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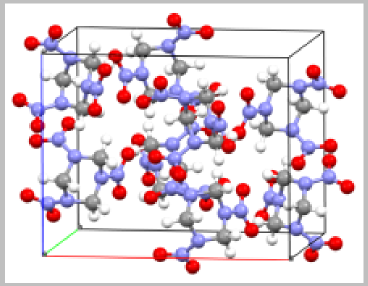

Electronic Properties of RDX Under Compression

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Sandia National Laboratories

APS SCCM 2017

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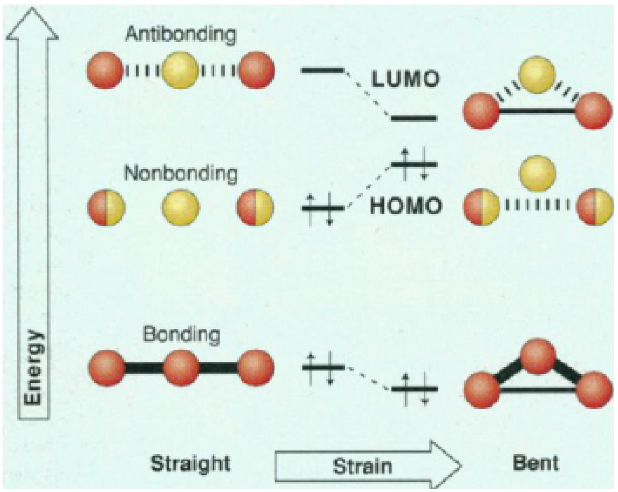
Electronic Properties Under Compression

Changes in electronic structure during shock compression have been investigated as a potential mechanism for initiating or assisting reaction in explosive materials



J. J. Gilman, *Science* **274**, 5284 (1996)

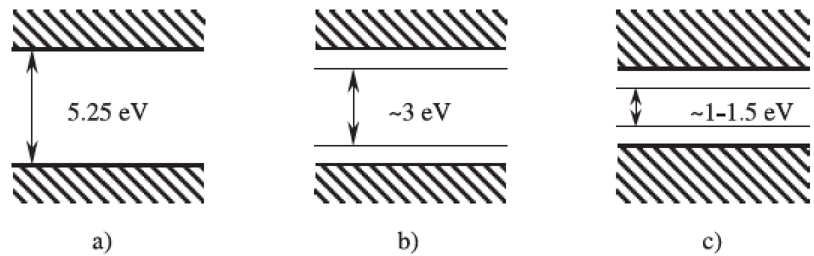


FIGURE 1 Schematic representation of the calculated bandgap of RDX: **a** perfect crystal; **b** RDX with edge dislocations; and **c** shocked RDX with edge dislocations

Kuklja, *Appl. Phys. A* **76**, 359 (2003)

Compression of lattice reduces band gap, enabling reactions

J. J. Gilman, *Science* **274**, 5284 (1996)
Kuklja, *Appl. Phys. A* **76**, 359 (2003); Kuklja *et al*, *J. Appl. Phys.* **89**, 4156 (2001);
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Margetis, Kaxiras, Elstner, Frauenheim, and Manaa, *J. Chem. Phys.* **117**, 788 (2002)
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Reed, Joannopolous, and Fried, *Phys. Rev. B* **62**, 16500 (2000)

\+ many others

Electronic Properties Under Compression

At Sandia, we are working on quantifying changes in electronic structure under compression experimentally.

Goal of this talk is to simulate changes in band gap and optical spectrum of RDX:

- Under hydrostatic compression
- Polymorphic differences
- Under uniaxial compression
- Directional dependence

Structure and Polymorphs of RDX

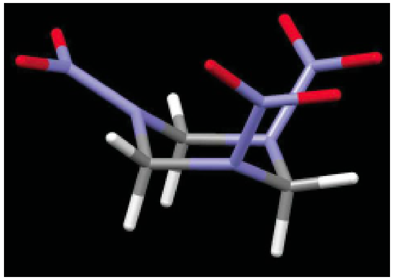
At ambient conditions, RDX exists in its α phase:

- Orthorhombic (*Pbca*), with lattice constants a = 13.182; b = 11.574; c = 10.709 Å, and cell volume V = 1633.9 Å^3.[1]

