# **Electronic Supplementary Information:**

Predicting the impact sensitivity of a polymorphic high explosive: the curious case of FOX-7

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# CONTENTS

S1. Computational Details p	g 2
S2. Experimental Details	g 3
S3. Vibrational Up-Pumping – theoretical framework p	og 4
S4. Setting Initial Conditions for Up-Pumping p	og 6
S5. Up-Pumping of FOX-7 polymorphs p	og 7
S6. Impact Sensitivity Measurements p	og 9
S7. References p	og 10

## **S1** Computational Details

Input structures were taken from experimentally determined geometries. Both  $\alpha$ - and  $\beta$ -FOX-7 structures were obtained from the Cambridge Crystallography Database (CCDC): REF (SEDTUQ03) and (SEDTUQ06). The coordinates for  $\gamma$ -FOX-7 were extracted from the low-temperature crystal structure reported in Ref<sup>1</sup>. All calculations were performed in the frame of plane wave Density Functional Theory (DFT) as implemented in CASTEP v19.<sup>2</sup> The electronic structure was sampled on a *k*-point mesh with spacing of approximately 0.05 A<sup>-1</sup>, and expanded in plane waves to a kinetic energy cut-off of 1200 eV. Dispersion interactions were accounted for using the Grimme D2 correction, which has been previously demonstrated to perform well for FOX-7.<sup>3–5</sup> The input structures were fully relaxed until residual atomic forces <  $1 \times 10^{-4}$  eV.Å<sup>-1</sup>, wave function self-consistency <  $1 \times 10^{-12}$  eV, and lattice vectors stresses < 0.01 GPa.

Phonon calculations were performed using the linear response method, as implemented in CASTEP v19.<sup>6</sup> For  $\gamma$ -FOX-7 a fine integration grid of 63.1626 Å<sup>-1</sup>, with grids of 31.5813 Å<sup>-1</sup> used for the other polymorphic forms. Phonon density of states were generated using a Gaussian smearing of 5 cm<sup>-1</sup>.

In all cases, the PBE-D2 relaxed structures for FOX-7 polymorphs, **Table S1.1**, are in good agreement with experiment. The structures for  $\alpha$  and  $\gamma$ -FOX-7 differ by < 3% from the low temperature experimental data, with  $\beta$ -FOX-7 within 4% of the 403 K structure.

**Table S1.1** Comparison of simulated and experimental crystallographic lattices for FOX-7 polymorphs. Experimental data are taken for structures at  $\alpha$ -FOX-7 (200 K),<sup>7</sup>  $\beta$ -FOX-7 (403 K),<sup>1</sup> and  $\gamma$ -FOX-7 (200 K)<sup>1</sup>. Note that  $\Delta$  values are calculated as  $100 \times (j^{calc} - j^{exp})/j^{exp}$ 

	<i>α</i> -FOX-7	eta-FOX-7	γ <b>-FOX-7</b>
a (calc)	7.01	7.027	13.428
a (exp)	6.9209(7)	6.986(1)	13.354(3)
∆a /%	+1.287	+0.583	+0.554
b (calc)	6.49	6.356	7.024
b (exp)	6.65515(9)	6.660(2)	6.895(1)
∆ <b>b /%</b>	-2.481	-4.565	+1.871
c (calc)	11.31	11.690	12.178
c (exp)	11.2741(14)	11.674(3)	12.050(2)
∆ <b>c /%</b>	+0.3184	+0.137	+1.062
$\beta$ (calc)	90.94	90	112.062
$\beta$ (exp)	90.060(11)	90	111.102(8)
Δβ /%	+0.977	0	+0.864
V (calc)	514.32	522.184	1064.5
V (exp)	511.19(11)	543.1(2)	1035.0(3)
∆ <b>v /%</b>	+0.6123	-3.85	+2.9

