SUPPORTING INFORMATION

Investigating the Photochemical Decomposition of Solid 1,3,5-Trinitro-1,3,5-Triazinane (RDX)

*Santosh K. Singh[a], Vasant Vuppuluri[b], Steven F. Son[b], Ralf I. Kaiser[a]**

[a] *Department of Chemistry, University of Hawaii, Honolulu, HI 96822, USA*

W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii, Honolulu, HI 96822, USA

[b] *Mechanical Engineering, Purdue Energetics Research Center, Purdue University, West Lafayette, IN 47907, USA*

Number of Pages: 11

Title Page: S1

Table of Contents: S2

Number of Figures: 5 (S3-S7)

Number of Tables: 2 (S8-S10)

*Corresponding author. E-mail: ralfk@hawaii.edu

Table of Contents

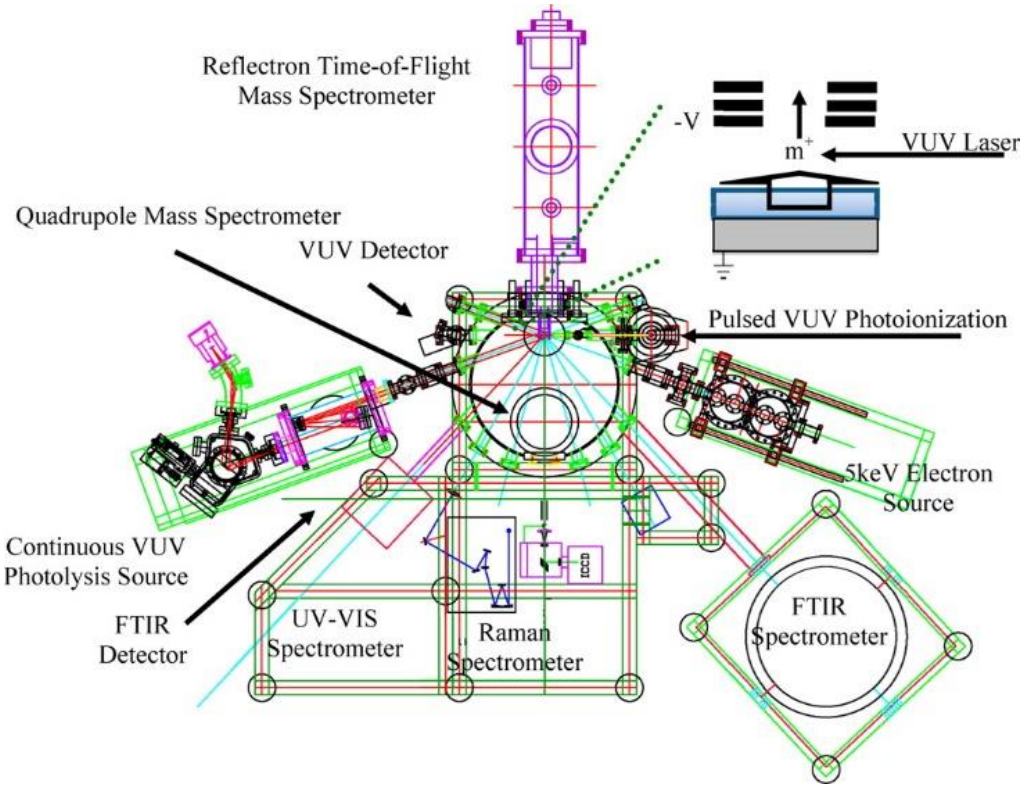

Figure S1. Schematic top view of the ultra-high vacuum chamber including the radiation sources (electron source), analytical instruments (FTIR, UV-VIS, ReTOF), and cryogenic target (point of convergence of the lines).[1]

