ABSTRACT: Energetic materials such as 1,3,5-trinitro-1,3,5-triazinane (RDX) are known to photodissociate when exposed to UV light. However, the fundamental photochemical process(es) that initiate the decomposition of RDX is (are) still debatable. In this study we investigate the photodissociation of solid-phase RDX at four distinct UV wavelengths (254 nm (4.88 eV), 236 nm (5.25 eV), 222 nm (5.58 eV), 206 nm (6.02 eV)) exploiting a surface science machine at 5 K. We also conducted dose-dependent studies at the highest and lowest photon energy of 206 nm (6.02 eV) and 254 nm (4.88 eV). The products were monitored online and in situ via infrared spectroscopy. During the temperature-programmed desorption phase, the subliming products were detected with a reflectron time-of-flight mass spectrometer coupled with soft-photoionization at 10.49 eV (PI-ReTOF-MS). Infrared spectroscopy revealed the formation of small molecules including nitrogen monoxide (NO), nitrogen monoxide dimer ([NO]₂), dinitrogen trioxide (N₂O₃), carbon dioxide (CO₂), carbon monoxide (CO), dinitrogen monoxide (N₂O), water (H₂O), and nitrite group (−ONO) while ReTOF-MS identified 32 cyclic and acyclic products. Among these, 11 products such as nitryl isocyanate (CN₂O₃), 5-nitro-1,3,5-triazinan-2-one (C₃H₆N₄O₃) and 1,5-dinitro-1,3,5-triazinan-2-one (C₃H₅N₅O₅) were detected for the first time in photodecomposition of RDX. Dose-dependent in combination with wavelength-dependent photolysis experiments aid to identify key primary and secondary products as well as distinguished pathways that are more preferred at lower and higher photon energies. Our experiments revealed that N−NO₂ bond fission and nitro−nitrite isomerization are the initial steps in the UV photolysis of RDX. Reaction mechanisms are derived by comparing the experimental findings with previous electronic structure calculations to rationalize the origin of the observed products. The present study can assist in understanding the complex chemistry behind the photodissociation of electronically excited RDX molecule, thus bringing us closer to unraveling the decomposition mechanisms of nitramine-based explosives.

1. INTRODUCTION

Cyclic nitramines, such as 1,3,5-trinitro-1,3,5-triazinane (RDX), have wide applications as explosives and rocket propellants due to their high energy content.¹⁻³ Therefore, an understanding of the fundamental decomposition mechanisms of energetic materials at the molecular level is essential to increase the energy efficiency of nitramines in explosion and combustion applications. Over the past decades, copious studies have been devoted to investigate the fundamental chemical processes involved in the fragmentation of RDX (Scheme 1).¹⁻⁴³ Diverse methods ranging from shock waves, infrared (IR) lasers, electron beams to ultraviolet (UV) lasers have been employed to initiate the complex dissociation mechanism(s), but the very first reaction step(s) that initialize the decomposition is (are) still debated.⁴⁻¹⁵

The decomposition of condensed phase RDX via thermal energy, shock waves, and infrared laser exposure suggest that the N−NO₂ bond fission represents the primary pathway.⁴⁻¹³,¹⁴ On the contrary, infrared multiphoton dissociation of RDX in molecular beams in the gas phase reveals a triple C−N bond
rupture leading to three methylene nitramine molecules (H₂C−N−NO₂) as the dominating channel. This channel has also been observed in the decomposition of solid phase RDX via infrared laser leading eventually to the formation of ketene (H₂CCO) and water (H₂O). Thermal decomposition studies disclose yet another primary mechanism, which involves a concerted elimination of nitrous acid (HONO) along with the formation of triazine (C₃H₃N₃). Very recently, the dissociation of RDX conducted via energetic electrons revealed that the products involving the N−NO₂ homolysis and HONO elimination are more prevailing than the triple dissociation. Although several discrepancies revolve around the initial step of decomposition, the proposed reaction schemes in the aforementioned studies could elucidate the decomposition of RDX from its ground electronic state (S₀). However, the primary/secondary steps responsible for the fragmentation of nitramine-based energetic materials from their excited electronic states could be quite different.

Previous experiments demonstrated that excited electronic states (S₁, S₂) of energetic materials could play a fundamental role in their decomposition and also in the ignition processes. In the laboratory, these excited states are readily accessible once the sample is exposed to ultraviolet (UV) photons. However, only a few studies have been pursued to unravel the fragmentation processes of RDX that occur after electronic excitation (Table S1). Herein, the majority of the UV photolysis experiments are conducted in the gas phase by Bernstein and co-workers. Here, the majority of the UV photolysis experiments are conducted in the gas phase by Bernstein and co-workers. These studies investigated the photodissociation of RDX from its excited electronic states upon photoexcitation at three distinct wavelengths of 230, 228, and 226 nm; in each case, only nitrogen monoxide (NO) was observed. Their observation of rotationally cold, but vibrationally hot excitation spectra of NO (nitrogen monoxide) suggests that RDX dissociates in the S₁ state after rapid internal conversion from the Sₐ state. Calculations on the excited-state potential energy surface (PES) revealed that following electronic excitation, the RDX molecules undergo nitrone−nitrite isomerization after passing through a series of conical intersections (CIs) and finally dissociate from the S₁ state via simple O−NO bond rupture processes. Im et al. conducted femtosecond pump−probe experiments to demonstrate that photodecomposition dynamics of RDX at 226 nm involves a time scale faster than 180 fs. Lemire et al. also conducted photodissociation of RDX at 226 nm in the gas phase and primarily observed only the nitrogen monoxide (NO) fragment.

Although gas phase studies by Bernstein and co-workers convincingly suggested nitrone−nitrite isomerization to be a major fragmentation channel involving initially excited state dynamics, evidence of such isomerization mechanism upon photoexcitation has not been observed in the condensed phase yet. The infrared spectrum of RDX collected by Alix et al. in the argon matrix at 10 K after photodissociation with a broadband UV light did not reveal any vibrational features corresponding to the nitrite group (−ONO). Only features attributed to nitrogen monoxide (NO), formaldehyde (H₂CO), dinitrogen monoxide (N₂O), carbon monoxide (CO), dinitrogen trioxide (N₂O₃), methane (CH₄), and ozone (O₃) were reported. Gares et al. recorded the deep-ultraviolet resonance Raman (DUVRR) spectra of solution and solid phase RDX after photolysis at 229 nm (5.41 eV) and observed a decrease in the N−NO₂ band intensity along with evidence of the formation of nitrate ion (−NO₃⁻) and carbon nitrides (C≡N) moieties. However, no vibrational signature of nitrite group (−ONO) or nitrogen dioxide (NO₂) were reported; therefore, the authors predicted that the N−NO₂ bond cleavage represents the dominant pathway. Tang et al. also proposed the N−NO₂ bond fission as a primary step in the dissociation of solid RDX at 266 nm (4.66 eV) based on the detected products such as NO₂ (nitrogen dioxide), NO (nitrogen monoxide), and (a)cyclic species carrying C≡N moieties.

In summary, previous UV photolysis studies have not elucidated the role of the nitro−nitrite isomerization mechanism in the decomposition of RDX. This is due to the lack of the identification of higher molecular weight products that could result from the nitro−nitrite isomerization process. In the gas phase, the higher molecular weight species formed via the nitro−nitrite isomerization plus nitrogen monoxide (NO) elimination could be undetected considering the low number densities and absence of (state) specific detection schemes such as laser induced fluorescence (LIF) and resonance enhanced multiphoton ionization (REMPI); this is evident from the works of Bernstein et al. reporting solely NO (nitrogen monoxide) as the primary product, whose LIF scheme is well established, but no heavier cofragments. On the other hand, condensed phase studies could provide a significantly more complex chemistry (Table S1). However, a systematic experimental approach is required to shed fundamental insight on the complex chemistry of the decomposition of RDX upon UV photofragmentation, i.e., pathways which may involve multiple reaction channels such as N−NO₂ bond fission, nitro−nitrite isomerization, and/or HONO elimination. Furthermore, a complete spectrum of the wavelength-dependent photodissociation products of RDX in the condensed phase is scarce.

Herein, we investigate the photofragmentation of solid RDX at four distinct UV wavelengths (254 nm (4.88 eV), 236 nm (5.25 eV), 222 nm (5.58 eV), and 206 nm (6.02 eV)) exploiting a surface science machine at 5 K to trap the products within the low temperature solid. These energies are well below the adiabatic ionization energy of RDX determined to be between 9.9 and 10.2 eV in the gas phase. At the highest and lowest photon energy of 206 nm (6.02 eV) and 254 nm (4.88 eV), we also conducted time (dose) dependent studies to gauge the effects of higher order reaction products. By employing four different wavelengths, distinct electronic transitions of RDX, i.e., n → π* and π → π* are accessed. The weak n → π* transition involves an excitation of a nonbonding electron located at the oxygen atom and can be excited via 254 nm (4.88 eV) and 222 nm (5.58 eV). The significantly stronger π → π* absorption promotes an electron located in the π orbital of the ring-nitrogen to the π* orbital at the NO₂ group. The 236 nm (5.25 eV) and 206 nm (6.02 eV) excitation can readily activate this π → π* transition. The calculated oscillator strengths of these transitions are provided in Table 1. Thus, the discrete choice of excitation wavelengths enables us to cover critical and major transitions that populate the electronic spectrum of RDX. During the photolysis, chemical changes in the RDX samples were monitored via Fourier transform infrared spectroscopy (FTIR). A reflection time-of-flight mass spectrometry coupled with UV photolysis (PI-ReTOF-MS) was employed to record the mass spectra of the photolysed samples during temperature-programmed desorption (TPD) following the photolysis of the RDX.
experiments revealed a wide spectrum of photoproducts of RDX. The FTIR spectroscopy detects small decomposition products and the nitrite (-ONO) functional group, while the acyclic products were identified through PI-ReTOF-MS. Among these, 11 products at m/z values of 59 (C2H5NO), 72 (C2H4N2O) 73 (C2H7N3), 88 (CN2O3), 99 (C2H5NO), 117 (C3H8N3O2), 118 (C2H6N4O2), 119 (C3H5N5O5), 146 (C3H6N4O3), 149 (C4H11N3O3), and 191 (C3H5N3O3) in the mass spectrum were detected for the RDX. The FTIR spectroscopy detects small decomposition products and the nitrite (-ONO) functional group, while the acyclic products were identified through PI-ReTOF-MS. Among these, 11 products at m/z values of 59 (C2H5NO), 72 (C2H4N2O) 73 (C2H7N3), 88 (CN2O3), 99 (C2H5NO), 117 (C3H8N3O2), 118 (C2H6N4O2), 119 (C3H5N5O5), 146 (C3H6N4O3), 149 (C4H11N3O3), and 191 (C3H5N3O3) in the mass spectrum were detected for the RDX.

Table 1. Calculated Transition Energies (ΔE) and Gas Phase Oscillator Strengths (f) of the Excited States of RDX Probed in This Study

<table>
<thead>
<tr>
<th>wavelength (nm)</th>
<th>photon energy (eV)</th>
<th>state</th>
<th>transition</th>
<th>transition energy (ΔE, eV)</th>
<th>oscillator strength (f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>234</td>
<td>4.88</td>
<td>1E</td>
<td>n → π*</td>
<td>4.54</td>
<td>0.000</td>
</tr>
<tr>
<td>236</td>
<td>5.25</td>
<td>2E</td>
<td>π → π*</td>
<td>5.24</td>
<td>0.064</td>
</tr>
<tr>
<td>222</td>
<td>5.58</td>
<td>1A1</td>
<td>n → π*</td>
<td>5.36</td>
<td>0.025</td>
</tr>
<tr>
<td>206</td>
<td>6.02</td>
<td>1A1</td>
<td>π → π*</td>
<td>6.01</td>
<td>0.126</td>
</tr>
</tbody>
</table>

*Values reproduced from ref 50.