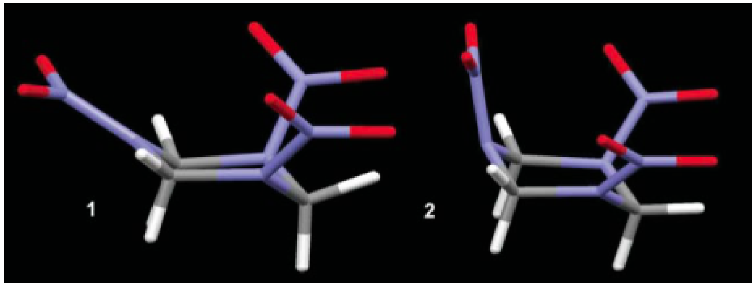
Around 4 GPa[2], α-RDX converts to γ-RDX:

- Orthorhombic ($Pca2_1$), with lattice constants a = 12.5650, b = 9.4769, c = 10.9297 Å, and cell volume V = 1301.5Å^3.[3]

Under shock conditions, conversion is observed at 3.9 GPa after 100 ns induction period.



α-RDX conformation
(from Ref. 3)



γ-RDX conformation
(from Ref. 3)

[1] Choi and Prince, *Acta Cryst. B* **28**, 2857 (1972)
[2] Ciezak, Jenkins, Liu, and Hemley, *J. Phys. Chem. A* **111**, 59 (2007)
[3] Davidson *et al*, *Cryst. Eng. Comm.* **10**, 141 (2008)
[4] Bedroff, Hooper, Smith, and Sewell, *J. Chem. Phys.* **131**, 034712 (2009)
[5] Patterson, Dreger, and Gupta, *J. Phys. Chem.* **111**, 10897 (2007)

DFT Calculations

Calculations are performed using VASP 5.4[1] (in MedeA[2]), using the generalized gradient approximation with the PBE revised for solids functional[3].

- PAW pseudopotentials[4] (hard) with 1250 eV cutoff
- Van der Waals corrections are made using the D3 method of Grimme[5].
- Pre- and post-processing is accomplished using the MedeA[2] software package by Materials Design.

[1] Kresse and Hafner, *Phys. Rev. B* **47**, 558 (1993); ibid. **49**, 14251 (1994); Kresse and Furthmueller, *Comput. Mat. Sci.* **6**, 15 (1996); Kresse and Furthmueller, *Phys. Rev. B* **54**, 11169 (1996)
[2] www.materialsdeisgn.com/medea
[3] Perdew, *et al*, *Phys. Rev. Lett.* **100**, 136406 (2008)
[4] Blochl, *Phys. Rev. B* **50**, 17953 (1994); Kresse and Joubert, *Phys. Rev. B* **59**, 1758 (1999)
[5] Grimme, *et al*, *J. Chem. Phys.* **132**, 154104 (2010)

DFT Calculations

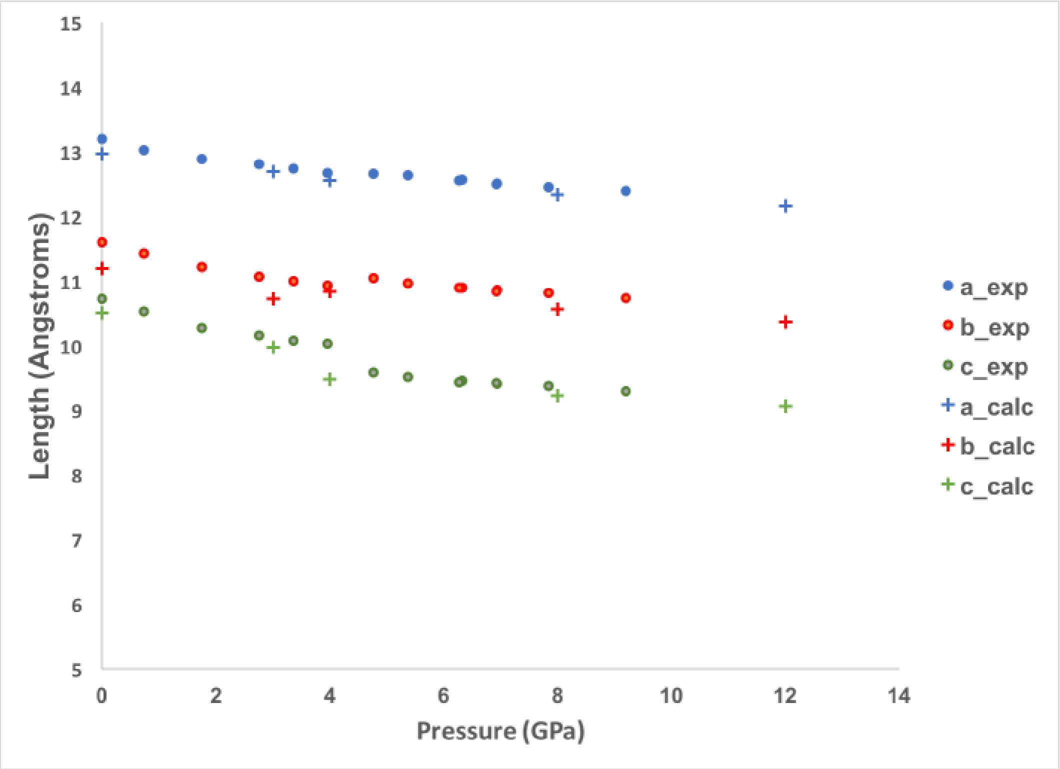
Hydrostatic compression is simulated by iterative optimization to increasing external pressure:

