nu_5$), and the vibrational mode at ~1620 cm^{-1} can be identified as a newly formed peak, which is assigned to Fermi resonance between NH_2 and NO_2 scissoring vibrations[25]. In contrast to other H-bonded energetic materials, such as 1,3,5-triamine-2,4,6-trinitrobenzene (TATB)[17], the weakening of H-bonding effect in most vibrational bands is inconspicuous with increasing temperature below 105 ℃.

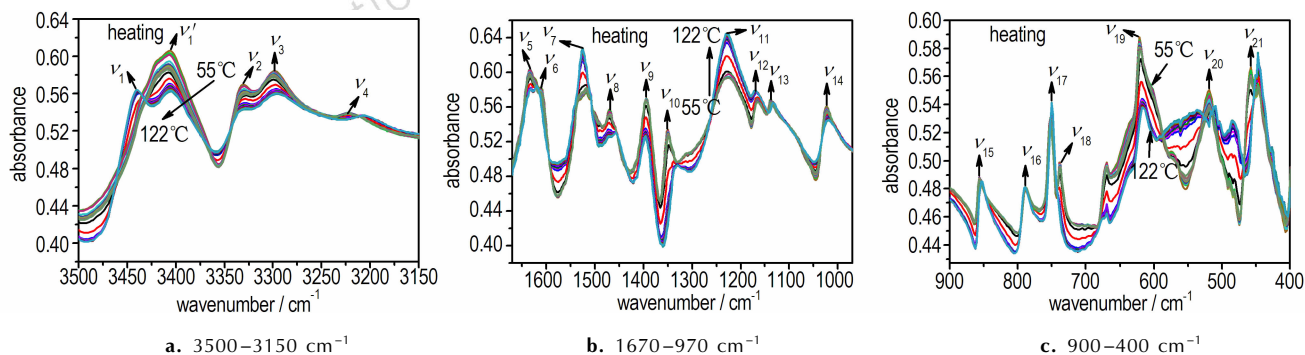**a.** 3500–3150 cm^{-1} **b.** 1670–970 cm^{-1} **c.** 900–400 cm^{-1}

Fig. 1 FTIR spectra of FOX-7 while the temperature increases from 55 ℃ to 122 ℃

Table 1　Assignments of vibrational bands in spectra of FOX-7

band/cm^{-1}	vibration modes	wavenumber/cm^{-1}	band/cm^{-1}	vibration modes	wavenumber/cm^{-1}
$\nu_1{'}$	NH$_2$(ν_{as})	3406	$\nu_{11}\,\nu_{12}\,\nu_{13}$	C—NH$_2$(ν)	1226,1170,1137
$\nu_2\,\nu_3$	NH$_2$(ν_s)	3329,3298	ν_{14}	NH$_2$(ρ)	1023
ν_4	Fermi resonance	3223	ν_{15}	NO$_2$(γ)	855
ν_5	NH$_2$(γ)	1632	$\nu_{16}\,\nu_{17}\,\nu_{18}$	C—NO$_2$(ν)	788,750,737
ν_6	C＝C(ν)	1610	ν_{19}	NH$_2$(ω)	621
$\nu_7\,\nu_8$	NO$_2$(ν_{as})	1526,1470	ν_{20}	NO$_2$(ω)	518
$\nu_9\,\nu_{10}$	NO$_2$(ν_s)	1394,1350	ν_{21}	NO$_2$(ρ)	458

Note：ν=stretching, ν_{as}=asymmetric stretching, ν_s=symmetric stretching, γ=scissoring, ρ=rocking, ω=wagging.

3.1.2　Effects of Intermolecular Hydrogen Bonding Interaction and Molecular Structure

Above 105 ℃, the NH$_2$(ν_{as}) peak near 3443 cm^{-1} abruptly shifts to higher wavenumber, as shown in Fig.1a. The intensity of NO$_2$(ν_s) ν_{10} sharply decreases and shifts toward lower wavenumber (Fig.1b). As shown in Fig.1c, ν_{18} disappears above 105 ℃. Spectral bands in the lower spectral range (650−467 cm^{-1}) undergo significant changes in the range of 100 ℃ to 120 ℃. The smoothing ν_{20} is replaced by a broad medium strong peak above 105 ℃. The band at 458 cm^{-1} vanishes, and a peak at 447 cm^{-1} grows at about 111 ℃ and reaches the same intensity of the band near 458 cm^{-1}. FTIR spectra of FOX-7 experience some abrupt changes on heating at 105 ℃, indicating that the $\alpha\rightarrow\beta$ transition occurs.