Table 2. Parameters Utilized to Calculate the Dose (D; eV molecule⁻¹) at the Photolysis Wavelengths of 254 nm (4.88 eV), 236 nm (5.25 eV), 222 nm (5.58 eV), and 206 nm (6.02 eV)

<table>
<thead>
<tr>
<th>wavelength (λ, nm)</th>
<th>integrated absorption coefficient (Aeq, cm molecule⁻¹)</th>
<th>penetration depth (δp, μm)</th>
<th>laser intensity (P, μJ cm⁻²)</th>
<th>photon energy (Eph, J)</th>
<th>irradiation time (t, s)</th>
<th>photons molecule⁻¹</th>
<th>dose (D, eV molecule⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>254</td>
<td>2.3 × 10⁻¹⁵</td>
<td>11.1 ± 0.7</td>
<td>(7.8 ± 0.5) × 10⁻¹³</td>
<td>7.82 × 10⁻¹⁹</td>
<td>3600</td>
<td>8.0 ± 1.0</td>
<td>39.0 ± 5.0</td>
</tr>
<tr>
<td>236</td>
<td>5.8 × 10⁻¹⁵</td>
<td>9.4 ± 0.6</td>
<td>(7.8 ± 0.5) × 10⁻¹³</td>
<td>8.42 × 10⁻¹⁹</td>
<td>3600</td>
<td>12.7 ± 1.3</td>
<td>66.8 ± 7.0</td>
</tr>
<tr>
<td>222</td>
<td>3.3 × 10⁻¹⁵</td>
<td>9.3 ± 0.6</td>
<td>(7.8 ± 0.5) × 10⁻¹³</td>
<td>8.95 × 10⁻¹⁹</td>
<td>3600</td>
<td>9.1 ± 1.0</td>
<td>50.8 ± 5.0</td>
</tr>
<tr>
<td>206</td>
<td>8.4 × 10⁻¹⁵</td>
<td>8.1 ± 0.5</td>
<td>(7.8 ± 0.5) × 10⁻¹³</td>
<td>9.64 × 10⁻¹⁹</td>
<td>3600</td>
<td>13.8 ± 1.4</td>
<td>83.0 ± 8.0</td>
</tr>
</tbody>
</table>

*Integrated absorption coefficients (Aeq) of RDX is derived by integrating the molar absorptivity (ελ; L mol⁻¹ cm⁻¹) vs wavelength graph acquired from the ref 49.
Table 3. Parameters Utilized to Calculate the Dose (D; eV molecule⁻¹) for the Dose-Dependent Experiments Conducted at the Photolysis Wavelengths of 254 nm (4.88 eV) and 206 nm (6.02 eV)

<table>
<thead>
<tr>
<th>Wavelength (λ), nm</th>
<th>Integrated Absorption Coefficient ( (A_{\text{exp}} \text{ cm molecule}^{-1}) )^a</th>
<th>Laser Intensity ( (P, \text{ J s}^{-1} \text{ cm}^{-2}) )</th>
<th>Photon Energy ( (E_p, \text{ J}) )</th>
<th>Irradiation Time ( (t, \text{s}) )</th>
<th>Photons Molecule⁻¹</th>
<th>Dose ( (D, \text{ eV molecule}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>254</td>
<td>( 2.3 \times 10^{-15} )</td>
<td>( (4.4 \pm 0.5) \times 10^{-3} )</td>
<td>( 7.82 \times 10^{-19} )</td>
<td>1800</td>
<td>2.2 ± 0.2</td>
<td>10.7 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>( 2.3 \times 10^{-15} )</td>
<td>( (1.1 \pm 0.5) \times 10^{-3} )</td>
<td>( 7.82 \times 10^{-19} )</td>
<td>300</td>
<td>0.1 ± 0.02</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>( 2.3 \times 10^{-15} )</td>
<td>( (0.2 \pm 0.05) \times 10^{-3} )</td>
<td>( 7.82 \times 10^{-19} )</td>
<td>300</td>
<td>0.020 ± 0.004</td>
<td>0.10 ± 0.02</td>
</tr>
<tr>
<td>206</td>
<td>( 8.4 \times 10^{-15} )</td>
<td>( (4.4 \pm 0.5) \times 10^{-3} )</td>
<td>( 9.64 \times 10^{-19} )</td>
<td>1800</td>
<td>3.7 ± 0.4</td>
<td>22.3 ± 2.0</td>
</tr>
<tr>
<td></td>
<td>( 8.4 \times 10^{-15} )</td>
<td>( (1.1 \pm 0.5) \times 10^{-3} )</td>
<td>( 9.64 \times 10^{-19} )</td>
<td>300</td>
<td>0.15 ± 0.02</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>( 8.4 \times 10^{-15} )</td>
<td>( (0.2 \pm 0.05) \times 10^{-3} )</td>
<td>( 9.64 \times 10^{-19} )</td>
<td>300</td>
<td>0.030 ± 0.005</td>
<td>0.20 ± 0.02</td>
</tr>
</tbody>
</table>

*aIntegrated absorption coefficients \( (A_{\text{exp}}) \) of RDX is derived by integrating the molar absorptivity \( (\epsilon_{\nu}; \text{ L mol}^{-1} \text{ cm}^{-1}) \) vs wavenumber graph acquired from the ref 49.

\[
\text{dose (D)} = \frac{\text{number of photons}}{\text{molecule}} \times E_p \ (\text{eV molecule}^{-1}) \tag{3}
\]

Here, \( P \) is the laser intensity \( (\text{J s}^{-1} \text{ cm}^{-2}) \), \( E_p \) is the energy of a photon \( (\text{J}) \), \( t \) is the total irradiation time \( (\text{s}) \), \( N \) is the column density \((\text{molecules cm}^{-2})\) and \( E_{\nu \nu} \) is the energy of a photon in units of \( \text{eV} \). To determine the value of \( N \), we used modified Lambert–Beer law equation \( ^{55} \) (4) which is given as

\[
N = \frac{\ln 10 \int_{\nu_1}^{\nu_2} A_{\nu} \ d\nu \cos(30^\circ)}{A_{\text{exp}}} \tag{4}
\]

where \( \int_{\nu_1}^{\nu_2} A_{\nu} \ d\nu \) is the integral peak area of the absorbance in the region \( \nu_1 - \nu_2 \) in \( \text{cm}^{-1} \), \( A_{\text{exp}} \) is the integrated absorption coefficient in units of \( \text{cm molecule}^{-1} \). The value of absorbance \( (A_{\nu}) \) at a given wavenumber in UV region is obtained from the UV–vis spectrum of RDX measured at 5K \( (\text{Figure S2}) \) employing a modified UV–vis spectrophotometer \( (\text{Evolution 600}) \). The UV–vis measurement was performed at an angle of 30° relative to the normal of the substrate in an absorption–reflection–absorption mode. The integrated absorption coefficient \( A_{\text{exp}} \) of RDX in the UV region is derived by integrating the molar absorptivity \( (\epsilon_{\nu}; \text{ L mol}^{-1} \text{ cm}^{-1}) \) vs wavenumber graph acquired from the work of Orloff et al. \( ^{39} \). The penetration depth \( (\delta_p) \) of a UV light is determined using eq 5 provided below \( ^{58} \) where \( t \) is the thickness of the RDX film, and \( A \) is the absorbance at a certain wavelength \( (\lambda) \). \( ^{58} \)

\[
\delta_p = \frac{2t}{2.303A_{\nu}} \tag{5}
\]

We subsequently investigated the effect of the dose on the decomposition mechanism of RDX by tuning the dose over 2 orders of magnitude, i.e., from 10.7 ± 1.0 to 0.10 ± 0.02 eV molecule⁻¹ at 254 nm \( (4.88 \text{ eV}) \) irradiation and from 22.3 ± 2.0 to 0.20 ± 0.02 eV molecule⁻¹ at 206 nm \( (6.02 \text{ eV}) \) irradiation wavelength \( (\text{Table 3}) \). After the irradiation, the exposed samples were annealed from 5 to 320 K at a rate of 1 K min⁻¹ \( (\text{temperature-programmed desorption; TPD}) \); temperature increase was halted at 320 K until all the products sublimed. During the TPD phase, the molecules subliming from the substrate were monitored exploiting a photoionization reflectron time-of-flight mass spectrometer \( \text{(PI-}

Figure 1. Difference infrared spectra of RDX collected at 5K after exposure to (a) 254, (b) 236, (c) 222, and (d) 206 nm light at doses of 39.0 ± 5.0, 66.8 ± 7.0, 50.8 ± 5.0, and 83.0 ± 8.0 eV molecule⁻¹ respectively. The assignments of the bands depicted in (c and d) correspond to those provided in (a and b) and are represented through dotted lines.
ReTOF-MS). In the PI-ReTOF-MS setup, we utilized pulsed vacuum ultraviolet (VUV) light at 10.49 eV to softly photoionize the subliming molecules. The ions produced in the photoionization process of the neutrals are then separated in the reflectron time-of-flight tube based on their mass-to-charge ratio and eventually detected via a dual chevron configured microchannel plate (MCP) detector (Jordan TOF Products Inc.). The MCP detector generates the signal, which is amplified via a preamplifier (Ortec 930S) and shaped with a 100 MHz discriminator (Advanced Research Instruments Corporation; F-100TD). A computer-based multichannel scaler receives the signal from the discriminator and records it using 4 ns bin widths triggered at 30 Hz by a pulse delay generator (Quantum Composer 9518). 3600 sweeps are collected per mass spectrum per 1 K increase in the temperature during the TPD phase.

2.2. Sample Preparation. RDX samples were procured from BAE Systems, Inc. prepared according to the MIL-DTL-398 D (Military Specification, Detail Specification RDX, 12 DEC 1996); this specifies an HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane; C4H8N8O8) impurity in RDX at levels from 4% to 17%. The maximum permissible quantity of other impurities if present is 0.08%. The impurities were removed from the production grade RDX through recrystallization process in acetone (Fisher Scientific, Inc.). Nuclear magnetic resonance (NMR) spectrum was measured to characterize the recrystallized RDX. The 13C NMR spectra of the crude and recrystallized RDX measured using a Spinco 60 Carbon benchtop 60 MHz NMR spectrometer after dissolving in dimethyl sulfoxide-d6 (DMSO-d6) solvent are depicted in Figure S3. The peaks associated with the chemical shift of dimethyl sulfoxide-d6 (DMSO-d6) solvent are depicted in Figure S3. The peaks associated with the chemical shift of dimethyl sulfoxide-d6 (DMSO-d6) solvent are depicted in Figure S3. The peaks associated with the chemical shift of dimethyl sulfoxide-d6 (DMSO-d6) solvent are depicted in Figure S3.

3. RESULTS AND DISCUSSION

3.1. IR Spectroscopy. 3.1.1. Qualitative Analysis. Figures 1 and 2 display infrared (IR) difference spectra of RDX collected at 5 K after exposure to 254 nm at doses of 10.7 ± 1.0 and 0.5 ± 0.1 eV molecule⁻¹ and (b) 206 nm at doses of 22.3 ± 2.0 eV and 0.9 ± 0.02 eV molecule⁻¹. For clarity, only assignments of the bands corresponding to the products observed at low dose experiments are provided. For the assignments of other bands, please refer to Figure 1.