1. Optimize experimental structure (at 0 GPa for α-RDX; 4 GPa for γ-RDX)
2. Increment pressure
3. Optimize structure
4. Repeat steps 2 and 3.
5. Calculate band gap and optical spectrum for each optimized structure.

Uniaxial compression is simulated by optimizing iteratively contracted unit cells:

1. Start with optimized structure from #1 above
2. Contract unit cell along axis
3. Optimize atom positions
4. Repeat steps 2 and 3, for compression along *a, b,* and *c* axes.
5. Calculate band gap and optical spectrum for each optimized structure.

1. Unit Cells – Hydrostatic Compression



α-RDX at 0 GPa	Calculated:	a = 12.96476	b = 11.19769	c = 10.50650 Å
	Experiment[1]:	a = 13.182	b = 11.574	c = 10.709 Å
γ-RDX at 4 GPa	Calculated:	a = 12.54961	b = 9.47896	c = 10.84014 Å
	Experiment[2]:	a = 12.5650	b = 9.4769	c = 10.9297 Å

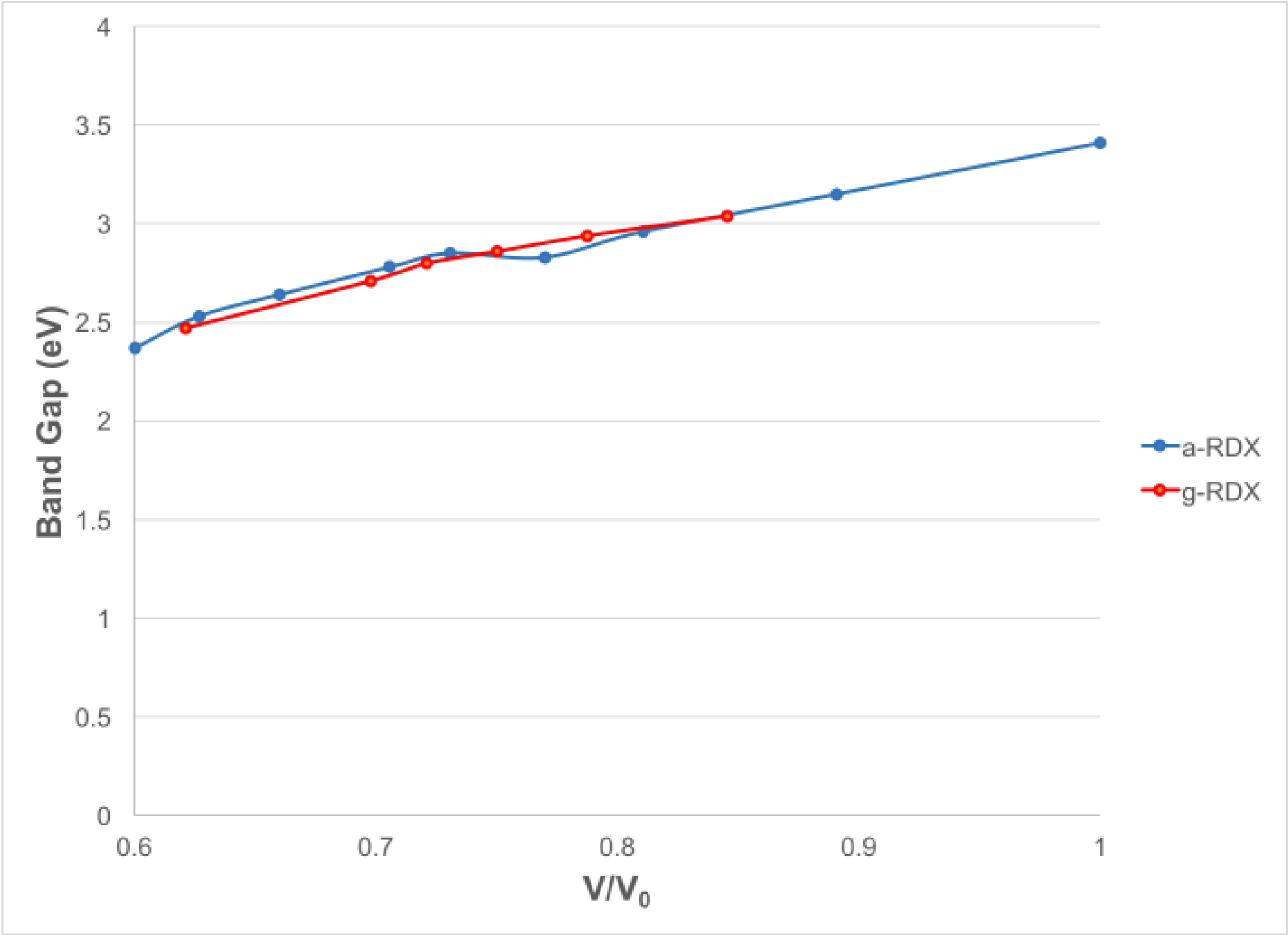
1 Choi and Prince, *Acta Cryst. B* **28**, 2857 (1972)
2 Davidson *et al*, *Cryst. Eng. Comm.* **10**, 141 (2008)
3 Olinger, Roof, and Cady, *Proc. Symposium (Intern.) on High Dyn. Press,* C.E.A. Paris, France 1978, pp. 3-8.