## **S2 Experimental Details**

**S2.1 FOX-7 Synthesis.** 1,1-diamino-2,2-dinitroethene (DADNE, FOX-7) was synthesized as outlined in **Scheme S2.1**.<sup>8</sup> 2-Methyl-4,6-pyrimidinedione (6.0 g, 0.05 mol) was dissolved in cooled ( $< 30^{\circ}$ C) concentrated H<sub>2</sub>SO<sub>4</sub> (95%, 45 mL). Dropwise addition of concentrated HNO<sub>3</sub> (99%, 20 mL) was performed whilst maintaining temperatures  $< 20^{\circ}$ C. The solution was stirred for 3 hours. The precipitated material was rinsed with concentrated H<sub>2</sub>SO<sub>4</sub>, and subsequently added to deionized water (100 mL). The hydrolysis reaction was conducted by stirring in water for 2h. The resulting precipitate was analysed by 1H and 13C NMR in DMSO. The solid was analyzed by X-ray powder diffraction.



Scheme S2.1| Synthetic approach to preparation of FOX-7.

A sample of  $\gamma$ -FOX-7 was prepared by heating the above prepared  $\alpha$ -form to 190 °C. The powder was held at this temperature for *ca* 2 h and quench cooled. Successful conversion to  $\gamma$ -FOX-7 was confirmed by X-ray powder diffraction.

#### **S2.2** Powder X-ray Diffraction.

Powder X-ray diffraction (PXRD) patterns were collected in Bragg Brentano geometry using a D2 Phase Diffractometer. Data were collected with  $^{Cu_{K_{\alpha}}}$ radiation. We note that PXRD analysis of the  $\gamma$ -FOX-7 samples used as a control for BAM hammer testing was stored at room conditions for 72 h prior to testing, ensuring handling and storage were not responsible for the observed phase transition.

#### S2.3 Inelastic Neutron Scattering Spectroscopy.

INS spectra were collected using the TOSCA indirect geometry spectrometer at the ISIS Neutron and Muon source.<sup>9–11</sup> Samples (*ca.* 1.5 g) were placed in aluminium sample holders. Samples were cooled to *ca.* 10 K and data over a period of *ca* 3 hr each. Both forward and back-scattered data were accumulated and corrected for scattering from the sample holder and background. All data processing was done using Mantid.<sup>12</sup> INS spectra were simulated using ABINS,<sup>13</sup> as implemented in Mantid. Only first-order quantum events (*i.e.* the fundamentals) are considered in the simulation of INS spectra.

#### S3 Vibrational Up-Pumping – theoretical framework

The up-pumping model used here follow from our recent developments in reference <sup>4</sup> where full details can be obtained. For completeness, we provide a brief overview here.

In this model, we make the assumption that each of the polymorphs of FOX-7 has equivalent compressibility and anharmonic Gruneisen parameters,  $\gamma$ . These are reasonable assumptions particularly in the present context, wherein the crystal packing is largely conserved across the three polymorphic forms, and the energetic molecule is not changed. The initial conditions for up pumping are assumed to follow from adiabatic compression, wherein a crystal at temperature  $T_0$  and volume  $V_0$  is compressed to volume  $V_f$ . The final equilibrium temperature of this adiabatically compressed material  $T_f$  follows,

$$\left(\frac{T_f}{T_0}\right) = \left(\frac{V_f}{V_0}\right)^{-\gamma}$$
 Equation S1

We next assume that the quasi-temperature of the phonon states (which absorb the mechanical shock),  $\phi_{ph}(0)$ , is a state of the bulk temperature-volume curve, such that

$$C_{ph[\phi_{ph}(0) - T_0]} = \int_{T_0}^{T_f} dT C_{tot}(T)$$

Finally, this quasi-temperature is applied to populate all phonon frequencies below the threshold  $\Omega_{max}$  according to the Bose-Einstein statistical populations,

$$n = \left[ \exp\left(\frac{\hbar\omega}{k_B T}\right) - 1 \right]^{-1}$$
 Equation S3