Figure 2. Difference infrared spectra of RDX collected at 5K after exposure to (a) 254 nm at doses of 10.7 ± 1.0 and 0.5 ± 0.1 eV molecule⁻¹ and (b) 206 nm at doses of 22.3 ± 2.0 eV and 0.9 ± 0.02 eV molecule⁻¹. For clarity, only assignments of the bands corresponding to the products observed at low dose experiments are provided. For the assignments of other bands, please refer to Figure 1.

corresponds to antisymmetric stretching modes of −NO2 (nitro) group. The characteristic stretching vibration of nitramine bond (N=NO2) appears at 1323 cm⁻¹ adjacent to 1267 cm⁻¹ band ascribed to symmetric stretching mode of −NO group. The in-plane and out-of-plane bending modes of CH2 group are observed at 1442 and 1377 cm⁻¹ respectively. The ring vibrations of RDX prevail the spectral regions 1100–1000 and 900–700 cm⁻¹.

After the irradiation new vibrational features appear in the regions 3500–3100, 2340, 2231, 2138, 2079, 1861, and 1756 cm⁻¹, which can be ascribed to photolysis products of RDX (Table 4). A broad absorption feature covering the spectral range from 3500 to 3100 cm⁻¹ arises from OH stretching modes of water (H2O) and nitrous acid (HONO). Prominent bands at 2340, 2231, 2138, 2079, 1861, and 1756 cm⁻¹ are assigned to carbon dioxide (CO2), dinitrogen monoxide (N2O), carbon monoxide (CO), formyl radical (HCO), nitrogen monoxide (NO), and the nitrogen monoxide dimer ([NO2]2), respectively. The observed vibrational features of these products are in excellent agreement with those reported by Alix et al. after photodecomposition of RDX employing a broadband UV light. An absorption feature at 1300 cm⁻¹ is also observed (see Figure 2) which can be assigned to O=N=O symmetric stretching mode of either dinitrogen trioxide (N2O3) and/or nitrogen dioxide (NO2). However, the symmetric stretch of NO2 is very weak in intensity; therefore, based on the observed intensity of 1300 cm⁻¹ band in our IR spectrum, it could be assigned to N2O3. It is important to mention that dinitrogen trioxide (N2O3) could either form via a barrier-less radical recombination of nitrogen monoxide (NO) and nitrogen dioxide (NO2) or through bimolecular reaction of nitrous acid (HONO); the latter pathway has a barrier of about 66 kJ mol⁻¹. The barrierless radical–radical recombination seems to be favorable since under UV exposure, nitrous acid (HONO) dissociates rapidly to OH and NO radicals.
Table 4. (a) Infrared Features of RDX before Irradiation and (b) New Vibrational Bands Appeared after Irradiation at 5 K

<table>
<thead>
<tr>
<th>Wavenumber observed (cm⁻¹)</th>
<th>Wavenumber literature (cm⁻¹)</th>
<th>Assignments</th>
<th>Carrier</th>
</tr>
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<tr>
<td>(a) Before Irradiation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3066</td>
<td>3068</td>
<td>ν(CH₂)</td>
<td>C–H asymm. stretch</td>
</tr>
<tr>
<td>2989</td>
<td>3004</td>
<td>ν(CH₂)</td>
<td>C–H symm. stretch</td>
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<td>1581</td>
<td>1576</td>
<td>ν(NO₂)</td>
<td>NO₂ asymm. stretch</td>
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<td>1442</td>
<td>1435</td>
<td>β(CH₂)</td>
<td>CH₂ bending in plane</td>
</tr>
<tr>
<td>1377</td>
<td>1391</td>
<td>γ(CH₂)</td>
<td>CH₂ bending out of plane</td>
</tr>
<tr>
<td>1323</td>
<td>1322</td>
<td>ν(N=NO₂)</td>
<td>N–N symm. stretch</td>
</tr>
<tr>
<td>1267</td>
<td>1275</td>
<td>ν(NO₂)</td>
<td>NO₂ symm. stretch</td>
</tr>
<tr>
<td>1218</td>
<td>1219</td>
<td>ν(N=C-N)</td>
<td>ring skeletal vibrations</td>
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<tr>
<td>1083</td>
<td>1040</td>
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<td>1020</td>
<td>ν(ring)</td>
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<td>779</td>
<td>790</td>
<td>ν(C=N-C)</td>
<td>ring skeletal vibrations</td>
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<th>Wavenumber observed (cm⁻¹)</th>
<th>Wavenumber literature (cm⁻¹)</th>
<th>Assignments</th>
<th>Carrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>(b) After Irradiation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3500–3100</td>
<td>2340</td>
<td>ν(H₂O)</td>
<td>O–H stretch of H₂O</td>
</tr>
<tr>
<td>2331</td>
<td>2227</td>
<td>ν₂(N₂O)</td>
<td>N=O stretch of N₂O</td>
</tr>
<tr>
<td>2138</td>
<td>2140</td>
<td>ν₂(CO)</td>
<td>C=O stretch of CO</td>
</tr>
<tr>
<td>2079</td>
<td>2085</td>
<td>ν(HCO)</td>
<td>C=O stretch of HCO</td>
</tr>
<tr>
<td>1861</td>
<td>1864</td>
<td>ν₁(NO)</td>
<td>N=O stretch of NO</td>
</tr>
<tr>
<td>1756</td>
<td>1757</td>
<td>ν₁([NO]₂)</td>
<td>N=O stretch of [NO]₂</td>
</tr>
<tr>
<td>1300</td>
<td>1305</td>
<td>ν₁(N₂O₃)</td>
<td>O=N=N=O stretch of N₂O₃</td>
</tr>
<tr>
<td>804</td>
<td>812</td>
<td>ν(–ONO)</td>
<td>N–O stretch of –ONO</td>
</tr>
</tbody>
</table>

It is intriguing to analyze the infrared spectra recorded during the dose-dependent photolysis experiments conducted at irradiation wavelengths of 254 nm (4.88 eV) and 206 nm (6.02 eV). Figure 2a reveals the IR spectra recorded after exposure to 254 nm UV light at a dose of 10.7 ± 1.0 eV molecule⁻¹ (high dose) and 0.5 ± 0.1 eV molecule⁻¹ (low dose). At the low dose experiment, only product corresponding to NO (nitrogen monoxide, 1857 cm⁻¹), [NO]₂ (nitrogen monoxide dimer, 1755 cm⁻¹), and N₂O₃ (dinitrogen trioxide, 1292 cm⁻¹) are prominent. This may imply that these products (NO and N₂O₃) rapidly develop during the initial stage of the decomposition relative to alternative products like CO₂, N₂O, CO, and H₂O, which are considered “end members” of the decomposition. The IR spectrum recorded after exposure to 206 nm at a dose of 0.9 ± 0.1 eV molecule⁻¹ reveals product bands corresponding to nitrogen monoxide (NO), nitrogen monoxide dimer ([NO]₂), dinitrogen trioxide (N₂O₃) along with dinitrogen monoxide (N₂O) carbon dioxide (CO₂), and water (H₂O). A new absorption feature emerges at 804 cm⁻¹ which can be attributed to stretching mode of the nitrite (–ONO) group. Although the IR spectra investigated after irradiation at 254 and 206 nm are qualitatively similar for both high dose experiments, we observe noticeable difference in low dose studies. Even at a dose of 0.9 ± 0.1 eV molecule⁻¹, the exposure to 206 nm results in the formation of CO₂, N₂O, and H₂O, which were not observed at 254 nm at a similar dose; this suggests that the decomposition of RDX is faster at a shorter wavelength, i.e., close to the absorption maximum of RDX. When exposed to the lowest doses of 0.10 ± 0.02 and 0.20 ± 0.02 eV molecule⁻¹ at 254 and 206 nm, respectively, the absorptions of the new products are not detectable in the IR spectrum; the intensity of the RDX bands decreases by only 15 ± 2%. The photolysis at 254 nm at a dose of 10.7 ± 1.0 eV molecule⁻¹ results in the decomposition of (5.6 ± 0.6) × 10¹⁵ molecules cm⁻² of RDX, i.e., 73 ± 8%. The amount of NO ((1.0 ± 0.1) × 10¹⁵ molecules cm⁻²), [NO]₂ ((3.1 ± 0.4) × 10¹⁴ molecules cm⁻²), N₂O₃ ((3.0 ± 0.3) × 10¹⁴ molecules cm⁻²), N₂O ((7.9 ± 0.8) × 10¹⁴ molecules cm⁻²), CO ((3.9 ± 0.4) × 10¹⁴ molecules cm⁻²), CO ((3.9 ± 0.4) × 10¹⁴ molecules cm⁻²), and

Formed during the photolysis, we calculated their column densities using a modified Lambert–Beer law equation. The integrated absorption coefficients are acquired from the literature as 5.1 × 10⁻¹⁷ cm molecule⁻¹ for the NO₂ asymmetric stretching mode of RDX at 1581 cm⁻¹. The N=O stretch of nitrogen monoxide (NO; ν₁; 1861 cm⁻¹) and of the nitrogen monoxide dimer ([NO]₂; ν₁; 1756 cm⁻¹) hold integrated band strengths of 5.2 × 10⁻¹⁷ and 9.3 × 10⁻¹⁷ cm molecule⁻¹, respectively. The dinitrogen trioxide (N₂O₃) was identified via its O–N≡O stretching mode (ν₂; 1300 cm⁻¹), which has an integrated absorption coefficient of 4.6 × 10⁻¹⁷ cm molecule⁻¹. The column density of N₂O (dinitrogen monoxide) is measured at 2231 cm⁻¹ (ν₁; N≡N stretching mode) using an integrated band strength of 5.2 × 10⁻¹⁷ cm molecule⁻¹. The C=O stretch of carbon dioxide (CO₂; ν₁; 2340 cm⁻¹) and carbon monoxide (CO; ν₁; 2138 cm⁻¹) holds integrated band strengths of 7.6 × 10⁻¹⁷ and 1.1 × 10⁻¹⁷ cm molecule⁻¹, respectively. The broad absorption band in the region 3500–3100 cm⁻¹ attributed to O–H stretch of water has an averaged absorption coefficient of 2.0 × 10⁻¹⁶ cm molecule⁻¹. The integrated area of the vibrational bands of the reactant/products and their corresponding integrated absorption coefficients are utilized to determine the column densities in the photolysis experiments conducted at 254 and 206 nm; these findings are listed in Table S2 of the Supporting Information.
Table 5. Rate Constants Derived by Solving the Reaction Scheme Shown in Figure 4