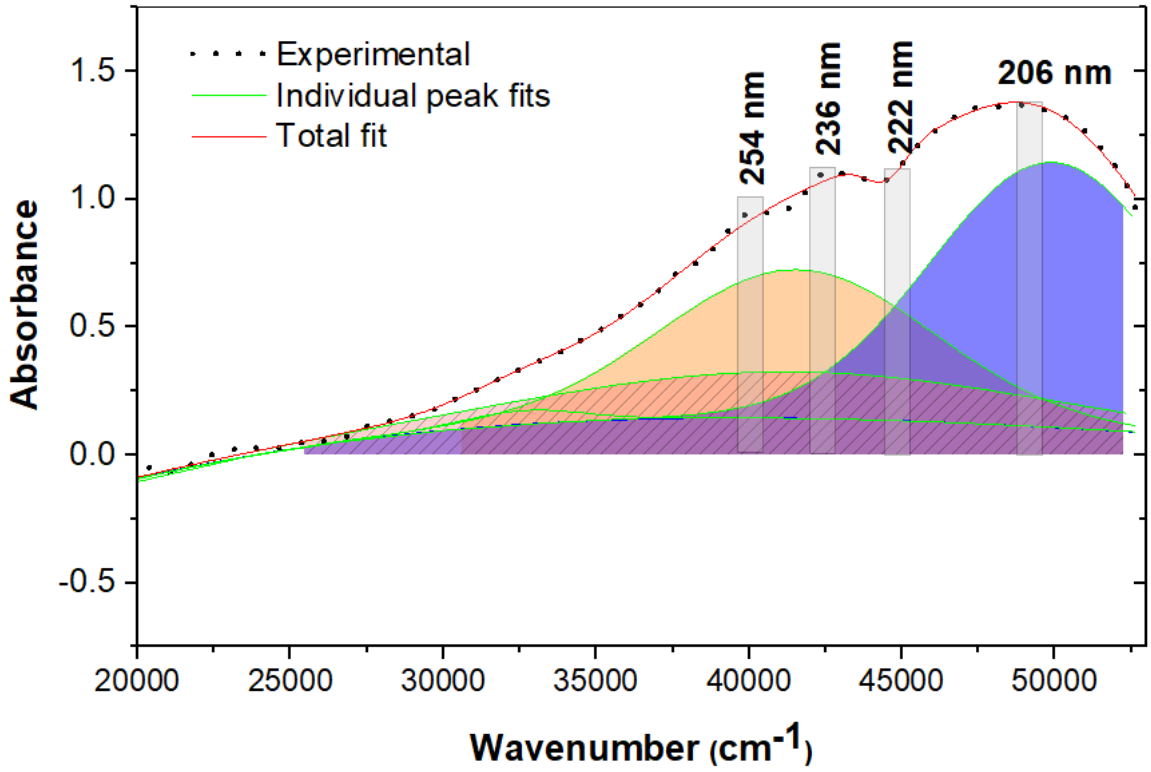

Figure S2. Deconvoluted UV-Vis spectrum of RDX collected at 5K. The most intense absorption appears at around 206 nm with a shoulder at around 236 nm. The shaded regions depict the absorptions at the wavelengths employed for the decomposition of RDX. Spectrum is plotted in wavenumber to obtain the individual peak areas in cm^{-1}.