The molecular conformations and packing arrangements of α and β polymorphs can provide some insight. The α and β-FOX-7 have similar structures of two-dimensional wave-shaped layers (CCDC, SEDTUQ03 and SEDTUQ06), as shown in Fig.2. However, heating of the FOX-7 molecules to 120 ℃ flattens the wave-shaped layers. Within the layers, there are strong H-bonds. Indeed, the spectral changes of

a. α-FOX-7(25 ℃)

b. β-FOX-7(120 ℃)
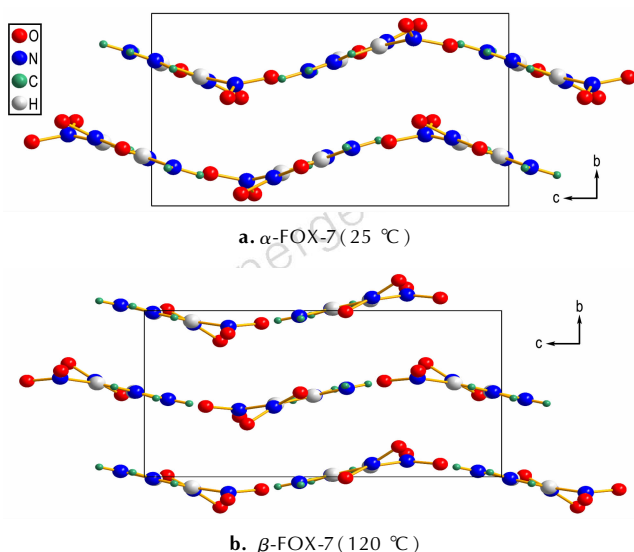
Fig.2　View along a axis of α-FOX-7 at 25 ℃ and β-FOX-7 at 120 ℃

NH$_2$(ν_{as}) at 3443 cm^{-1} are attributed to the restructing of the H-bonding network in the $\alpha\rightarrow\beta$ phase transition[4]. The C＝C and amino nitrogen atoms form a molecular plane, and the nitro oxygen atoms deviate strongly from the molecular plane. The results have been previously reported[8] that the NO$_2$ twist angle does not vary significantly on heating up to 100 ℃, but it increases abruptly above 100 ℃. The unique spectra signature of ν_{10} is likely associated with changes of the NO$_2$ twist angle when the temperature increases. The analytical results of the IR spectra indicate that intermolecular hydrogen bonding interactions change in the phase transitions of the FOX-7, which cause the changes of the molecular structure. The results confirm that the $\alpha\rightarrow\beta$ is a displacive transition with minor structural distortions[8].

3.1.3　Transition State

Most materials experience relatively modest expansions with increasing temperature, resulting from the increasing anharmonic vibration amplitudes of the ingredient atoms or molecules[26]. The degree of linear thermal expansion has been quantified using a coefficient defined as $\alpha=(l_T-l_0)/(l_0(T-T_0))$[27], where l_T is the axis length at the final temperature, and l_0 is the axis length at the initial temperature. The average linear thermal expansion coefficients of α-FOX-7 are $\alpha_a=2.18\times10^{-5}$℃$^{-1}$, $\alpha_b=12.71\times10^{-5}$℃$^{-1}$ and $\alpha_c=4.29\times10^{-5}$℃$^{-1}$. The average linear thermal expansion coefficients of β-FOX-7 are $\alpha_a=0.84\times10^{-5}$℃$^{-1}$, $\alpha_b=16.89\times10^{-5}$℃$^{-1}$ and $\alpha_c=3.85\times10^{-5}$℃$^{-1}$[28]. Similarly, the H-bonding length is formulated as $l_T=l_0+\alpha\Delta T$[27], where l_T is the H-bonding length at final temperature, l_0 is the H-bonding length at initial temperature, α is the coefficient of thermal expansion, and ΔT is the change of temperature. Here, the value of α for α- and β-FOX is almost equal to 1×10^{-5}℃$^{-1}$. The intermolecular H-bonds of FOX-7 at 25 ℃ and 120 ℃ are presented in Fig.3, and their length are displayed in Table 2. The average H-bonds length between FOX-7 molecules is 2.58 Å at 25 ℃ and 2.76 Å at 120 ℃. We find that $l_0+\alpha\Delta T=$ $(2.58+1\times10^{-5}\times95)$ Å≈2.58Å$=l_0\neq l_T=2.76$ Å. As described in Section 3.1.1, the length of H-bonding remains constant