<table>
<thead>
<tr>
<th>wavelength (λ, nm)</th>
<th>equation</th>
<th>rate constant</th>
<th>value</th>
<th>units</th>
</tr>
</thead>
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<td>C₃H₆N₆O₆ → 3NO + C₆H₆N₆</td>
<td>k₁</td>
<td>(2.0 ± 0.2) × 10⁻¹⁶</td>
<td>cm³ molecule⁻¹ s⁻¹</td>
</tr>
<tr>
<td></td>
<td>C₃H₆N₆O₆ → 3NO + C₆H₆N₆O₅</td>
<td>k₂</td>
<td>(2.2 ± 0.1) × 10⁻⁵</td>
<td>s⁻¹</td>
</tr>
<tr>
<td></td>
<td>NO₂ + NO → N₂O₢</td>
<td>k₃</td>
<td>(3.6 ± 0.4) × 10⁻⁸</td>
<td>cm³ molecule⁻¹ s⁻¹</td>
</tr>
<tr>
<td></td>
<td>NO + NO → N₂O₂</td>
<td>k₄</td>
<td>(3.1 ± 0.3) × 10⁻⁵</td>
<td>s⁻¹</td>
</tr>
<tr>
<td></td>
<td>C₃H₆N₆O₆ → 3NO₂ + 3H₂CO</td>
<td>k₅</td>
<td>(6.3 ± 0.6) × 10⁻¹</td>
<td>s⁻¹</td>
</tr>
<tr>
<td></td>
<td>H₂CO → 2H + CO</td>
<td>k₆</td>
<td>(2.6 ± 0.3) × 10⁻¹⁰</td>
<td>cm³ molecule⁻¹ s⁻¹</td>
</tr>
<tr>
<td></td>
<td>OH + H → H₂O</td>
<td>k₇</td>
<td>(5.1 ± 0.5) × 10⁻⁵</td>
<td>s⁻¹</td>
</tr>
<tr>
<td></td>
<td>C₃H₆N₆O₆ → X</td>
<td>k₈</td>
<td>(1.6 ± 0.2) × 10⁻⁴</td>
<td>s⁻¹</td>
</tr>
<tr>
<td></td>
<td>C₃H₆N₆O₆ → 3NO₂ + C₆H₆N₆</td>
<td>k₉</td>
<td>(3.0 ± 0.3) × 10⁻⁴</td>
<td>s⁻¹</td>
</tr>
<tr>
<td></td>
<td>NO₂ + NO → N₂O₂</td>
<td>k₁₀</td>
<td>(9.9 ± 1.0) × 10⁻¹⁰</td>
<td>cm³ molecule⁻¹ s⁻¹</td>
</tr>
<tr>
<td></td>
<td>NO + NO → N₂O₢</td>
<td>k₁₁</td>
<td>(5.0 ± 0.5) × 10⁻¹⁰</td>
<td>cm³ molecule⁻¹ s⁻¹</td>
</tr>
<tr>
<td></td>
<td>C₃H₆N₆O₆ → X</td>
<td>k₁₂</td>
<td>(1.6 ± 0.2) × 10⁻³</td>
<td>s⁻¹</td>
</tr>
</tbody>
</table>

Figure 3. Temporal evolution of the column densities of the reactant at 1581 cm⁻¹ (RDX) and of the products at 1861 cm⁻¹ (NO), 1757 cm⁻¹ (NO₂), 1305 cm⁻¹ (N₂O), and 3500–3100 cm⁻¹ (H₂O) during the photodissociation of RDX at (a) 206 nm at a dose of 0.9 ± 0.02 eV molecule⁻¹ and (b) 254 nm at a dose of 0.5 ± 0.1 eV molecule⁻¹. Solid line represents the kinetic fits obtained solving the coupled differential equations leading to the reaction scheme defined in Figure 4 and Table 5.

H₂O ((5.8 ± 0.6) × 10¹⁴ molecules cm⁻²) formed during photolysis accounts for 69 ± 7% of the decomposed RDX molecules. This implies that 30% of the decomposed molecules could not be identified via infrared spectroscopy; these molecules could belong to higher order products and/or are obscured by the fundamentals of the RDX. In the low dose experiment, the amount of RDX molecules destroyed is (1.2 ± 0.2) × 10¹⁵ molecules cm⁻³, which is only 43 ± 5% of the initial column density (2.9 ± 0.2) × 10¹⁵ molecules cm⁻³. At this dose, the quantity of the NO (2.1 ± 0.3) × 10¹⁴ molecules cm⁻²), [NO]₂ ((2.8 ± 0.3) × 10¹³ molecules cm⁻³), and N₂O₃ ((2.2 ± 0.2) × 10¹⁴ molecules cm⁻²) products formed accounts for only 36 ± 3% of the photolyzed RDX molecules. Therefore, we can conclude that almost 74% of the decomposed products were unidentified through IR spectroscopy.

Upon photolysis at 206 nm at a dose of 22.3 ± 2.0 eV molecule⁻¹, about (4.5 ± 0.5) × 10¹³ RDX molecules cm⁻² dissociate; this corresponds to 83 ± 8% of the initial column density ((5.4 ± 0.5) × 10¹⁵ molecules cm⁻³). The amount of products such as NO ((5.2 ± 0.7) × 10¹⁴ molecules cm⁻³), [NO]₂ ((2.2 ± 0.2) × 10¹⁴ molecules cm⁻³), N₂O₃ ((5.5 ± 0.6) × 10¹⁴ molecules cm⁻³), N₂O ((1.0 ± 0.1) × 10¹⁵ molecules cm⁻³), CO₂ ((6.9 ± 0.7) × 10¹⁴ molecules cm⁻³), CO ((5.6 ± 0.6) × 10¹⁴ molecules cm⁻³) products formed accounts for only 36 ± 3% of the photolyzed RDX molecules.
× 10^{14} \text{ molecules cm}^{-2}, \text{ and } \text{H}_2\text{O} \left( (4.3 \pm 0.4) \times 10^{14} \text{ molecules cm}^{-2} \right) \text{ formed during photodecomposition accounts for } 87 \pm 8\% \text{ of the decomposed RDX molecules. It is intriguing to compare the high and low dose photodissociation studies conducted at 206 nm. On the basis of column density calculations, the amount of RDX molecules photolyzed at a dose of 0.9 \pm 0.1 \text{ eV molecule}^{-1} \text{ is } (1.5 \pm 0.2) \times 10^{15} \text{ molecules cm}^{-2}, \text{ which is only } 55 \pm 5\% \text{ of the initial number of molecules } (2.7 \pm 0.2) \times 10^{15} \text{ molecules cm}^{-2}). \text{ Products formed during photodecomposition including NO } \left( (3.2 \pm 0.3) \times 10^{14} \text{ molecules cm}^{-2} \right), [\text{NO}]_2 \left( (7.8 \pm 0.8) \times 10^{13} \text{ molecules cm}^{-2} \right), \text{N}_2\text{O}_3 \left( (2.6 \pm 0.2) \times 10^{14} \text{ molecules cm}^{-2} \right), \text{N}_2\text{O} \left( (7.7 \pm 0.8) \times 10^{15} \text{ molecules cm}^{-2} \right), \text{ and } \text{H}_2\text{O} \left( (1.2 \pm 0.2) \times 10^{14} \text{ molecules cm}^{-2} \right) \text{ accounts for } 62\% \text{ of the decomposed RDX molecules. The comparison of the column densities of the reactant versus products between 254 and 206 nm reveal that the amount of decomposed RDX molecules and that of products formed is higher at later wavelength. These findings are indicative of higher decomposition rates at the shorter wavelength, where } \pi \rightarrow \pi^* \text{ transitions occur.}

### 3.1.3. Quantitative Analysis: Kinetic Fitting.

Having identified the species formed during the photolysis of RDX, we are now proposing the underlying mechanism of their formation. This is achieved by exploiting a set of coupled differential equations to numerically fit the temporal profiles of the column densities of the new species formed during the photolysis. A MATLAB script was used to solve the equations and determine the rate constants. Initially assuming first-order and second-order kinetics, the rate constants were optimized to reduce the error between experimentally observed column densities and those predicted from the numerical solutions. The resulting rate constants are listed in Table 5 with the numerical fits plotted in Figure 3 along with the observed column densities. The kinetic scheme is compiled in Figure 4. It is important to mention here that only low dose photolysis experiments conducted at 206 and 254 nm have been considered here. At high dose, the rate of decomposition may drastically change after some duration because the accumulated products also absorb the UV photons.

As mentioned previously, the FTIR spectrometer detects five products when the sample was exposed to 206 nm light at a dose of 0.9 \pm 0.1 \text{ eV molecule}^{-1}. \text{ To rationalize the formation of these products and account for the mass balance, nine key pathways have been considered. First, reaction } k_9 \text{ which involves decomposition of RDX into nitrogen dioxide (NO) and a higher molecular weight intermediate } (\text{C}_3\text{H}_2\text{N}_3) \text{, has a rate constant of } (7.7 \pm 0.8) \times 10^{-4} \text{ s}^{-1}. \text{ RDX could also decompose to nitrogen monoxide and intermediate } \text{C}_3\text{H}_2\text{N}_3\text{O}_2; \text{ this reaction has a rate constant value of } (2.2 \pm 0.2) \times 10^{-5} \text{ s}^{-1} (k_2). \text{ The third decomposition pathway includes elimination of } \text{HONO}, \text{ which could rapidly decompose into nitrogen monoxide (NO) and hydroxyl (OH) radicals as mentioned above } (k_1 = (3.2 \pm 0.4) \times 10^{-4} \text{ s}^{-1}). \text{ The resulting NO and NO}_2 \text{ may react to form dinitrogen trioxide } \text{N}_2\text{O}_3 \text{ which } \pi \rightarrow \pi^* \text{ reaction has a rate constant of } k_1 = (3.6 \pm 0.4) \times 10^{-18} \text{ cm}^{-2} \text{ molecule}^{-1} \text{ s}^{-1}. \text{ Nitrogen monoxide molecules can undergo self-reaction to form nitrogen monoxide dimer } \text{(NO)}_2; \text{ this bimolecular reaction has a rate constant of } k_1 = (3.6 \pm 0.4) \times 10^{-18} \text{ cm}^{-2} \text{ molecule}^{-1} \text{ s}^{-1}. \text{ It is important to note here that NO molecules formed in the second and third reactions could also combine to form the } \text{(NO)}_2 \text{ dimer. RDX could dissociate directly to dinitrogen oxide } \text{(NO)}_2 \text{ and formaldehyde } \text{(H}_2\text{CO}) \text{ } (k_2 = (3.1 \pm 0.3) \times 10^{-5} \text{ s}^{-1}). \text{ Formaldehyde rapidly decomposes to form carbon monoxide } \text{(CO)} \text{ and atomic/molecular hydrogen } (k_1 = (6.3 \pm 0.6) \times 10^{-1} \text{ s}^{-1}). \text{ The OH (hydroxy radical) and hydrogen can combine to form water } (k_5 = (2.6 \pm 0.3) \times 10^{-10} \text{ cm}^{-2} \text{ molecule}^{-1} \text{ s}^{-1}). \text{ Finally, a generic reaction involving decomposition of RDX into products which could not be identified through IR spectroscopy has been considered to account for the mass balance as discussed above } (k_9 = (5.1 \pm 0.5) \times 10^{-4} \text{ s}^{-1}).

When the RDX samples are exposed to 254 nm light at a low dose \((0.10 \pm 0.02 \text{ eV molecule}^{-1})\), only three products \((\text{NO}, \text{NO})_2, \text{ and } \text{N}_2\text{O}_3\) are detected via IR spectroscopy. Their origin can be justified by four key pathways. (i) stepwise decomposition of RDX leading to three nitrogen dioxide \((\text{NO})_2\) molecules and intermediate \(\text{C}_3\text{H}_2\text{N}_3\) \((k_1')\), (ii) RDX decomposition into nitrogen monoxide \((\text{NO})\) and intermediate \(\text{C}_3\text{H}_2\text{N}_3\text{O}_3\) \((k_2')\), (iii) reaction of NO and NO molecules to form \(\text{N}_2\text{O}_3\) \((k_3')\), (iv) reaction of two nitrogen monoxide \((\text{NO})\) molecules to form the dinitrogen dioxide \((\text{NO})_2\) \((k_4')\). Finally, a fifth pathway for the decomposition of RDX into products which are unidentified through IR spectroscopy has been considered and expressed generically via the rate constant } k_5'. \text{ The aforementioned reaction mechanisms have also been exploited to fit the temporal profiles of the products NO, } (\text{NO})_2, \text{ and } \text{N}_2\text{O}_3 \text{ observed in the 206 nm photolysis experiment. Figure 3 further reveals that the profiles of } \text{nitrogen monoxide (NO)} \text{ and dinitrogen monoxide dimer can be fit with fast kinetics, while products such as dinitrogen monoxide } \text{(NO)}_2 \text{ and water } \text{(H}_2\text{O}) \text{ exhibit slower rises. This suggests that the NO and } \text{N}_2\text{O}_3 \text{ products are likely formed rapidly at the early stage of decomposition. It is important to note here that the total concentration of nitrogen monoxide } \text{(NO)} \text{, i.e., column density of } \text{NO} + (\text{NO})_2 \text{ in the reaction medium is always higher than the other products such as dinitrogen oxide } \text{(N}_2\text{O}_3) \text{, carbon monoxide } \text{(CO}_2) \text{, water.
are depicted in Figures 7 and 8 respectively. It is essential to
pro
upon further photolysis. The mass spectra and the TPD
191, could decompose to any lower molecular weight products
molecular weight products holding
observed. This proposed that these species, especially higher
60, 87, 98, 105, 117, 118, 119, 130, 146, 149, and 191 are not
products are revealed in Table 6 and Figure 6.
10.23,26 our recent investigation on RDX
isomer selective soft-photoionization
decomposition exploiting isomer selective soft-photoionization
technique enabled us to assign it to ketene (H2CCO; IE = 9.62 eV).
The ion signal at m/z = 44 can be ascribed to dinitrogen
monoxide (N2O; IE = 12.89 eV) and/or methane diazene
holding the molecular formula CH4N2 (IE = 8.81 eV). The
photoionization energy of 10.49 eV used in this experiment is

(H2O) and dinitrogen trioxide (N2O3), even at the low dose
experiments.