2. Band Gaps – Hydrostatic Compression

Calculated (0 GPa): 3.4 eV

Measured[1]: 3.6 eV

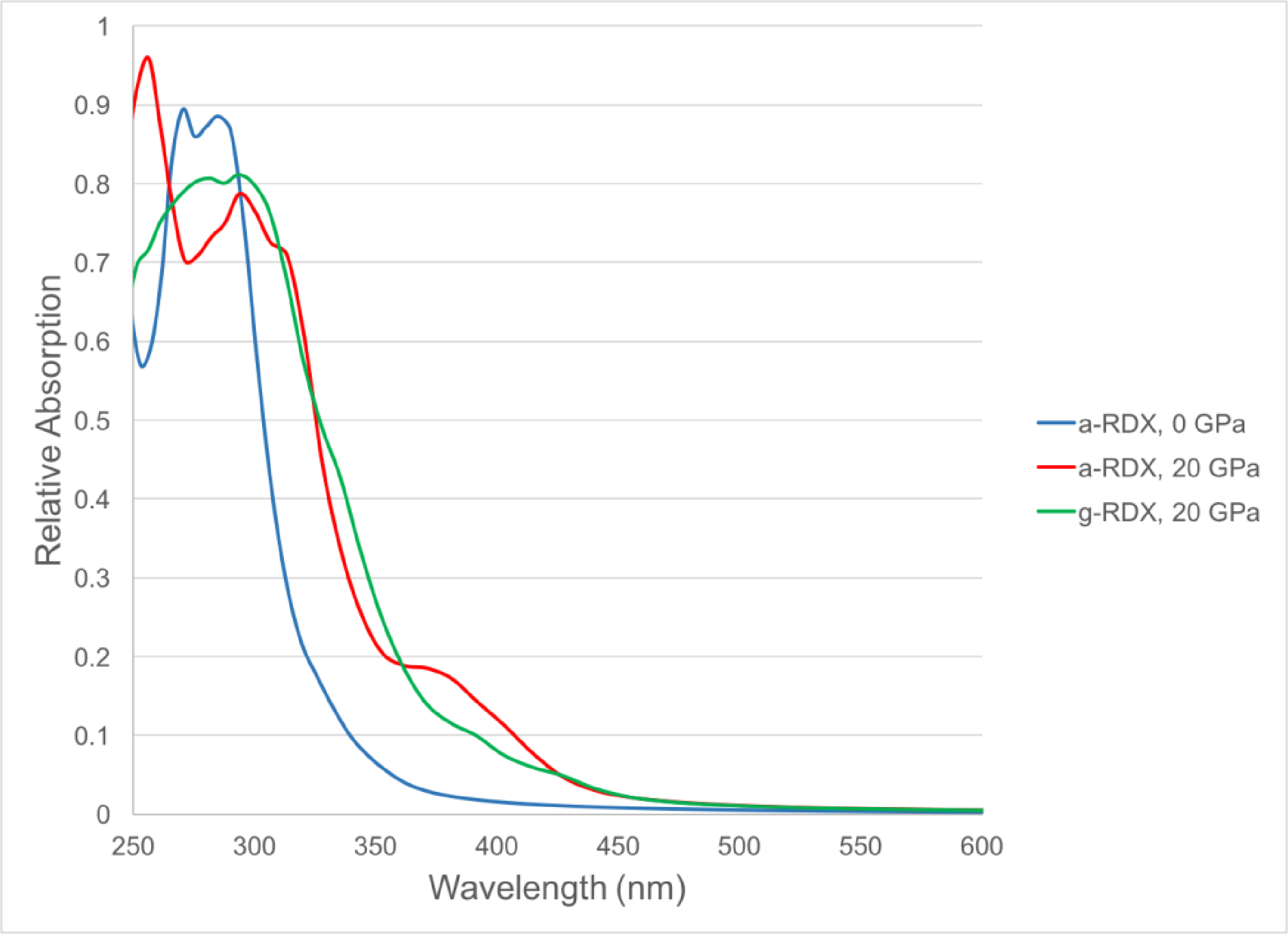
Prev. Calc.[2]: 3.45 eV



[1] Whitley, *AIP Conf. Proc.* **845**, 1357 (2006)