during heating from 55 to 100 ℃. We conclude that a intermediate l_{trans} occurs in the $\alpha \rightarrow \beta$ transition, as is followed: $l_T = l_0 + \alpha \Delta T + l_{trans}$, where l_T is the H-bonding length at final temperature, l_0 is the H-bonding length at initial temperature, α is the coefficient of thermal expansion, ΔT is the change of temperature, l_{trans} is the H-bonding length incremental resulting from the phase transition and increase gradually when the temperature increases from 100 ℃ to 110 ℃. Besides, the evolution of selected peaks frequencies with increasing temperature is presented. As shown in Fig. 4, the frequencies of FOX-7 in all

vibrational bands show abrupt changes during heating in the range of 100 ℃ to 110 ℃. Three or more points are observed in the range of 100 ℃ to 110 ℃, and each one of them is neither α-FOX-7 nor β-FOX-7, which giving more evidence of the occurrence of a transition state in the phase transition. It is the transition state that makes the change of H-bonding length with temperatures, not consistent with the formula ($l_T = l_0 + \alpha \Delta T$). The intermediate should be a necessary step in the transition from α-FOX-7 to β-FOX-7. Traditionally, phase transition is considered to be one-step reaction.
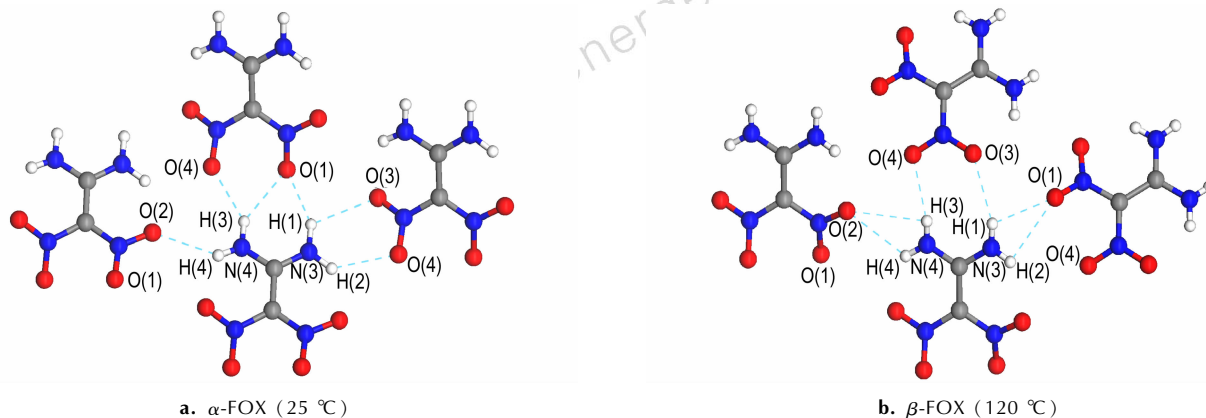

a. α-FOX (25 ℃)

b. β-FOX (120 ℃)

Fig. 3   H-bonding interactions of FOX-7

Table 2   H-bonds length between FOX-7 molecules at 25 ℃ and 120 ℃

D—H⋯A	α-FOX (25 ℃)			β-FOX (120 ℃)		
	D—H/Å	H⋯A/Å	D⋯A/Å	D—H/Å	H⋯A/Å	D⋯A/Å
N(4)—H(4)⋯O(2)	0.849	2.341	3.027	0.862	2.483	2.945
N(4)—H(3)⋯O(4)	0.904	2.143	2.921	0.795	2.209	2.979
N(4)—H(3)⋯O(2)	0.904	3.105	3.027	0.795	2.782	2.945
N(4)—H(3)⋯O(1)	0.904	2.390	3.193	0.795	4.157	3.925
N(3)—H(1)⋯O(1)	0.945	2.145	3.016	0.793	2.532	2.988
N(3)—H(1)⋯O(3)	0.945	2.446	3.008	0.793	2.396	3.156
N(3)—H(2)⋯O(4)	0.943	2.291	3.013	0.805	2.703	3.414
N(3)—H(2)⋯O(1)	0.956	3.771	3.016	0.805	2.795	2.988

