**Response to Reviewer Comments**

**Reviewer #1:**

In this Frontiers Article, the authors reviewed the existing literature on the decomposition of nitromethane both in the gas and condensed phases and presented their own results on state-of-the-art studies of this species in the solid state using FTIR and EPR spectroscopies and single-photon photoionization mass spectrometry (PIReTOF-MS) accompanied with quantum chemical calculations. A detailed analysis of possible decomposition pathways is given based both on theoretical and experimental data. The results show, in addition to the 'classical' pathways observed in the gas phase, new reaction channels including the formation of O and H atoms, carbene loss, and multiple mass growth processes via consequent CH2 insertions into single bonds and recombination of of various radicals formed as the primary decomposition products. The study using the advanced experimental techniques clearly demonstrates the difference between the gas and solid state decomposition mechanisms and shows a necessity of further solid state studies for various prototype high energy materials. Future challenges and research directions are clearly laid out in the last section of the manuscript. I believe that this Frontiers Article will be of high interest to the readership of Chemical Physics Letters, especially, to the physical chemistry, high energy materials, and combustion/explosion communities. I have few suggestions for the authors to consider, which may further improve this paper:

1) Since the reported studies are carried out with nitromethane ices at 5 K, it is important to mention that "the crystalline structure of nitromethane at atmospheric pressure, from 4.2 K to the melting point, is orthorhombic, with four molecules per unit cell" and thus, apparently, molecular packing does not change with temperature, making the work relevant to higher temperatures as well (see J. Phys. Chem. B 2008, 112, 4, 1095-1103).

**Response:** We thank the reviewer for his suggestion. We have included the following sentence “*Previous investigation suggest that the molecular packing of the solid nitromethane (CH3NO2; 1) does not change with the temperature from 4.2 K to the melting point, making the current experimental work relevant to higher temperature as well.”* in the revised manuscript and cited the above-mentioned reference.

***Relevant changes in the manuscript (On Page No. 6): “****Previous investigation suggest that the molecular packing of the solid nitromethane (CH3NO2; 1) does not change with the temperature from 4.2 K to the melting point, making the current experimental work relevant to higher temperature as well.”*

2) Figures 5 and 6 are very nice and useful. But because this is a Frontiers Article describing prospectives in research, it would be useful to also sketch and describe potential  
decomposition pathways of not only RDX (Fig. 6) but also HMX and CL-20 mentioned in the text as subjects for future studies.

**Response:** Following the reviewer suggestion, the primary decomposition pathways of HMX and CL-20 are sketched in Figure 6b-c and are also described in the text.

***Relevant changes in the manuscript (On Page No. 17). Following sentences are added. “*** *For instance, unimolecular decomposition of RDX, HMX and CL-20 can initiate through four primary steps 1) N-NO2 bond cleavage resulting in the formation of nitrogen dioxide (NO2) along with a N-centered radical, 2) molecular elimination channel yielding nitrous acid (HONO) and unsaturated ring species, 3) nitro-nitrite rearrangement followed by NO loss and 4) ring opening pathway leading to methylene nitramine (H2CNNO2) (Figure 6a-c). These reaction steps are often accompanied by several secondary reactions leading to large number of products for example, dissociation of RDX generate products having molecular weight ranging from 18 to 191 amu.”*

***(On Page No. 30).*** *Modified figure 6.*

3) Generally, the paper is nicely and clearly written but I noticed few errors/typos:  
Page 6, line 15: "Torr" is misspelled.  
Page 7, line 41: a word (probably, "study") is missing after "photochemical".  
Page 7, line 55: only one "." should be after "et al".  
The abbreviation "PI-ReTOF-MS" is defined twice, first in p. 6 and then again in p. 8.  
Page 17, line 27: parentheses are not needed around "PI-ReTOF-MS".

**Response:** We thank the reviewer for pointing these errors. We have now corrected all the above-mentioned errors/typos in the revised manuscript.

***Relevant changes in the manuscript***

*(On Page No. 6). “Tor” is replaced by “Torr”*

*(On Page No. 7). “photochemical computationally” is replaced by “photochemical study computationally”*

*(On Page No. 7). “Shin et al..’ replaced by “Shin et al.”*

*(On Page No. 8). Repeated abbreviation of PI-ReTOF-MS is removed.*

*(On Page No. 17). “(PI-ReTOF-MS)” replaced by “PI-ReTOF-MS”.*

**Reviewer #2:**

This manuscript summarizes the decomposition, isomerization and molecular mass growth processes of nitromethane in the solid phase. Following exposure to ionizing radiation, nitromethane ice is warmed and probed by FTIR, EPR, and PI-Re-TOF MS. Quantum chemical calculations have been employed to support the observed findings. This work demonstrates the strength of this approach to study exotic chemistry that cannot be captured in the gas phase such as high-energy reactions involving O-atom, H-atom and carbene insertion channels which are necessary for a complete understanding of energetic processes and materials. I recommend publication. Some minor points of clarification would be helpful:

I understand this Feature Article relies heavily upon recently published work, but it is not obvious what level of theory was used for Figure 2 (neither in the caption nor within the text). Pease make this explicit.

**Response:** Isomerization pathways of nitromethane depicted in Figure 2 are calculated at the B3LYP/cc-pVTZ//CCSD(T)/CBS level of theory.We have now mentioned this in the figure 2 caption.

***Relevant changes in the manuscript (On Page No. 25).*** *In Figure 2 caption “Isomerization of distinct isomers of nitromethane (CH3NO2;* ***1****) calculated at the B3LYP/cc-pVTZ//CCSD(T)/CBS level of theory.”*

The observation of dimers is interesting. Although it is noted that further work is required to understand the nature of these dimers, can anything be said as to whether these  
are formed in the gas phase, or in the ice?