[2] Oleynik, Conroy, and White, *AIP Conf. Proc.* **955**, 401 (2007)

3. Optical Spectra – Hydrostatic Compression



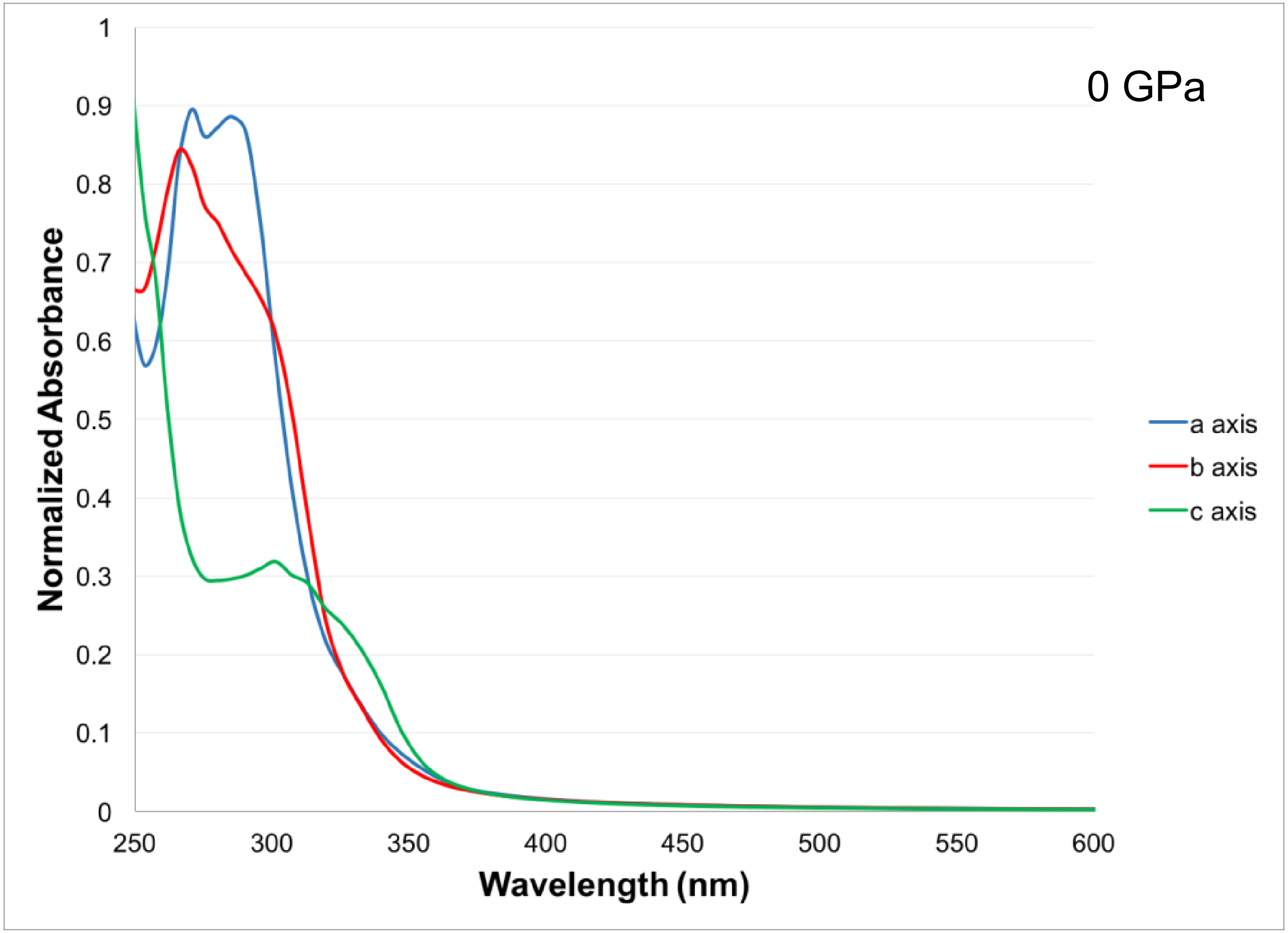
* Absorption calculated along *a*-axis of crystal