3.2 $\beta \rightarrow \gamma$ **Phase Transition**

With further application of temperature to 190 ℃, spectra were acquired and displayed in Fig. 5. In β-phase, the two NH$_2$(ν_{as}) peaks are well separated and dramatically shifted to higher frequencies. As temperature increases, the two peaks are broad and strongly overlapped with each other in the range of 3500-3350 cm^{-1} as well as being accompanied by the loss of NH$_2$(ν_s) modes at ~3329 cm^{-1}. NO$_2$-related vibrations such as ν_{12} and ν_{20} exhibit significant changes, indicating that the γ transition was obtained. Compared to the changes observed in the $\alpha \rightarrow \beta$ transition, the frequencies of most vibrational bands remain nearly constant in the $\beta \rightarrow \gamma$ transition, implying no further weakening of the H-bonding network. The changes in NO$_2$-related vibrations are smaller during the $\beta \rightarrow \gamma$

transition than the $\alpha \rightarrow \beta$ transition. The previous results[9] showed that the displacement of the nitro groups with respect to the molecular plane remains invariant in β- and γ-FOX-7. FTIR spectra of FOX-7 exhibit minor changes in the $\beta \rightarrow \gamma$ transition. A combination of stable H-bonding network and structural similarities is responsible for subtle differences in the FTIR spectra for two polymorphs over the whole temperature range from 122 ℃ to 190 ℃.

Standard FTIR spectra of α, β and γ polymorphs of FOX-7 are identified and confirmed by X-ray diffraction patterns (see in Fig. 6). The FTIR spectra of α-, β- and γ-FOX-7 exhibit significant changes including NH$_2$ and NO$_2$-related vibrations such as ν_{12}, ν_{18}, ν_{20} and ν_{21}. The former is due to the restructing of the H-bonding network, and the latter is due to the changes in the displacement of nitro groups with respect to the

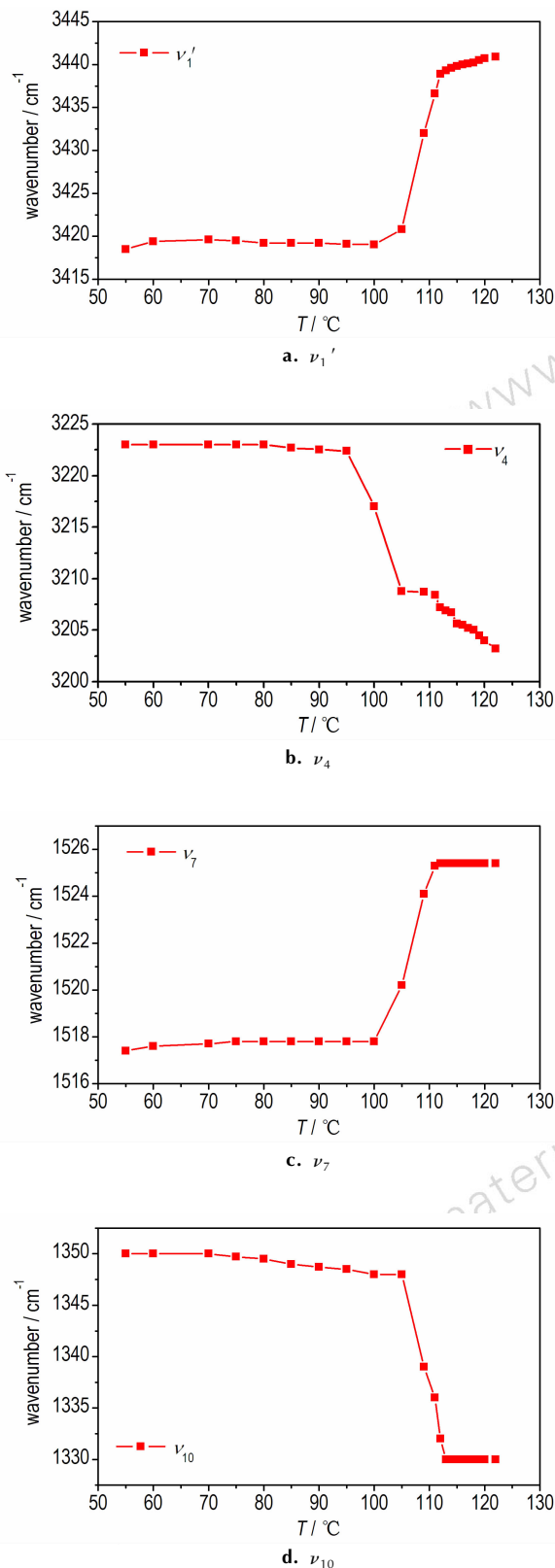molecular plane. The characteristic FTIR absorption bands of each phase of FOX-7 are presented in Table 3.

a. $\nu_1{}'$

b. ν_4

c. ν_7

d. ν_{10}

Fig. 4 Peak positions of different vibrational modes as a function of temperature

Table 3 The characteristic FTIR absorption bands of each phase of FOX-7

	3440 cm^{-1} NH$_2$(ν_{as})	3329 cm^{-1} NH$_2$(ν_s)	1170 cm^{-1} C—NH$_2$(ν)	737 cm^{-1} C—NO$_2$(ν)	650–467 cm^{-1} (ν_{19},ν_{20}) NH$_2$(ω), NO$_2$(ω)
α	×	√	√	√	sharp peaks
β	√	√	√	×	broad peaks
γ	√	×	×	×	another broad peaks