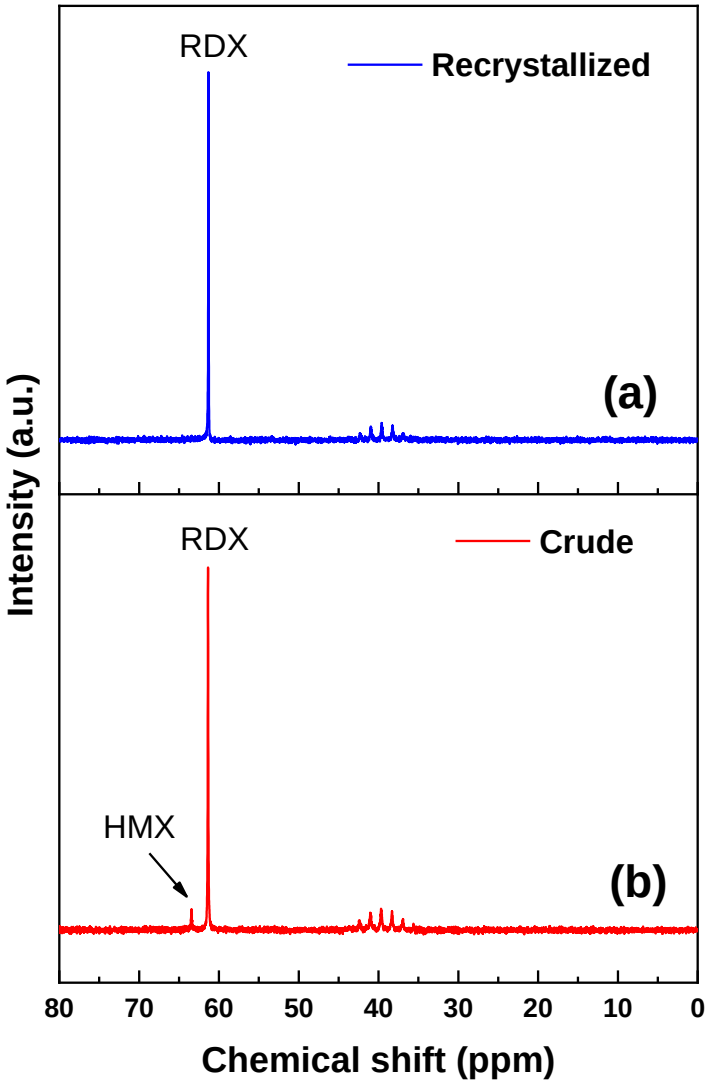

Figure S3. ^{13}C NMR spectra of (a) recrystallized RDX (b) crude RDX. Peak at 63.47 ppm in the NMR spectra of crude RDX corresponds to HMX impurity which is absent is the NMR spectra measured after recrystallization of RDX.

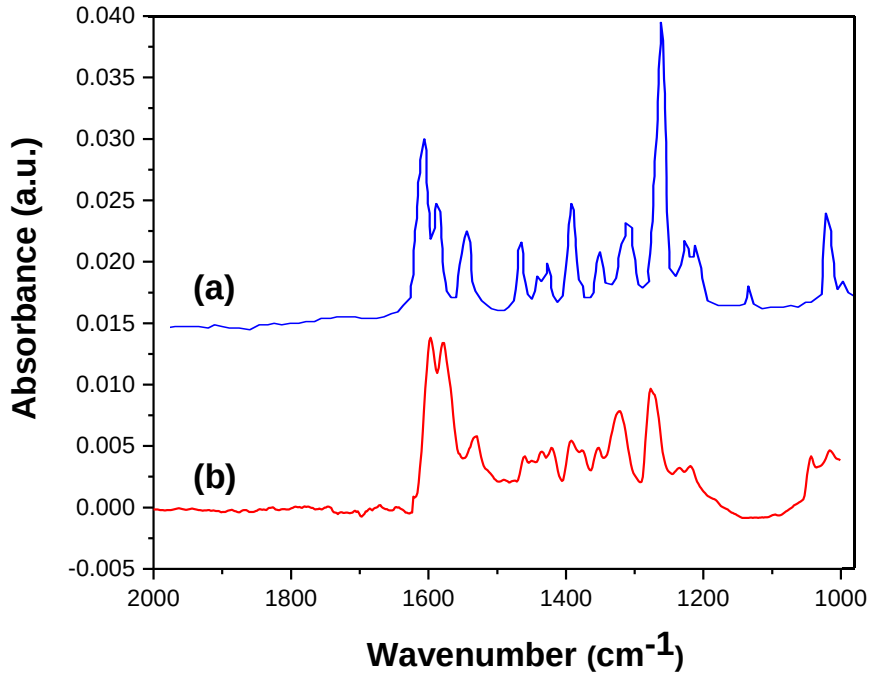

Figure S4. Infrared spectra of (a) crystalline phase of RDX film measured by Botcher, T. R. *et al*. (b) amorphous phase of RDX film measured in this study. Fig (a) is adapted with permission from Botcher, T. R.; Wight, C. A. *J. Phys. Chem.* **1993,** *97*, 9149-9153. Copyright (1993) *American Chemical Society*.

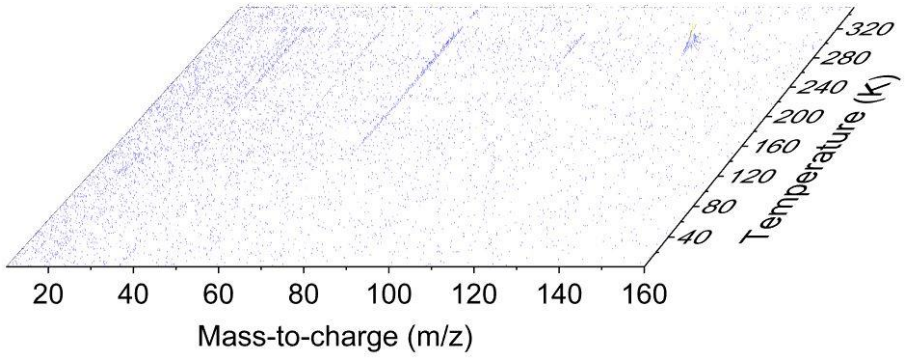

Figure S5. PI-ReTOF mass spectrum measured as a function of temperature in a blank experiment at a photoionisation energy of 10.49 eV.