4. Band Gaps – Uniaxial Compression

V/V_0 or L/L_0	Compression	Band Gap	Δ Gap
1	None	3.41	
0.75	Hydrostatic	2.86	-0.55
0.75	*a* axis	2.55	-0.86
0.75	*b* axis	2.75	-0.66
0.75	*c* axis	2.65	-0.76
0.55	*a* axis	1.74	-1.67

- Calculations predict some differences in electronic structure, depending on axis of compression
- Band gap decreases more with uniaxial compression

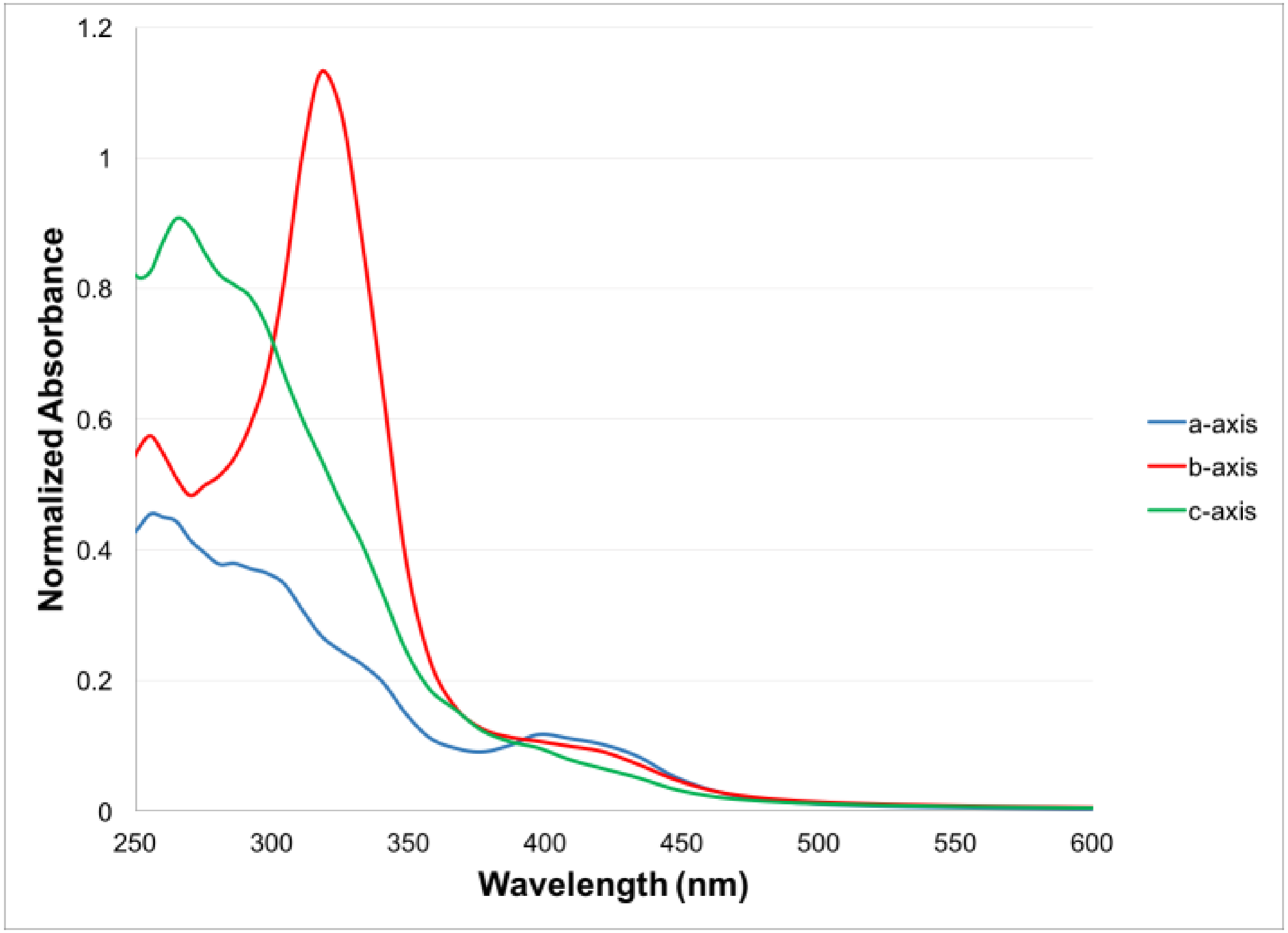
5. Optical Spectra – Directional Dependence