Owing to restrictions in momentum and energy conservation, the excited phonon states (population  $n_{ph}$ , with upper bound  $\Omega_{max}$ ) are initially scattered amongst themselves to populated doorway states (population  $n_d$ , with  $\Omega_{max} < \omega < 2\Omega_{max}$ ) with rate

$$\tau_1 = \Omega^{(2)} \left( \omega = \omega_{\frac{T}{2}} \right) \times [n_{ph} - n_d]$$
Equation S4

The doorway states can subsequently scatter into higher frequency vibrational modes (population  $n_T$ ) to a maximum of  $3\Omega_{max}$  with rate

$$\pi_2 = \Omega^{(2)} \times [n_{ph} + n_d - n_T]$$
 Equation S5

Across each step of up-pumping ( $\tau_1$  and  $\tau_2$ ), the up-pumped density is normalized to the number of independent molecules in the unit cell, to reflect the localized nature of these vibrational states. Finally, the total amount of up-pumped density in the region  $\Omega_{max} < \omega < 3\Omega_{max}$  is taken to be indicative of the relative amount of vibrational energy available to induce chemistry in the system, and hence correlated with impact sensitivity.

As input for our model, we take harmonic vibrational frequencies generated through DFT simulation (see Section S1), to which a Gaussian smearing of 5 cm<sup>-1</sup> is applied. Given that the number of wave vectors k contained within a crystal follow

$$g(k)dk = \frac{V}{2\pi^3} 4\pi k^2 dk$$

**Equation S6** 

**Equation S2** 

the simulated vibrational frequency spectrum is normalized such that

$$\int_{0}^{\Omega_{max}} d\omega g(\omega) = \frac{Z(6+Y)}{V_0}$$

**Equation S7** 

where Z(6+Y) is the number of external lattice vibrations for a unit cell comprising Z molecules, each containing Y amalgamated vibrational modes. This normalization approach better reflects the relative number of states included in the uppumping across systems with differently sized unit cells.

Energetic Material	$\Omega_{max}$ /cm <sup>-1</sup>	$\phi_{\it ph}$ /K
HNB	145	3423.3
<i>€</i> -CL-20	222	3278.0
$\beta_{-HMX}$	196	3487.8
α <sub>-FOX-7</sub>	175	3278.0
$\beta$ -fox-7	160	3278.0
<i>Υ</i> -FOX-7	160	3125.2
α <sub>-NTO</sub>	204	2642.1
ТАТВ	145	4399.1

**Table S3.1** | Characteristic vibrational features of the selected energetic materials. Shock temperatures ( $\phi_{ph}$ ) are taken to be<br/>consistent with our previous model.<sup>4</sup>

#### S4 Setting Initial Conditions for Up-Pumping

The adiabatic heating that initiates up-pumping in EMs follows from the consideration of both the bulk and phonon heat capacities. By considering only the Gaussian broadened zone centre vibrational frequencies, we assume wave vector dispersion (see EM dispersion curves in our previous work<sup>5</sup>) is negligible. However, we do note that heat capacity is dominated by low frequency bands and thus neglecting particularly the acoustic branches at  $k \neq 0$  leads to overestimation of the material heat capacity. Moreover, we do not explicitly consider thermal expansion, leading to additional error in our approximate heat capacity calculations.

Based on the Gaussian broadened phonon density of states (Figure 2 in the main text), the heat capacities used in this work were calculated according to

$$C_v = \int \frac{\partial n}{\partial T} \hbar \omega g(\omega) d\omega$$
 Equation S8

wherein the integral was evaluated across the entire vibrational spectrum, **Table 1** in the main text. The cumulative heat capacities define the relative contribution of the phonon and internal modes to the total heat capacity, **Figure S4.1**. A value of  $C_{tot}$  (**Table 1** in main text) is obtained by integrating **Equation S8** across all vibrational modes, whereas  $C_{ph}$  (**Table 1** in main text) is obtained by placing an upper bound on the integral at  $\Omega_{max}$ . In the high temperature limit, each vibration contributes  $k_BT$  to  $C_{tot}$ . Correspondingly, the theoretical heat capacity for each polymorph is expected to be equal. As shown in **Table 1** of the main text, there is a small underestimation for the value of  $C_{tot}$  for  $\gamma$ -FOX-7, but does not affect the overall up-pumping predictions (see **Table S5.1**)



**Figure S4.1** Cumulative heat capacities (T=3000 K) for the three FOX-7 polymorphs. The position for the total ( $C_{tot}$ ) and phonon ( $C_{ph}$ ) heat capacities are indicated.