3.2. Mass Spectrometry. Single-photon reflectron time-
of-flight mass spectrometry enables the detection of wide range
of photodecomposition products of RDX based on their mass-
to-charge (m/z) ratio and sublimation temperature. Parts a–c
of Figures 5 reveal the temperature-dependent mass spectra
measured after exposing the RDX samples to 254 nm (4.88
eV) at doses of 10.7 ± 1.0, 0.5 ± 0.1, and 0.10 ± 0.02 eV
molecule−1 respectively. Parts d–f Figure 5 show the data after
photolysis of RDX at 206 nm (6.02 eV) at doses of 22.3
± 0.90, 0.50, and 0.20 ± 0.02 eV molecule−1. It is apparent from
Figure 5 that the ion counts corresponding to lower molecular
weight species are enhanced at the high dose experiment
compared to low dose study; higher molecular weight products
are more prominent at lower doses. This suggests that higher
mass (primary) products eventually decompose to lower
weight species as the dose increases. Overall, we observed
products holding m/z values of 30, 31, 42, 44, 45, 46, 57, 58,
59, 60, 71, 72, 73, 74, 75, 81, 87, 88, 89, 97, 98, 99, 101, 105,
117, 118, 119, 128, 130, 146, 149, and 191. The assigned
molecular formulas and potential structures of all these
products are revealed in Table 6 and Figure 6.

It is intriguing to note here that when RDX samples are
exposed to very high doses of 39.0 ± 5.0, 66.8 ± 7.0, 50.8 ± 5.0,
and 83.0 ± 8.0 eV molecule−1 at 254, 236, 222, and 206
nm respectively, products corresponding to m/z values of 57,
60, 87, 98, 105, 117, 118, 119, 130, 146, 149, and 191 are not
observed. This proposed that these species, especially higher
molecular weight products holding m/z = 130, 146, 149, and
191, could decompose to any lower molecular weight products
upon further photolysis. The mass spectra and the TPD
profiles of the individual masses recorded in these experiments
are depicted in Figures 7 and 8 respectively. It is essential to
mention here that the ReTOF mass spectrum collected in a
blank experiment—that is an experiment conducted without
exposing the RDX sample to UV light—did not reveal any
signal (Figure S5). This ensures that the product signals
observed in the photolysis experiments are solely due to the
to the action of UV photons.

Figure 9 display the TPD traces of the photoproducts of
RDX observed after exposure to 254 nm at a dose of 10.7 ±
1.0, 0.5 ± 0.1, and 0.10 ± 0.02 eV molecule−1. Signal at m/z =
30 and m/z = 31 can be allocated to nitrogen monoxide (NO;
IE = 9.26 eV) and methylamine (CH3NH2; IE = 8.90 eV),
respectively. The maximum intensity at m/z = 31 at 260 K
correlates with the second sublimation event of m/z = 30 at
260 K, proposing that at least some of the ion counts recorded
at m/z = 30 at 260 K could be due to the fragment of
CH3NH2+, i.e., CH3NH+. The appearance energy (AE) of
10.18 eV for CH3NH+ from CH3NH2 has been reported by
Losing et al., which further corroborates our assignment.6
In previous experimental studies, ion signal at m/z = 30 has been
assigned to formaldehyde (H2CO) based on electron impact
ionization. In the present study, the photoionization energy of
10.49 eV is lower than the ionization energy of formaldehyde
(H2CO, IE = 10.88 eV); therefore, the signal at m/z = 30 has
to be assigned to nitrogen monoxide (NO; IE = 9.26 eV).
Product signal at m/z = 42 has been observed in several studies
investigating the decomposition of RDX. Although, m/z = 42 is
assigned to diazomethane (H2CNN; IE = 8.99 eV) in most
of the studies,10,23,26 our recent investigation on RDX
decomposition exploiting isomer selective soft-photoionization
technique enabled us to assign it to ketene (H2CCO; IE = 9.62 eV).46 The ion signal at m/z = 44 can be ascribed to dinitrogen
monoxide (N2O; IE = 12.89 eV) and/or methane diazene
holding the molecular formula CH4N2 (IE = 8.81 eV). The
photoionization energy of 10.49 eV used in this experiment is

Figure 5. Temperature-dependent ReTOF mass spectra collected during the sublimation phase after exposure to 254 nm at doses of (a) 10.7 ± 1.0,
(b) 0.5 ± 0.1, and (c) 0.10 ± 0.02 eV molecule−1. Exposure to 206 nm at doses of (d) 22.3 ± 2.0 eV, (e) 0.9 ± 0.02, and (f) 0.20 ± 0.02 eV
molecule−1.
lower than the ionization energy of dinitrogen monoxide (N₂O); therefore, the signal at \( m/z = 44 \) should be due to CH₃NNH (methane diazene). A broad signal at \( m/z = 45 \) can be associated with the structural isomers of molecular formula CH₃NO: nitrosomethane (CH₃NO; IE = 9.30 eV), formamide (HCONH₂; IE = 10.16 eV), and formaldehyde oxime (H₂CNOH; IE = 10.11 eV). Behrens et al. also observed a product signal at \( m/z = 45 \), which was assigned to molecular formula CH₃NO based on isotopic scrambling experiment.⁸,⁹

The peak maxima of the TPD profile measured at \( m/z = 45 \) at 256 and 316 K correlates with the second and third sublimation events recorded at \( m/z = 30 \) implying that the NO⁺ fragment of CH₃NO⁺ (nitrosomethane) could contribute to some of the ion counts at \( m/z = 30 \) at 256 and 316 K.

Table 6. Probable Molecular Formulas of the Masses Observed in the ReTOF Mass Spectrometer after Photodecomposition of RDX at 254 and 206 nm⁶

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<th>Molecular formula</th>
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“High, low and lowest denotes the dose strength. Presence and absence of a signal at a given m/z value is represented by (+) and (−) signs respectively. Ion signal intensities of the m/z values marked with blue color are enhanced at a high dose while that of marked with red color are enhanced at a low dose."
Therefore, we can propose that at least a fraction of the ion counts measured at $m/z = 45$ and $m/z = 30$ at around 256 and 316 K could be due to CH$_3$NO$^+$ and its fragment ions NO$^+$, respectively. Dose-dependent experiments show a significant decrease in the ion intensity at $m/z = 30$ and $m/z = 45$ at low dose. Signal at $m/z = 31$ and 44 also disappears in low dose experiments, indicating that these products must be originating from higher molecular weight products at later stage of the photolysis process. On the other hand, ion counts at $m/z = 42$ are enhanced in low dose experiments ($0.5 \pm 0.1$ and $0.10 \pm 0.02$ eV molecule$^{-1}$) revealing that this product could form at an early stage of decomposition.

The TPD profile recorded at $m/z = 46$ can be allocated to nitrogen dioxide (NO$_2$; IE = 9.58 eV). Furthermore, the

Figure 6. Probable structures and molecular formulas of the masses observed in ReTOF mass spectrometer.
Figure 7. Temperature-dependent ReTOF mass spectra collected during the sublimation phase measured after exposure to (a) 254, (b) 236, (c) 222, and (d) 206 nm at doses of 39.0 ± 5.0, 66.8 ± 7.0, 50.8 ± 5.0, and 83.0 ± 8.0 eV molecule⁻¹ respectively.

Figure 8. TPD profiles of the ion counts recorded at mass-to-charge ratios of 30, 42, 44, 45, 46, 58, 59, 71, 72, 73, 74, 75, 81, 87, 88, 97, and 128 at a photoionization energy of 10.49 eV, after exposure to 254, 236, 222, and 206 nm photons at doses of 39.0 ± 5.0, 66.8 ± 7.0, 50.8 ± 5.0, and 83.0 ± 8.0 eV molecule⁻¹ respectively.
sublimation events measured at \( m/z = 46 \) at around 284 and 316 K correlate with two peaks observed at \( m/z = 30 \) at around 284 and 316 K, signifying that fragments of NO\(_2\), i.e., NO\(^+\), may contribute to the ion counts measured at \( m/z = 30 \) at these temperatures. The signal at \( m/z = 58 \) can be assigned to an amine with the molecular formula C\(_2\)H\(_6\)N\(_2\) or to a nitroso derivative of methylene nitramine (CH\(_2\)N\(_2\)O). In several experimental and computational studies, the product at \( m/z = 58 \) has been assigned to CH\(_2\)N\(_2\)O. The ion signal at \( m/z = 59 \) can be attributed to a molecular formula C\(_2\)H\(_5\)NO based on previous assignments reported by Behrens and co-workers. The product corresponding to \( m/z = 60 \) can be allocated to N\(_2\)O\(_2\) or designated as the hydrogenated form of the amine moiety allocated to \( m/z = 58 \) and hence might be linked to the molecular formula C\(_2\)H\(_8\)N\(_2\) (N-methylmethanediamine). The former (N\(_2\)O\(_2\); 60 amu) could form via self-reaction of nitrogen monoxide (NO). The TPD profiles measured at \( m/z = 59 \) and 60 are very similar suggesting that some of the ion counts at \( m/z = 59 \) could be due to C\(_2\)H\(_8\)N\(_2\) \(^{+}\) generated via fragmentation of internally "hot" C\(_2\)H\(_8\)N\(_2\) \(^{+}\) (N-methylmethanediamicine; \( m/z = 60 \)) ions. Although the appearance energy (AE) for C\(_2\)H\(_8\)N\(_2\) \(^{+}\) from C\(_2\)H\(_8\)N\(_2\) \(^{+}\) (N-methylmethanediamicine ion) is not known, the AE of fragment C\(_2\)H\(_8\)N\(_2\) \(^{+}\) from ethylenediamine (C\(_2\)H\(_8\)N\(_2\)) \(^{+}\) ion at a photoionization energy of 9.20 eV has been reported. Therefore, fragmentation of C\(_2\)H\(_8\)N\(_2\) \(^{+}\) (N-methylmethanediamicine ion) into C\(_2\)H\(_8\)N\(_2\) \(^{+}\) at a photoionization energy of 10.49 eV is likely. The ion counts at \( m/z = 46 \) and \( m/z = 58 \) are reduced by a factor of 2 at low dose (0.5 \( \pm \) 0.1 eV molecule\(^{-1}\)) and show almost negligible counts at the lowest dose (0.10 \( \pm \) 0.02 eV molecule\(^{-1}\)). Similarly, no signal is observed at \( m/z = 59 \) and 60 in low dose experiments. These findings provide evidence that species corresponding to \( m/z = 46, 58, 59, \) and 60 could be defined as secondary products. Ions recorded at \( m/z = 71 \) are likely linked to an amine holding the molecular formula C\(_2\)H\(_8\)N\(_3\). Ions at \( m/z = 72 \) can be linked to 1-methyleneara with the molecular formula C\(_2\)H\(_5\)NO. The signal at \( m/z = 71 \) has also been observed in electron impact fragmentation of RDX by Yinon et al. Product at \( m/z = 73 \) is likely linked to C\(_2\)H\(_8\)N\(_3\) \(^{+}\) which is hydrogenated counterpart of C\(_2\)H\(_8\)N\(_2\) \(^{+}\) (\( m/z = 71 \)). The TPD traces measured at these channels (\( m/z = 71, 72 \)) show peak maxima at same temperatures of 310 K. This could be either due to cosublimation of the products or photofragmentation of one species into another. Fragmentation of C\(_2\)H\(_8\)N\(_2\)O\(^+\) to C\(_2\)H\(_8\)N\(_2\)O\(^{+}\) is viable. The TPD profile measured at \( m/z = 74 \) can be certainly associated with the monomeric unit of RDX i.e. methylene nitramine (H\(_2\)CNNO\(_2\)), based on assignments reported by previous studies. The ion signal at \( m/z = 75 \) can be assigned to a molecular formula C\(_2\)H\(_7\)N\(_3\) based on the appearance energy of 9.20 eV.
be allocated to an amine \( \text{C}_2\text{H}_9\text{N}_3 \) or \( \text{c-hydroxyl-N-methyl formamide} \) \( \text{C}_2\text{H}_5\text{NO}_2 \). The latter \( \text{C}_2\text{H}_5\text{NO}_2^+ \); \( m/z = 75 \) has been observed in the thermal decomposition of RDX.21 Ion counts for species at \( m/z = 71 \) and 72 increase at a dose of \( 0.5 \pm 0.1 \text{ eV molecule}^{-1} \), suggesting that these species could be generated at the early stage of decomposition. On the other hand, intensity of ions signals at \( m/z = 74 \) and 75 are reduced by a factor of 2 at medium dose and by a factor of 5 at the lowest dose \( (0.10 \pm 0.02 \text{ eV molecule}^{-1}) \) providing evidence that products corresponding to \( m/z \) values of 74 and 75 should be originating at a later stage of the photolysis.