Note: √ represents the emergence of peak, × represents the disappearance of peak.
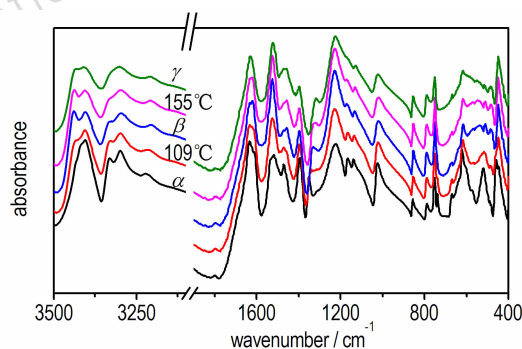
Fig. 5 FTIR spectra of FOX-7 at five different temperatures (α-FOX-7 at 55 ℃; β-FOX-7 at 122 ℃; γ-FOX-7 at 190 ℃)
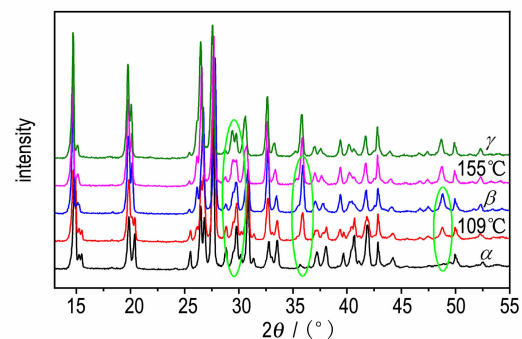
Fig. 6 XRD patterns of FOX-7 at five different temperatures (α-FOX-7 at 55 ℃; β-FOX-7 at 122 ℃, γ-FOX-7 at 190 ℃)

4　Conclusions

Temperature-dependent FTIR spectroscopy has been employed to study the phase transitions of FOX-7 in real time. The main conclusions are as follows:

(1) In the process of phase transitions of the FOX-7, intermolecular hydrogen bonding interactions change, which caused the changes of the molecular structure.

(2) The transition state was confirmed by the special thermal expansion properties of H-bonding length and the special frequencies of $\nu_1{}'$, ν_4 [Fermi resonance between the NH$_2$(ν_{as}) and the overtone mode of the NH$_2$ scissor ($2\nu_5$)], ν_7 and ν_{10} [NO$_2$(ν_{as})] in the $\alpha\rightarrow\beta$ transition with increasing temperature. α-FOX-7 does not directly transforms to β-FOX-7, the transition state should be a necessary step.

(3) Standard FTIR spectra of α, β and γ-FOX-7 were iden-

tified and confirmed *in-situ* by powder X-ray diffraction (XRD). Several characteristic peaks of ν_{12}[C—NH$_2$(ν)], ν_{18}[C—NO$_2$(ν)] and ν_{20}[NO$_2$(ω)] can be used to identify each phase of FOX-7.

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变温红外光谱法研究 FOX-7 的相变

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摘　要：采用变温红外光谱法对高能钝感炸药1,1-二氨基-2,2-二硝基乙烯(FOX-7)$\alpha\rightarrow\beta$ 和 $\beta\rightarrow\gamma$ 两种晶型转变进行了研究,讨论了 FOX-7 相变过程中的分子间氢键作用和分子结构。55～122 ℃,ν_{11}[NH$_2$(ν_{as})]和 ν_{10}[NO$_2$(ν_s)]频率移动为 20 cm^{-1}左右,ν_{18}[C—NO$_2$(ν)]消失；122～190 ℃,ν_{12}[C—NH$_2$(ν)]消失,ν_{20}[NO$_2$(ω)]转变为新的宽峰。红外光谱结果表明：在 FOX-7 相变过程中,分子间氢键作用发生改变,分子结构改变。此外,随着温度的升高,在 $\alpha\rightarrow\beta$ 的相转变中,氢键长度变化不符合线性热膨胀公式,并且 ν_{11}、ν_4[NH$_2$(ν_{as})] 与 $2\nu_5$ NH$_2$(γ)的费米共振）、ν_7[NO$_2$(ν_{as})]和 ν_{10} 等谱带表现出与 α-和 β-FOX-7 均不同的特征频率,表明 FOX-7 在 $\alpha\rightarrow\beta$ 相变过程中要经历一种过渡态。

关键词：相变；1,1-二氨基-2,2-二硝基乙烯(FOX-7)；变温红外光谱；分子结构；氢键

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