## S5 Up-Pumping of FOX-7 polymorphs

Only up-pumped density which is coherent with fundamental vibrational modes can be 'captured'. Correspondingly, the uppumped density captured by  $\Omega^{(2)}$  via Equations S4 and S5 are projected onto the Gaussian-broadened phonon density of states derived from DFT, **Figure S5.1**. Only the populations which map onto the fundamental frequencies between  $\Omega_{max}$  and  $3\Omega_{max}$  are integrated and taken to be indicative of impact sensitivity, **Table S5.1**.



**Figure S5.1** Up-pumped vibrational density for the three polymorphic forms of FOX-7. The total up-pumped density following the two-step process (Equations S4 and S5) is shown on the left, and its projection onto the fundamental modes is given on the right. Note that the projected densities are approximately 1/Z the values of the total up-pumped density, thereby accounting for

projection onto Z isolated molecules. Hence,  $\alpha$  and  $\beta$ -FOX-7 (Z=4) exhibit projected  $\rho^{(2)}$  approximately twice that of  $\gamma$ -FOX-7 (Z=8)

We note in Section S4 that the heat capacity obtained for  $\gamma$ -FOX-7 is lower than expected based on the high temperature limit. Correspondingly, we calculated also the up-pumping value for  $\gamma$ -FOX-7 assuming a corrected heat capacity, equivalent to the  $\alpha$  and  $\beta$  polymorphs, Table S5.1.

**Table S5.1** Integrated up-pumped density in the region  $\Omega_{max} < \omega < 3\Omega_{max}$  for FOX-7 polymorphs using the values of  $\phi_{ph}$  defined according to **Section S4** (see Table 1 main text), alongside the value for  $\gamma$ -FOX-7 based on a corrected heat capacity.

	<i>α</i> -FOX-7	$\beta$ -FOX-7	γ <b>-FOX-</b> 7
Up-pumped density	4.23	3.323	1.192
$\phi_{ph}$ as in Table 1			
Up-pumped density	4.23	3.323	1.196
$\phi_{ph} = 3278 \text{ K}$			

# S6 Impact Sensitivity

Impact sensitivity measurements were conducted using a BAM Fall Hammer BFH-12. Testing was performed using the 1-in-6 go/no-go method, resulting in measurement of the  $E_0$  values for both polymorphs of FOX-7, **Table S6.1-6.2**. Both polymorphic phases exhibit the same impact sensitivity to within the resolution of the instrument.

			Trial Number					
Mass /kg	Height /cm	Energy /J	1	2	3	4	5	6
5	22.4	11.20	~					
	17.8	8.90	~					
1	89.1	8.91	×	×	×	×	×	✓
	79.4	7.94	×	~				
	70.8	7.08	×	×	×	×	×	×

**Table S6.1** BAM impact sensitivity results for  $\alpha$ -FOX-7. A 'go' is indicated as  $\checkmark$  and 'no-go' by **x**.

Table S6.2| BAM impact sensitivity results for  $\gamma$ -FOX-7. A 'go' is indicated as  $\checkmark$  and 'no-go' by  $\varkappa$ .

				Trial Number				
Mass /kg	Height /cm	Energy /J	1	2	3	4	5	6
5	31.6	15.80	✓					
	28.2	14.10	~					
	25.1	12.55	~					
	22.4	11.20	~					
	20	10.00	×	×	✓			
1	89.1	8.91	×	✓				
	79.4	7.94	×	×	×	×	×	×

#### **S5** References

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