**Response:** These dimers are formed in the ice upon exposure to ionizing radiation.

***Relevant changes in the manuscript (On Page No. 12).*** *These dimerization reactions could take place in the condensed phase upon exposure to energetic electrons and photons.*

"Toward lower T….a detailed analysis of the data reported that this section of the TPD profile links to the aci- nitromethane isomer with possible contributions…" What is the  
analysis that supports this? Page 8 line 55.

**Response:** The sublimation eventpeaking at 185 K disappears when photoionization energy is switched from 9.80 to 9.14 eV. This sublimation region could be attributed to aci-nitromethane (H2C=N(O)OH; **3**) and/or formohydroxamic acid (HCONHOH; IE = 9.42-9.66 eV, **6-7**) isomers as their ionization energies exist between 9.80 and 9.14 eV. Based on the potential energy surface depicted in Figure 2, it could be suggested that aci-nitromethane (H2C=N(O)OH; **3**) would originate from nitromethane (CH3NO2; **1**), while formohydroxamic acid (HCONHOH; **6-7**) would generate from nitrosomethanol (H2C(NO)OH; **4**) via hydrogen migration. Since nitrosomethanol (H2C(NO)OH; **4**) itself can only originate from aci-nitromethane (H2C=N(O)OH; **3**) via hydroxyl group migration therefore, we can link the sublimation profile peaking at 185 K to the aci-nitro­methane (H2C=N(O)OH; **3**) isomer with possible contri­butions from formohydroxamic acid (OHCNH(OH)).

***Relevant changes in the manuscript (On Page No. 8-9).*** *We have added the following sentences. “This sublimation region could be attributed to aci-nitromethane (H2C=N(O)OH; 3) and/or formohydroxamic acid (HCONHOH; IE = 9.42-9.66 eV, 6-7) isomers as their ionization energies exist between 9.80 and 9.14 eV. Based on the potential energy surface depicted in Figure 2, it could be suggested that aci-nitromethane (H2C=N(O)OH; 3) might originate from nitromethane (CH3NO2; 1), while formohydroxamic acid (HCONHOH; 6-7) could form from nitrosomethanol (H2C(NO)OH; 4) via hydrogen migration. Since nitrosomethanol (H2C(NO)OH; 4) itself can only originate from aci-nitromethane (H2C=N(O)OH; 3) via hydroxyl group migration therefore, we can link the sublimation profile peaking at 185 K to the aci-nitro­methane (H2C=N(O)OH;* ***3****) isomer with possible contri­butions from formohydroxamic acid (OHCNH(OH)).*

What is the ice thickness used in these experiments?

**Response:** The ice thickness in these experiments range from 380-450 nm.

***Relevant changes in the manuscript (On Page No. 6). “****Considering the low temperature of 5 K, the ice target having a thickness in the range of 380-450 nm, re­pre­sents a ‘closed system’ as reaction products - including atomic and molecular hydrogen – re­main trap­ped in the cryogenic sample.”*

Also, there are several small typos, some of which are listed below. The authors should more carefully review this manuscript for additional grammatical errors.  
page 5 line 21 missing period between "nitromethane" and "Considering" and remove "the" before nitromethane  
page 5 line 48 and 59 nomenclature for 4) missing  
page 6 line 14 missing "the" after "ionizing radiation in…"  
page 6 line 28 erase comma after (CNT)  
page 8 lines 32 and 41 add space between kJ mol^1  
page 9 line 58 "excluding" doesn't make sense in this sentence as it is written  
page 10 line 38 "fly apart and" — should get rid of "and"  
page 10 line 58 missing "the"…should be "ionizing radiation in the form of"…  
page 11 line 40 missing "the"…should be "in the form of"  
page 11 line 57 add space in kJ mol^-1  
page 14 line 33, typo, "…to ethylnitrite or if…"  
page 14 line 56, typo, "collisionless collision conditions…"  
page 15 line 8 add spaces in between the two kJ mol^1

**Response:** We thank the reviewer for pointing these errors. We have now corrected all the above-mentioned errors/typos in the revised manuscript.

***Relevant changes in the manuscript.***

*(On Page No. 5).”…the nitromethane Considering…” is replaced by “…nitromethane. Considering…”*

*(On Page No. 5). Nomenclature of compound 4 “nitrosomethanol” is added.*

*(On Page No. 6). “After the irradiation” is replaced by “After the exposure to ionizing irradiation”.*

*(On Page No. 7).” (CNT),. “ is replaced by “(CNT).”*

*(On Page No. 8). “kJmol-1” is replaced by “kJ mol-1”.*

*(On Page No. 9). “(excluding)” is removed.*

*(On Page No. 10). “fly apart and undisturbed” is replaced by “fly apart undisturbed”*

*(On Page No. 11). “to ionizing radiation in” is replaced by “to the ionizing radiation in”.*

*(On Page No. 11). “in form of (E)-azodioxymethane” is replaced by “in the form of (E)-azodioxymethane”.*

*(On Page No. 12). “kJmol-1” is replaced by “kJ mol-1”.*

*(On Page No. 14). “to ethylnitrite of if nitromethane” is replaced by “to ethylnitrite or if nitromethane”.*

*(On Page No. 15). “collisionless collision conditions” is replaced by “collision less conditions”.*

*(On Page No. 16). “kJmol-1” is replaced by “kJ mol-1”*