Table S1. Mass and molecular formula of the decomposition products of RDX previously reported in gas-phase and condensed-phase UV photolysis studies.

Methods				Products observed	
References	**Photolysis Wavelength**	**Method of ionization**	**Method of detection**	**Mass (amu)**	**Assignments**
Greenfield M. et al.[2]	230 nm 228 nm 226 nm	Photoionization	Time of flight mass spectrometer	30	Nitrogen monoxide (NO)
Lemire G. W. et al.[3]	226 nm	Photoionization	Time of flight mass spectrometer	30	Nitrogen monoxide (NO)
Wynn C. M. et al.[4]	236 nm	-	Laser induced fluorescence	30	Nitrogen monoxide (NO)
Tang T. B. et al.[5]	266 nm	Photoionization	Time of flight mass spectrometer	16	O
				17	Hydroxy (OH)
				18	Water (H_2O)
				26	Cyanide (CN)
				28	Carbon monoxide (CO)
				30	Nitrogen monoxide (NO)
				40	Carbon nitrides (NCN)
				41	HCNN
				42	Diazomethane (H_2CNN)
				46	Nitrogen dioxide (NO_2)
				82	($C_3N_3H_4$)
				83	($C_3N_3H_5$)
				85	$C_2N_2O_2H$)
				86	$C_2N_2O_2H_2$)
				90	(C_3N_3H)
				93	(C_3N_4H)
				98	($C_3N_4H_6$)
				134	($H_2CN_4O_4$)
				176	($H_6C_3N_5O_4$)

Alix J. et al.[6]	UV Broadband	-	FTIR spectrometer	30 42 28 30 60 76 15 48 26	Nitrogen monoxide (NO) Dinitrogen monoxide (N_2O) Carbon monoxide (CO) Formaldehyde (H_2CO) Nitrogen monoxide dimer ($(NO)_2$ Dinitrogen trioxide (N_2O_3) Methane (CH_4) Ozone (O_3) Acetylene (C_2H_2)
Gares K. L. et al.[7]	229 nm	-	Diffuse UV resonance Raman spectrometer	62 81 -	Nitrate ions (NO_3^{-1}) Triazine ($C_3N_3H_3$) Carbon nitrides (C≡N)
Dickinson, J. T.*et al.*[8]	248 nm	Electron impact ionization	Time of flight mass spectrometer	2 17 18 27 30 30 42 42 44 46 46 74 81	Hydrogen (H_2) Hydroxyl radical (OH) Water (H_2O) Hydrogen cyanide (HCN) Formaldehyde (H_2CO) Nitrogen monoxide (NO) Diazomethane (H_2CNN) Ethanenitrilium (C_2H_4N) Nitrous oxide (N_2O) Nitrogen dioxide (NO_2) Diazaoethane ($CH_2CH_2N_2$) Methylene nitramine (H_2CNNO_2) s-triazene ($C_3N_3H_3$)

Table S2. Column densities of decomposed RDX and its products calculated using their integral absorption coefficients and integrated peak area of the vibrational bands.