TPD traces observed via their ion counts at \( m/z = 81 \) and 87 can be attributed to species carrying ring moieties of RDX. \( m/z = 81 \) has been often associated with triazine \( \text{C}_3\text{H}_3\text{N}_3 \); \( \text{IE} = 9.80 \text{ eV} \)8,80 while \( m/z = 87 \) is likely associated as a fully hydrogenated counterpart of \( 1,3,5\)-triazine, i.e., \( 1,3,5\)-triazinane \( \text{C}_3\text{H}_9\text{N}_3 \). Although \( m/z = 81 \) has been observed in several experiments,8,26 there is only a single report of product at \( m/z = 87 \). Signal at \( m/z = 88 \) can be ascribed to mononitro compound with the molecular formulas \( \text{CN}_2\text{O}_3 \) or \( \text{C}_2\text{H}_4\text{N}_2\text{O}_2 \) following the assignments reported by Schroeder. 78 Signal at \( m/z \) values of 89 and 97 can be linked to aminomethyl nitramine \( \text{CH}_3\text{N}_3\text{O}_2 \) and \( \text{oxy-sym-triazine} \) \( \text{OST} \); \( \text{C}_3\text{H}_3\text{N}_3\text{O} \), respectively. The later \( (m/z = 97) \) has been observed in thermal decomposition studies and was assigned to \( \text{C}_3\text{H}_3\text{N}_3\text{O} \). Products observed at \( m/z = 81, 87, 88, \) and 89 are generated during the later stages of the photodissociation based on the fact that ion counts of these species are reduced by a factor of 2–3 at low dose \( (0.5 \pm 0.1 \text{ eV molecule}^{-1}) \); nearly no counts are observed at the dose of \( 0.10 \pm 0.02 \text{ eV molecule}^{-1} \). It is crucial to mention here that fragmented ions of \( \text{CH}_3\text{N}_3\text{O}_2^+ \); \( m/z = 89 \), i.e., \( \text{CH}_3\text{N}_3\text{O}_2^+ \) and \( \text{CHN}_3\text{O}_2^+ \), could contribute to some of the ion counts at \( m/z = 88 \) and 87 respectively; this is evident as the peak maxima of the TPD profile recorded at \( m/z = 89 \) is in agreement with the sublimation peak observed at \( m/z = 88 \) and 87 at around 310 K.

The signal at \( m/z = 98 \) is allocated to a mononitroso compound holding the molecular formula \( \text{C}_2\text{H}_2\text{N}_4\text{O} \). Mono-nitroso species have been proposed to form during RDX decomposition in previous experimental studies.15,8 The TPD profile recorded at \( m/z = 99 \) can be associated with the hydrogenated form of \( \text{oxy-sym-triazine} \) \( \text{C}_3\text{H}_3\text{N}_3\text{O} \); \( m/z = 97 \), hence assigned to the molecular formula \( \text{C}_3\text{H}_5\text{N}_3\text{O} \). Although, \( m/z = 97 \) has been observed in previous condensed phase studies investigating the decomposition of RDX, the signature of \( m/z = 99 \) has not been observed before. It is also important to note that the maximum of the TPD profile at \( m/z = 99 \) corresponds to the data recorded at \( m/z = 98 \) and 97; this suggests that \( \text{C}_3\text{H}_3\text{N}_3\text{O}^+ \); \( m/z = 99 \) could fragment into \( \text{C}_3\text{H}_3\text{N}_3\text{O}^+ \) and \( \text{C}_3\text{H}_3\text{N}_3\text{O}^+ \). Signals at \( m/z = 101 \), 105, 117, and 118 may be allocated to mononitro species holding molecular formulas \( \text{C}_3\text{H}_3\text{N}_3\text{O}_2 \), \( \text{C}_2\text{H}_4\text{N}_2\text{O}_2 \), \( \text{C}_3\text{H}_3\text{N}_3\text{O}_2 \), and \( \text{C}_4\text{H}_5\text{N}_3\text{O}_2 \) respectively. Product at \( m/z = 101 \) has been reported by Yinon et al. investigating the fragmentation of RDX and was assigned to \( \text{C}_2\text{H}_3\text{N}_3\text{O}_2^+ \). Following similar
Figure 11. continued
assignment, we assigned mass signal at $m/z = 101$ to C$_2$H$_7$N$_3$O$_2$$^+$, $m/z = 105$ (C$_2$H$_6$N$_4$O$_2$) can be considered as hydrogenated counterpart of C$_2$H$_3$N$_3$O$_2$$^+$ ($m/z = 101$). It is important to note here that evidence of product species at $m/z = 105, 117,$ and 118 has been recently reported by our group; these species have not been addressed previously in experimental or computational studies. Their TPD profiles ($m/z = 105, 117,$ and 118) reveal maxima of the ion intensity at the same temperatures either due to cosublimation of the products or fragmentation of one species into another. The fragment ion C$_2$H$_7$N$_4$O$_2$$^+$ from C$_2$H$_6$N$_4$O$_2$$^+$ ($m/z = 118$) could contribute to the ion signal at $m/z = 117$. Ion signal at $m/z = 119$ has not been observed before; this new product can be assigned to nitro−nitroso moiety with the molecular formula.

Figure 11. Proposed decomposition mechanisms of RDX into products at (a) 30, 31, 42, 44, 46, 58, 59, 81, 87, 97, 105, and 130 amu and at (b) 45, 57, 59, 71, 72, 73, 74, 75, 81, 88, 97, 99, 117, 118, 128, 149, and 191 amu (masses shaded with color bars cyan, blue, and red). Reaction mechanisms predicted through previous theoretical calculations are shown in green. Pathways which are selectively favorable at 254 and 206 nm are differentiated using red- and blue-colored arrows, respectively. Products preferably observed at lower and higher photon energies are shaded with red- and blue-colored bars, respectively.
C\textsubscript{3}H\textsubscript{6}N\textsubscript{5}O\textsubscript{4}. Products holding nitro and nitroso groups have been proposed to form during decomposition of RDX\textsuperscript{8,10}. The signal at \textit{m/z} = 128 can be allotted to the cyclic mononitro moiety (C\textsubscript{4}H\textsubscript{6}N\textsubscript{4}O\textsubscript{2}). Evidence of \textit{m/z} = 128 has been reported in previous studies\textsuperscript{11,12}. The TPD profile measured at \textit{m/z} = 146 can be considered as the mononitro counterpart of oxy-sym-triazine, i.e., 5-nitro-1,3,5-triazinan-2-one; therefore, it might be assigned to molecular formula C\textsubscript{4}H\textsubscript{6}N\textsubscript{5}O\textsubscript{2}. Similarly, \textit{m/z} = 191 can be linked to dinitro form of OST (C\textsubscript{4}H\textsubscript{6}N\textsubscript{5}O\textsubscript{3}; \textit{m/z} = 97) holding molecular formula C\textsubscript{4}H\textsubscript{6}N\textsubscript{5}O\textsubscript{3}. The proposed molecular formulas of \textit{m/z} = 146 and 191 are in agreement with Yinon et al.\textsuperscript{80} Although species at \textit{m/z} values of 146 and 191 have been observed before in electron fragmentation study of RDX, these species have not been reported previously in UV photolysis experiments. Ion signal at \textit{m/z} = 149 can be allocated to molecular formula C\textsubscript{4}H\textsubscript{11}N\textsubscript{3}O\textsubscript{3}. To the best of our knowledge, signal corresponding to product \textit{m/z} = 149 can be allocated to molecular formula C\textsubscript{4}H\textsubscript{11}N\textsubscript{3}O\textsubscript{3}. The RDX molecules are electronically excited when exposed to UV light. Gas phase calculations suggest that excited molecules may relax from higher electronic states (S\textsubscript{1}, S\textsubscript{2}) to higher vibrational levels of its ground state (S\textsubscript{0} RDX\textsubscript{NO}) and finally dissociate from its S\textsubscript{0} RDX\textsubscript{NO} state following three primary reaction channels: (i) N\textsubscript{2}O bond fission, (ii) HONO elimination, and (iii) C–N bond cleavage. The calculated energy barriers for the N\textsubscript{2}O fission (163 kJ mol\textsuperscript{-1}) and HONO elimination (164 kJ mol\textsuperscript{-1}) are lower than that for C–N bond rupture, and hence the former two channels are more favorable at the ground state.\textsuperscript{35} On the basis of these mechanisms, we have proposed probable reaction channels in parts a and b of Figures 11 that could occur after electronic excitation of RDX. In Figure 11a, we depict reactions that could initiate due to N–N\textsubscript{2}O fission, C–N bond rupture, and HONO elimination at the ground state of RDX; these reactions have been previously proposed through theoretical calculations\textsuperscript{35,37,41,42} and certainly rationalize the products observed in our experiments.