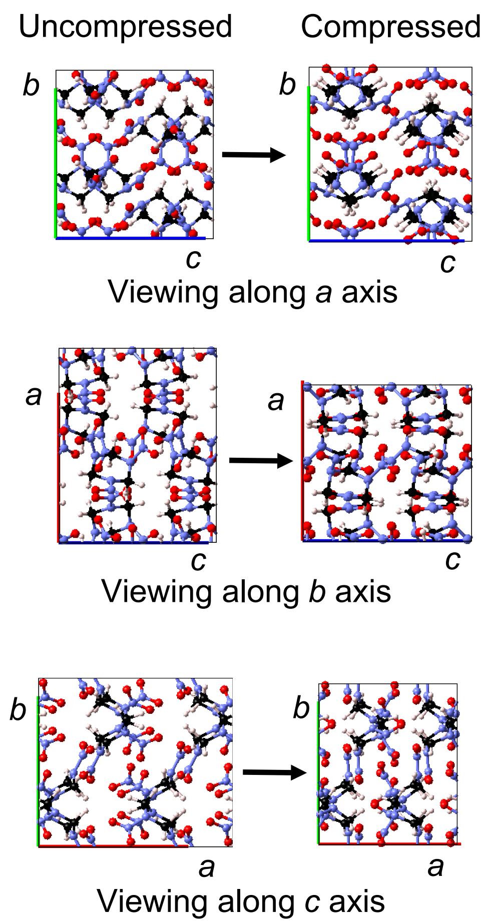


Optical spectra are different along *a*, *b*, *c* axes

5. Optical Spectra – Uniaxial Compression

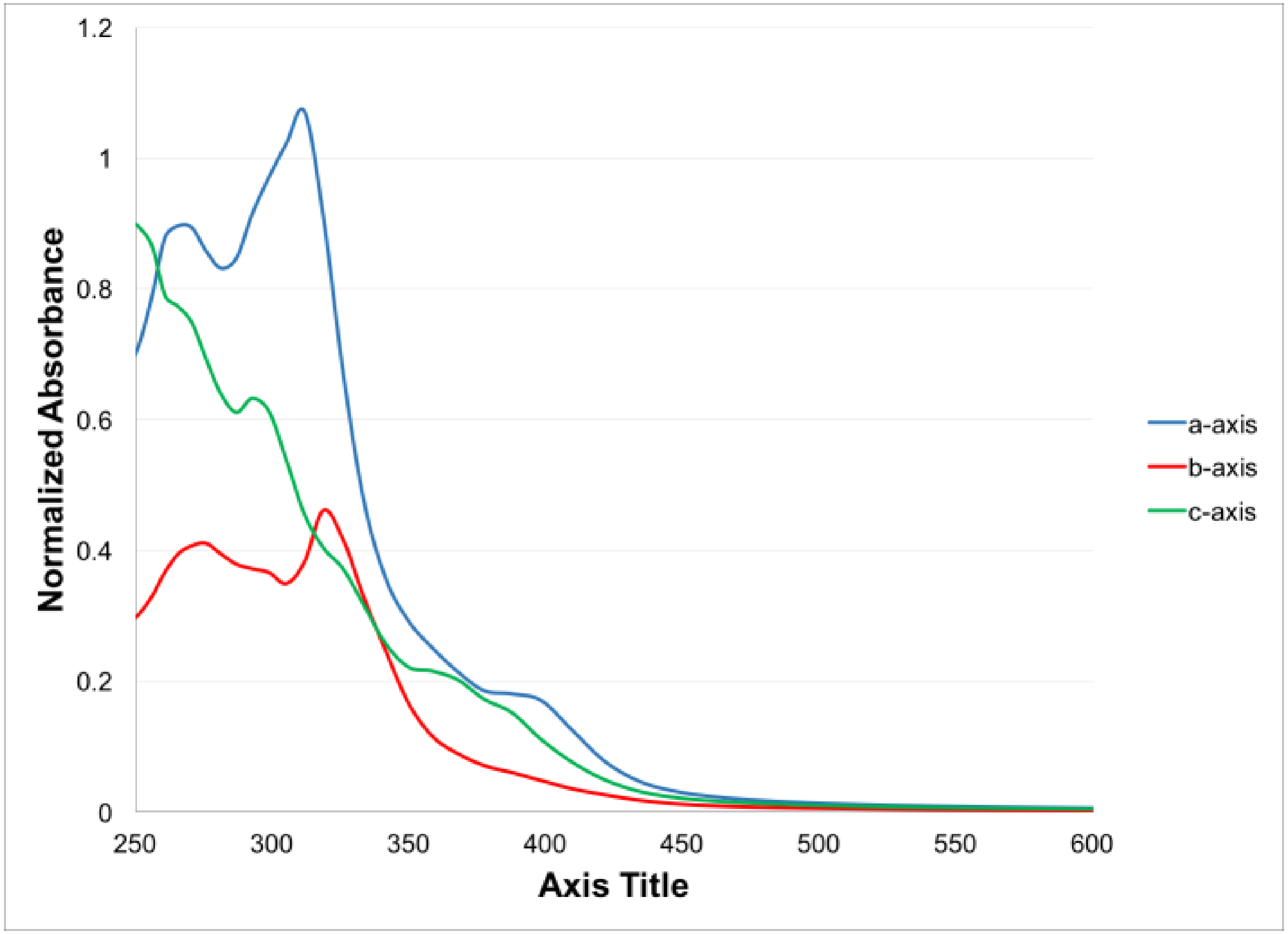
Compression along *a* axis

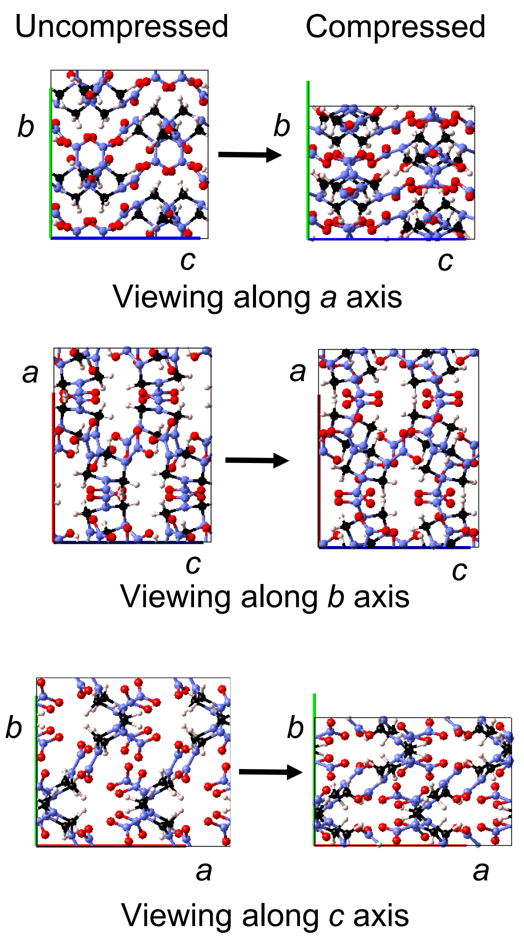




5. Optical Spectra – Uniaxial Compression

Compression along *b* axis





Conclusions

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Effects of hydrostatic and uniaxial compression of RDX have been simulated using density functional theory:

- Calculations predict compression of band gap from 3.4 eV to 2.4 eV at 50 GPa (V/V_0 = 0.6)
- Changes in band gap similar for α-RDX and γ-RDX under hydrostatic compression
- Optical spectra are directionally-dependent
- Changes in optical spectra are different for different directions under uniaxial compression

Acknowledgments

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