254 nm (dose: 10.7 ± 1.0 eV molecule^{-1})			
Wavenumber Observed (cm^{-1})	Assignment	Integrated Absorption Coefficient (A; cm molecule^{-1})	Column Density (molecule cm^{-2})
1581	ν^{as} (NO_2) RDX	5.1×10^{-17}	$5.6 \pm 0.6 \times 10^{15}$
3500-3100	ν_{OH} (H_2O)	2.0×10^{-16}	$5.8 \pm 0.6 \times 10^{14}$
2340	ν_3 (CO_2)	7.6×10^{-17}	$3.9 \pm 0.4 \times 10^{14}$
2231	ν_1 (N_2O)	5.2×10^{-17}	$7.9 \pm 0.8 \times 10^{14}$
2138	ν_1 (CO)	1.1×10^{-17}	$5.3 \pm 0.5 \times 10^{14}$
1861	ν_1 (NO)	5.2×10^{-17}	$1.0 \pm 0.1 \times 10^{15}$
1756	ν_5 ($[NO]_2$)	9.3×10^{-17}	$3.1 \pm 0.4 \times 10^{14}$
1300	ν_3 (N_2O_3)	4.6×10^{-17}	$3.0 \pm 0.3 \times 10^{14}$
254 nm (dose: 0.5 ± 0.1 eV molecule^{-1})			
1581	ν^{as} (NO_2) RDX	5.1×10^{-17}	$1.2 \pm 0.2 \times 10^{15}$
1861	ν_1 (NO)	5.2×10^{-17}	$2.1 \pm 0.3 \times 10^{14}$
1756	ν_5 ($[NO]_2$)	9.3×10^{-17}	$2.4 \pm 0.3 \times 10^{13}$
1300	ν_3 (N_2O_3)	4.6×10^{-17}	$2.2 \pm 0.2 \times 10^{14}$
206 nm (dose: 22.3 ± 2.0 eV molecule^{-1})			
1581	ν^{as} (NO_2) RDX	5.1×10^{-17}	$4.5 \pm 0.5 \times 10^{15}$
3500-3100	ν_{OH} (H_2O)	2.0×10^{-16}	$4.3 \pm 0.4 \times 10^{14}$
2340	ν_3 (CO_2)	7.6×10^{-17}	$6.9 \pm 0.7 \times 10^{14}$
2231	ν_1 (N_2O)	5.2×10^{-17}	$1.0 \pm 0.1 \times 10^{15}$
2138	ν_1 (CO)	1.1×10^{-17}	$5.6 \pm 0.6 \times 10^{14}$
1861	ν_1 (NO)	5.2×10^{-17}	$5.2 \pm 0.7 \times 10^{14}$
1756	ν_5 ($[NO]_2$)	9.3×10^{-17}	$2.2 \pm 0.2 \times 10^{14}$
1300	ν_3 (N_2O_3)	4.6×10^{-17}	$5.5 \pm 0.6 \times 10^{14}$
206 nm (dose: 0.9 ± 0.1 eV molecule^{-1})			
1581	ν^{as} (NO_2) RDX	5.1×10^{-17}	$1.5 \pm 0.2 \times 10^{15}$
3500-3100	ν_{OH} (H_2O)	2.0×10^{-16}	$1.2 \pm 0.2 \times 10^{14}$
2231	ν_1 (N_2O)	5.2×10^{-17}	$7.7 \pm 0.8 \times 10^{13}$
1861	ν_1 (NO)	5.2×10^{-17}	$3.2 \pm 0.3 \times 10^{14}$
1756	ν_5 ($[NO]_2$)	9.3×10^{-17}	$7.8 \pm 0.8 \times 10^{13}$
1300	ν_3 (N_2O_3)	4.6×10^{-17}	$2.6 \pm 0.2 \times 10^{14}$

References.

1. Jones, B. M.; Kaiser, R. I., Application of reflectron time-of-flight mass spectroscopy in the analysis of astrophysically relevant ices exposed to ionization radiation: Methane (CH_4) and D4-Methane (CD_4) as a case Study. *J. Phys. Chem. Lett.* **2013,** *4*, 1965-1971.
2. Greenfield, M.; Guo, Y. Q.; Bernstein, E. R., Ultrafast photodissociation dynamics of HMX and RDX from their excited electronic states via femtosecond laser pump–probe techniques. *Chem. Phys. Lett.* **2006**, *430*, 277-281.
3. Lemire, G. W.; Simeonsson, J. B.; Sausa, R. C., Monitoring of vapor-phase nitro compounds using 226-nm radiation: fragmentation with subsequent NO resonance-enhanced multiphoton ionization detection. *Anal. Chem.* **1993**, *65*, 529-533.
4. Wynn, C. M.; Palmacci, S.; Kunz, R. R.; Clow, K.; Rothschild, M., Detection of condensed-phase explosives via laser-induced vaporization, photodissociation, and resonant excitation. *Appl. Opt.* **2008**, *47*, 5767-5776.
5. Tang, T. B.; Chaudhri, M. M.; Rees, C. S.; Mullock, S. J., Decomposition of solid explosives by laser irradiation: A mass spectrometric study. *J. Mater. Sci.* **1987**, *22*, 1037-1044.
6. Alix, J.; Collins, S., The photochemistry of RDX in solid argon at 10 K. *Can. J. Chem.* **1991,** *69*, 1535-1538.
7. Gares, K. L.; Bykov, S. V.; Brinzer, T.; Asher, S. A., Solution and solid hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) ultraviolet (UV) 229 nm photochemistry. *Appl. Spectrosc.* **2015**, *69*, 545-554.
8. Dickinson, J. T.; Jensen, L. C.; Doering, D. L.; Yee, R., Mass spectroscopy study of products from exposure of cyclotrimethylene-trinitramine single crystals to KrF excimer laser radiation. *J. Appl. Phys.* **1990**, *67*, 3641-3651.