### 3.3.1. N–N\textsubscript{2}O Fission Channel

The first N\textsubscript{2}O bond fission of RDX (1) leads to a cyclic aminyl radical, 2a (C\textsubscript{3}H\textsubscript{6}N\textsubscript{4}O\textsubscript{2}; 176 amu) and nitrogen dioxide, 3 (NO\textsubscript{2}; 46 amu) which requires an energy of 163 kJ mol\textsuperscript{-1}.\textsuperscript{35} The later (NO\textsubscript{2}) can decompose to nitrogen monoxide, 4 (NO; 30 amu), via N–O bond cleavage. Radical 2a (C\textsubscript{3}H\textsubscript{6}N\textsubscript{5}O\textsubscript{2}; 176 amu) can undergo a second N–N\textsubscript{2}O bond fission followed by 1,2-hydrogen shift to yield a mononitro product, 5b (C\textsubscript{3}H\textsubscript{5}N\textsubscript{3}O\textsubscript{2}; 130 amu) after crossing an energy barrier of 187.4 kJ mol\textsuperscript{-1}; this pathway was predicted computationally by Goddard and co-workers.\textsuperscript{35} Alternatively, intermediate 5a can also accept two hydrogen atoms to form a cyclic mononitro product, 6 (C\textsubscript{4}H\textsubscript{6}N\textsubscript{5}O\textsubscript{2}; 132 amu). This mononitro moiety (6) may encounter N–N\textsubscript{2}O fission followed by hydrogen addition leading to 1,3,5-triazinane, 8 (C\textsubscript{3}H\textsubscript{8}N\textsubscript{4}O\textsubscript{2}; 87). Products corresponding to the molecular masses of 130 (C\textsubscript{3}H\textsubscript{6}N\textsubscript{5}O\textsubscript{2}), 87 (C\textsubscript{3}H\textsubscript{7}N\textsubscript{3}O\textsubscript{2}), and 46 (NO\textsubscript{2}) amu were observed in our experiments, signifying a high probability of N–N\textsubscript{2}O fission(s) of RDX. It is intriguing to note that species holding \textit{m/z} = 130 and 87 were not observed in the mass spectrum when exposed to 254 nm light at the lowest dose (0.10 ± 0.02 eV molecule\textsuperscript{-1}; Figure 9). On the contrary these species (\textit{m/z} = 130 and 87) were detected upon photolysis at 206 nm light at the lowest dose (0.20 ± 0.02 eV molecule\textsuperscript{-1}; Figure 10). This finding may indicate that pathways leading to products holding masses 130 and 87 amu, i.e., N–N\textsubscript{2}O fission of radical 2a followed by a 1,2-hydrogen shift or hydrogen addition, are (preferentially) formed at higher photon energy.

### 3.3.2. C–N Bond Rupture Channel

The cyclic aminyl radical, 2a (C\textsubscript{3}H\textsubscript{6}N\textsubscript{4}O\textsubscript{2}; 176 amu), could undergo a C–N bond rupture to form an acyclic intermediate, 2b (C\textsubscript{3}H\textsubscript{5}N\textsubscript{3}O\textsubscript{2}; 166 amu), via a barrier of 110 kJ mol\textsuperscript{-1}.\textsuperscript{35,37} This radical (2b) may encounter a second C–N bond cleavage which has an energy barrier of 103 kJ mol\textsuperscript{-1}, to yield a mononitro N-centered radical, 9 (C\textsubscript{3}H\textsubscript{7}N\textsubscript{4}O\textsubscript{2}; 102 amu), and methylene nitritane, 10 (CH\textsubscript{2}N\textsubscript{2}O\textsubscript{2}; 74 amu). Chakraborty et al. predicted this reaction sequence via \textit{ab initio} calculations.\textsuperscript{35} Radical 9 can eliminate a hydrogen atom to generate a mononitro product, 11 (C\textsubscript{3}H\textsubscript{6}N\textsubscript{5}O\textsubscript{2}; 101 amu). Radical intermediate 9 (C\textsubscript{3}H\textsubscript{7}N\textsubscript{3}O\textsubscript{2}) could undergo cyclization followed by elimination of N\textsubscript{2}O to generate an oxygen-
centered radical, 13 (C2H5NO); this pathway was predicted by Thynell and co-workers through quantum chemical calculations. This radical, 13, may accept a hydrogen atom leading to a product having mass 59 amu (C2H5NO; 14a), which is observed in the experiment.

Intermediate 2b may further undergo a hydrogen-shift to form yet another acyclic carbon-centered radical, 2c (C2H5NO2;*); this process requires an energy of 36 kJ mol−1. Radical intermediate 2c dissociates to yet another carbon-centered radical, 15 (C2H5NO2;*; 149 amu), and a hydrogen cyanide molecule (HCN) after crossing a barrier of 68 kJ mol−1; this pathway was proposed by Chakraborty et al. and Schweigert through ab initio calculation. This radical (C2H5NO2;*; 15) may eliminate a NO2 molecule via N−NO2 fission to yield a stable intermediate, 16 (C2H5NO2; 103 amu), which can accept two hydrogen atoms to form the product 17 (C2H5NO2; 105 amu). The latter (17) could experience yet another C−N bond cleavage leading to methylamine, 18 (CH3NH2; 31 amu) and methylene nitramine, 10 (CH2NNO2; 74 amu). Intermediate 16 could also dissociate to N-centered radical, 19 (C2H5N*; via N−NO2 fission; this radical could undergo C−N scission to form methylenimine (CH2N; 20). Addition of two hydrogen atoms to methylenimine could lead to its hydrogenated counterpart methylamine (CH3NH2; 18), which has been observed in the experiment. Radical 19 could also accept a hydrogen radical to form the product, 21a (C2H5N2), holding mass 58 amu. The resulting methylene nitramine (CH2NNO2; 10) molecules may dissociate to dinitrogen monoxide, 22 (N2O; 44 amu), and formaldehyde, 23 (H2CO; 30 amu). The N2O molecule may react with the CH2N* radical to produce diazomethane (CH2NN). This reaction pathway was predicted by Goddard and co-workers based on theoretical calculations. Furthermore, the diazomethane (CH2NN) molecules could undergo a hydrogen addition reaction to generate methane diazene (CH2NNH). H2CO (formaldehyde) either dissociates to CO (carbon monoxide; 26; 28 amu) and hydrogen and/or it reacts with another formaldehyde molecule to form ketene, 27 (H2CCO; 42 amu), and water (H2O; 18 amu). The later pathway, i.e., formation of ketene was predicted computationally and verified experimentally in our previous study. The detection of products holding masses of 105, 101, 74, 58, 59, 42, and 31 amu in our experiment (Figure 9) further validates the likelihood of the C−N bond rupture channel in the UV decomposition of RDX. The existence of these masses also reveals evidence of reactive radical intermediates such as C2H5N2O2* (9), C2H5NO* (13), C2H5NO2* (15), and C2H5N* (19), which have been predicted only through ab initio calculations. Interestingly, ion signals at m/z = 105 and 58 are not observed as the result of RDX photolysis at 206 nm; signals at m/z = 105 and 58 are rather distinct when exposed to 254 nm light even at the low dose (Figure 9). This finding implies that the underlying reaction mechanism yielding products corresponding to masses 105 and 58 amu is open at lower photon energy. On the other hand, reaction channel leading to a product of mass 59 amu appears to be more favorable at higher photon energy, since the signal at m/z = 59 is distinct when RDX is exposed to 206 nm light even at a low dose, while this signal is absent in a similar experiment (low dose) conducted at 254 nm.

3.3.3. HONO Elimination Channel. Molecular elimination of nitrous acid (HONO) could also initiate RDX decomposition. The first molecular HONO elimination results in the formation of a dinitro intermediate, 28 (C2H5N2O2; 175 amu), which can subsequently undergo a second HONO elimination to generate a cyclic mononitro product, 29 (C2H5N2O2; 128 amu). This product (29) may encounter yet a third HONO elimination yielding 1,3,5-triazine, 30 (C2H5N3; 81 amu). Gas phase calculations performed by Goddard and co-workers identified the HONO elimination pathway to be energetically most favorable for the formation of triazine (C2H5N3; 81 amu). Our observation of species holding masses at 128 and 81 amu are indicative of the HONO elimination channel occurring during the UV photolysis of RDX. It is intriguing to recall that the ion signal at m/z = 81 is not observed in the ReTOF-MS data after photodecomposition at 206 nm. However, the signal at m/z = 81 is observed when irradiated at 254 nm even in the low dose experiment. This observation proposes that HONO elimination from product 29 (C2H5N2O2; 128 amu) leading to 1,3,5-triazine (81 amu) is preferable at lower photon energy. At higher photon energy (206 nm), a mononitro product holding mass 128 amu (C2H5N2O2) may follow the HONO elimination pathway instead of the HONO elimination channel and generate oxy-sym-triazine, 31 (C2H5N3O2; 97 amu).

3.3.4. Bimolecular Reaction with Nitrogen Monoxide (NO). Once the concentration of nitrogen monoxide (NO) molecules increases, NO may react with residual (unreacted) RDX molecules to produce a mononitroso analogue of RDX, 32, i.e., 1-nitroso-3,5-hexahydro-s-triazine (ONDNTA; C3H4N4O2). Such reactions have been proposed previously in the condensed phase. ONDNTA may decompose via HONO elimination followed by C−N bond rupture to yield a mononitroso product N-methylene nitrosamide, 21b (C2H5N2O; 58 amu), and a mononitro product, 11 (C2H5N2O; 101 amu). This pathway has been computationally explored by Thynell and co-workers. ONDNTA could also lead to mononitroso intermediates such as C2H5N2O (98 amu); this has been previously discussed in ref 15.

3.3.5. Nitro–Nitrite Isomerization Channel. After electronic excitation, the excited RDX molecules may reach the ground state of RDX–nitrite (S0 RDX-ONO) from the excited electronic states (S1/S2) via conical intersections. The barrierless nature of this nonadiabatic pathway makes it highly favorable. It is important to mention that nitro–nitrite isomerization from the ground state of RDX (S0 RDX-NO2) is unfavorable due to a very high energy barrier (386 kJ mol−1).7 Once the excited RDX molecule relaxes to the ground state of RDX–nitrite (S0 RDX-ONO), it could dissociate via multiple fragmentation channels for example, NO elimination, N−NO2 fission, HONO elimination, and C−N bond rupture (see Figure 11b). Excited state potential energy surfaces (PES) explored computationally by Bernstein and co-workers revealed that elimination of nitrogen monoxide (NO) from the ground state of RDX-nitrite via O-NO bond fission requires an energy of 29 kJ mol−1.7,46 On the other hand, dissociation of RDX to nitrogen dioxide (NO2) from its ground state (S0 RDX-NO2) via N−NO2 fission requires an energy of at least 163 kJ mol−1.35 Thus, elimination of NO is more facile after the RDX molecule has isomerized to its nitrite form following electronic excitation. This theory supports our experimental observation of higher concentration of NO relative to NO2 in the IR (Figures 1 and 2) and mass spectra, even at the low dose experiments (Figures 9 and 10) suggesting that the nitro–nitrite isomerization occurred at the initial stage of decomposition.
Following nitro–nitrite isomerization, RDX could also undergo HONO elimination. The first HONO elimination would result in formation of a dinitro intermediate, $28 (C_3H_4N_4O_4; 175 \text{ amu})$. Subsequent elimination of second and third HONO molecules would generate a mononitro product, $29 (C_3H_3N_3O; 128 \text{ amu})$, and 1,3,5-triazine, $30 (C_3H_3N_5; 81 \text{ amu})$, respectively. Intermediate $1a$ can also decompose through a concerted elimination of HNO, yielding a dinitro product, $34 (C_3H_5N_5O_5; 191 \text{ amu})$. This product undergoes N−N$_2$O$_2$ fission to form an N-centered radical, $35a (C_3H_5N_4O_3; 145 \text{ amu})$, which can readily accept a hydrogen atom to produce a mononitro product, $36 (C_3H_5N_2O_3; 146 \text{ amu})$. The cyclic intermediate $35a (C_3H_5N_4O_3; 145 \text{ amu})$ could engage in ring opening reaction via C−N bond rupture to form an acyclic N-centered radical, $35b (C_3H_5N_2O_3; 145 \text{ amu})$. A radical intermediate, $35b$, may undergo yet another C−N bond breakage, which results in elimination of methylene nitramine (CH$_2$NNO$_2$; 74 amu) and formation of a nitrogen-centered radical, $37 (C_2H_2N_2O_2; 71)$. Radical 37 subsequently could accept a hydrogen atom to lead to a product N-nitro isocyanate, $38 (C_3H_3N_2O_2; 72 \text{ amu})$. Products holding masses 72 and 146 are observed in the mass spectrum. It is important to note here that elimination of HONO and HNO is highly likely since the oxygen atom of the nitrite group (−ONO) could easily interact with the neighboring hydrogen atom of the RDX ring. Electronic structure calculations also suggest that, during the nitro–nitrite isomerization, the NO$_2$ group at the active site interacts with the remainder of the molecule from a distance of 2.9 Å.

The oxy-sym-triazine (OST) molecule, $31 (C_3H_3N_5O_3; 97 \text{ amu})$, can emerge from the dinitro product, $34 (C_3H_3N_5O_5; 191 \text{ amu})$, via two successive HONO eliminations. The former product (OST; C$_3$H$_3$N$_3$O) can further accept two hydrogen atoms to form $39 (C_3H_3N_5O_5; 99 \text{ amu})$. Although product holding mass 97 amu (C$_3$H$_3$N$_3$O; 31) is observed during photolysis at 206 nm, the signature of its hydrogenated counterpart; i.e., a product corresponding to mass 99 amu (C$_3$H$_3$N$_5$O; 39) is not observed at 206 nm photolysis. Interestingly, ion signals corresponding to both the masses (m/z = 97 and 99) are observed at 254 nm implying that formation of product $39 (C_3H_3N_5O_5; 99 \text{ amu})$ from $34 (C_3H_3N_5O_5; 191 \text{ amu})$ through consecutive HONO elimination and hydrogen addition is preferred at lower photon energy. At higher photon energy, oxy-sym-triazine (97 amu) may originate via HNO elimination from product $29 (C_3H_3N_5O_2; 128 \text{ amu})$ as discussed above. $34$ may dissociate to product N-nitro isocyanate, $40 (C_2H_2N_2O_2; 88 \text{ amu})$, via intermediates, $35c (c-C_3H_3N_2O_2; 145 \text{ amu})$ and $35d (C_3H_5N_2O_3; 145 \text{ amu})$, after consecutive N−N$_2$O$_2$ and C−N bond rupture. The N-nitro isocyanate $40 (C_3H_2N_2O_2; 88 \text{ amu})$ may undergo N−NO$_2$ fission followed by addition of a methyl radical (CH$_3$) to produce N-methyl isocyanate product, $41 (C_3H_6N_2O_2; 57 \text{ amu})$. It is worth to recall that product at m/z = 57 is not observed during photolysis of RDX at 254 nm; on the other hand, this product is detected when RDX is exposed to 206 nm light even at the lowest dose (0.20 ± 0.02 eV molecule$^{-1}$; Figure 10). On the basis of this observation, we may propose that the aforementioned pathway leading to a product holding a molecular mass of 57 amu (C$_2$H$_5$NO) is more favorable at a higher photon energy. Product $40 (C_2H_2N_2O_2; 88 \text{ amu})$ could decompose rapidly to $41 (C_3H_4N_2O_2; 57 \text{ amu})$ at higher photon energy, therefore, the ion signal corresponding to m/z = 88 is not observed at 206 nm irradiation. Two consecutive C−N bond ruptures of dinitro moiety $34 (C_3H_3N_5O_5; 191 \text{ amu})$ may generate a C$_4$N$_2$-centered biradical, $42 (C_4H_5N_4O_4; 148 \text{ amu})$, which

Figure 12. Wavelength-selective decomposition pathways of RDX. Channels leading to products at 130, 87, 59, and 57 amu are preferable at a higher photon energy (denoted through blue color arrows). Pathways leading to products at 149, 105, 99, 89, 88, 81, 60, and 58 amu are more favorable at a lower photon energy (represented through red color arrows).
dissociates to two molecules of methylene nitramine, (CH$_3$N$\equiv$NO, 74 amu) following another C–N bond cleavage. Alternatively, biradical 42 (C$_2$H$_7$N$_3$O$_4$; 148 amu) may encounter a 1,2-hydrogen shift to form a dinitro intermediate, 44 (C$_2$H$_9$N$_3$O$_4$; 148 amu). This intermediate (44) reacts to develop a mononitro product, 45 (C$_2$H$_5$N$_2$O$_3$; 117 amu), via N–NO$_2$ fission and addition of a methyl radical (CH$_3$).

The nitro–nitrite isomerization process could be followed by a concerted elimination of NO (nitrogen monoxide) and CO (carbon monoxide) yielding a nitrogen-centered radical, 46 (C$_2$H$_5$N$_3$O$_4$; 164 amu), which may experience a N–NO$_2$ fission generating yet another biradical, 47a (C$_2$H$_7$N$_3$O$_4$; 118 amu). Biradical 47a undergoes a 1,2-hydrogen shift to form an acyclic mononitro product, 41b (C$_2$H$_4$N$_2$O$_2$), corresponding to mass 118 amu, which has been observed in the experiment. Biradical 47a may dissociate into a mononitro product, 48 (CH$_3$N$_2$O$_3$; 89 amu), and methanmine (CH$_3$NH) via C–N bond cleavage. Interestingly, the signal at m/z = 89 disappears during the photolysis with 206 nm photons (Figure 10). However, this product is observed during photodissociation at 254 nm even at the lowest dose of 0.10 ± 0.02 eV molecule$^{-1}$ (Figure 9). This suggests that the reaction pathway leading to product 48 (CH$_3$N$_2$O$_3$; 89 amu) could be feasible only at a lower photon energy. The HONO elimination from mononitro product 47b would yield a diamine product, 49 (C$_2$H$_5$N$_3$; 71 amu). Addition of two hydrogen atoms to a diamine moiety (49) could generate its hydrogenated counterpart, 50 (C$_2$H$_7$N$_3$; 73 amu). Alternatively, product 42 may accept four hydrogen atoms to form an amine moiety, 51 (C$_2$H$_9$N$_3$; 75 amu).

After the nitro–nitrite isomerization, 1a may eliminate NO (nitrogen monoxide) to form an oxygen-centered (aminooxy) radical 52 (C$_2$H$_7$N$_2$O$_4$; 192 amu). The aminooxy radical (C$_2$H$_7$N$_2$O$_4$) has been detected via electron spin resonance (ESR) technique by Darneze et al. during photolysis of RDX at 254 nm.$^{52,83}$ Calculations reveal that this reaction has an energy barrier of close to 29 kJ mol$^{-1}$. Radical intermediate 52 could further dissociate to methylene nitramine (CH$_3$N$\equiv$NO$_2$) and a carbon-centered radical, 47c (C$_2$H$_5$N$_3$O$_4$; 118 amu), via C–N bond cleavage. Radical 47c could decompose to methylene nitramine and a mononitroso radical, 53 (CH$_3$NO$_2$; 44 amu), following another C–N bond rupture. The latter (mononitroso radical, 53) can rapidly accept a hydrogen atom to form product 54 (CH$_3$NO; 45 amu) which is observed in the experiment. Radical 47c could also accept a hydrogen atom to yield a nitro–nitrosamino product, 55 (C$_2$H$_7$N$_3$O$_4$; 119 amu), which is detected in our mass spectrum. A product holding mass 149 amu (C$_2$H$_7$N$_2$O$_3$; 58) may originate from an aminooxy radical via intermediate 56 followed by bimolecular addition reaction with methyl (CH$_3$) and hydrogen radicals. This product (58) could further dissociate to species 54 (CH$_3$NO; 45 amu) and 14b (C$_2$H$_5$NO; 59 amu) via triple C–N bond cleavage. Products corresponding to these three masses, 149, 45, and 59 amu, are observed in the mass spectrum.

The wavelength-selective decomposition pathways of RDX are summarized in Figure 12. Channels leading to products corresponding to masses 130, 87, 59, and 57 amu are preferable at a higher photon energy (206 nm, 6.02 eV), while pathways leading to species at 149, 105, 99, 88, 89, 81, 60, and 58 amu are favorable at a lower photon energy (254 nm, 4.88 eV). These products might be considered as tracers of a wavelength-dependent photolysis of RDX. Overall, RDX could dissociate via N–NO$_2$ fission, HONO elimination, nitro–nitrite isomerization, and C–N bond rupture channels when exposed to UV light. The N–NO$_2$ fission and nitro–nitrite isomerization channels appear to be more dominant at the early stage of decomposition. The N–NO$_2$ fission channel yields products at 130, 87, 46, and 30 amu, whereas the HONO elimination channel generates products at 128, 97, and 81 amu, while the C–N rupture pathway following N–NO$_2$ fission leads to species holding masses 105, 101, 59, 58, 74, 44, 42, and 31. Nitro–nitrite isomerization in conjunction with successive reaction pathways is proposed to generate a variety of products including at 191, 146, 149, 117, 118, 119, 88, 71, 72, 73, 74, 75, 60, 59, 45, and 30 amu as discussed above. Our experimental observations suggest that besides the N–NO$_2$ fission, the nitro–nitrite isomerization could also play a major role to trigger the decomposition of RDX after electronic excitation. Most of the previously reported computational analyses address the thermal decomposition of RDX from its electronic ground state via N–NO$_2$. HONO elimination, C–N bond rupture or bimolecular reactions.$^{35,37,41,42,67}$ UV-photolysis of RDX is more complex as it involves excited state dynamics and ground states along with conical intersections. To the best of our knowledge, as of now, there has been no reported computational study that explores the excited-state potential energy surfaces of condensed-phase RDX.

4. CONCLUSIONS

In summary, the UV photodissociation of solid-phase RDX performed at 5 K exploiting different wavelengths (254 (4.88 eV), 236 (5.25 eV), 222 (5.58 eV), and 206 (6.02 eV) nm) and doses revealed a wide spectrum of photoproducts. Evidence of simple decomposition products such as CO$_2$, N$_2$O, CO, HCO, H$_2$O, NO, (NO)$_2$, N$_2$O$_3$, and the nitrite group (–ONO) were captured by FTIR spectroscopy in the condensed-phase during the photolysis. PI-ReTOF-MS collected during the warmup-phase identified 32 cyclic and acyclic products at m/z values ranging from 30 to 191. Low dose experiments suggest that NO and N$_2$O products rapidly develop during the initial stage of the decomposition relative to CO$_2$, N$_2$O, CO, and H$_2$O implying that N–NO$_2$ and nitro–nitrite isomerization could be the initial steps in the decomposition of RDX molecules following electronic excitation. Products observed at m/z values of 59, 72, 73, 88, 99, 117, 118, 119, 146, 149, and 191 were detected for the first time in photolysis experiments. Among those, products at m/z = 191, 149, 146, 119, and 72 are primary products which likely originate via nitro–nitrite isomerization. Wavelength-dependent studies revealed that pathways leading to products holding masses 130, 87, 59, and 57 amu are more prominent at a higher photon energy while reaction mechanisms yield products of masses 149, 105, 99, 81, 89, 58, and 60 amu are favorable at a lower photon energy (Figure 12). Finally, the decomposition mechanisms reported through gas-phase and condensed-phase calculations$^{34,35,37,41}$ were exploited to rationalize the formation of the observed species. Further experiments are planned, exploiting isomer-selective photoionization$^{34,35,41}$ to explicitly verify the structures of the decomposition products and hence the nature of the isomer(s) formed. Experimental results will be combined with theoretical simulations to unravel the complex decomposition pathways of RDX.
Experimental setup scheme, UV–vis spectrum, NMR spectra, IR spectra, mass spectrum, and column densities (PDF)

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1. Supporting Information

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