PRODUCTION AND POTENTIAL DETECTION OF FUNCTIONALIZED HEXAMETHYLENE-TETRAMINE COMPOUNDS IN SPACE. S. A. Sandford¹, P. P. Bera^{1,2}, M. Nuevo^{1,2}, T. J. Lee³, and C. K. Materese⁴, ¹NASA Ames Research Center, MS 245-6, Moffett Field, CA 94035, USA, ²BAER Institute, NASA Research Park, MS 18-4, Moffett Field, CA 94035, USA; ³NASA Ames Research Center, MS 245-3, Moffett Field, CA 94035, USA; ⁴NASA Goddard Space Flight Center, Code 691, Greenbelt, MD 20771, USA; E-mail: scott.a.sandford@nasa.gov.

Introduction: Laboratory studies have shown that exposure of mixed ices of astrophysical interest to ionizing radiation such as ultraviolet (UV) photons or energetic particles (electrons, protons) leads to the production of large numbers of new, more complex compounds. A significant portion of these new species appear to belong to a family of molecules that consist of hexamethylenetetramine (HMT; C₆N₄H₁₂; Fig. 1) and HMT to which different chemical side groups have been substituted for a peripheral H atom [1-4]. This work presents the identification of HMT-methanol (HMT-CH₂OH), one of these HMT variants, in organic residues produced from the UV irradiation of astrophysically relevant ice mixtures at < 20 K. We also present the infrared (IR) spectra of HMT, HMT-CH₂OH, and a number of other HMT variants computed using density functional theory (DFT) computations. These spectra can be compared with each other and show similarities that can be used to search for this family of compounds in space.

Methods: Several organic residues were produced in the laboratory by simultaneously depositing ice mixtures containing H₂O, CH₃OH, CH₄, NH₃, and purine ($C_5H_5N_4$) on a cold substrate (Al foil) at < 20 K under high vacuum ($\sim 2 \times 10^{-8}$ torr) and irradiating these ices with UV photons emitted by a microwavedischarge H₂ lamp. After slow warm-up to room temperature, the residues were recovered and analyzed with gas chromatography coupled to mass spectrometry (GC-MS). These experiments were repeated with isotopically labelled variants of the starting ices, namely, ¹³C-labeled CH₃OH and CH₄, ¹⁵N-labeled NH₃, and ¹⁸O-labeled H₂O and CH₃OH were used. The presence of purine in the starting ice mixtures is because these experiments were originally conducted for a different project studying the formation of purine-based nucleobases [5]. In addition, ab initio computations of the IR spectra of HMT, HMT-CH₂OH, HMT-OH, HMT-NH₂, HMT-CH₃, HMT-CN, HMT-OCN, HMT-OCH₃ HMT-CH(OH)CHO, and HMT-NHCHO were also performed using density functional theory (DFT) calculations with a ωB97X-D functional and a cc-pVTZ basis set.

Results: HMT-CH₂OH was tentatively identified in all the residues produced from the UV irradiation of ice mixtures containing H₂O, CH₃OH, CH₄, and NH₃ [6]. It was determined that purine is not required for

the formation of the photoproducts discussed in this work because the product also shows up in experiments in which no purine was added to the starting ice. Residues isotopically labelled with $^{13}\mathrm{C},~^{15}\mathrm{N},~\text{and}~^{18}\mathrm{O}$ (Fig. 2) allowed us to confirm its mass (242 Da) and chemical formula (C₇H₁₄N₄O). The yield of HMT-CH₂OH was found to increase with the concentration of CH₃OH in the starting ice mixtures. In particular, the absence of CH₃OH in the ices led to no HMT-methanol at all. However, its identification cannot be unambiguously proven, as no commercial standard of HMT-CH₂OH is available for direct comparison.

Ab initio computations of the IR spectra of HMT, HMT-CH₂OH, and the other HMT variants show that all these compounds share vibrational modes associated with the HMT cage-like structure that they have in common [7]. The coaddition of all these spectra (Fig. 3) show intense bands around 1065 and 1300 cm⁻¹ that are associated with the cage-like structure [6,7].

Implications: The presence of HMT and HMTrelated compounds in astrophysical environments is of astrobiological importance, as HMT is a chemical precursor to many organic molecules, including amino acids [8], N-heterocycles [9], and nitriles [1,10,11], after thermodegradation, photodegradation, or acid hydrolysis. HMT variants in which one or more peripheral H atoms are substituted with some other chemical functional group would be expected to produce additional, but similar, suites of compounds. In particular, the presence of HMT-related compounds in meteorite parent bodies like asteroids and comets may be of importance as some of these objects experienced periods of heating and/or aqueous alteration during which HMT-related compounds may have led to the formation of organic molecules of astrobiological significance. These compounds may then have played a role in the origin of life on our planet after they were delivered in the form of cosmic dust and meteorites

In addition, HMT-related compounds all produce a number of IR bands that fall at similar positions and have similar strengths, which may make them easier to detect in space as a family. Each molecular HMT variant also produces additional unique bands due to its attached side group, so that it may also be possible to distinguish between different variants.

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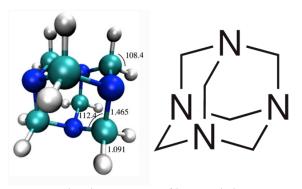


Fig. 1. Molecular structure of hexamethylenetetramine (HMT). (Left) Structural parameters computed using the ωB97X-D/cc-pVTZ method (bond lengths in Å, bond angles in degrees). (Right) Conventional structure of HMT showing its cage-like structure and high symmetry. Variants on this structure can be made by replacing a peripheral H atom with a new chemical side group.

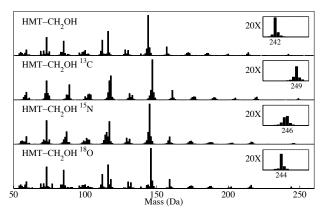


Fig. 2. Mass spectra of the normal, ^{13}C , ^{15}N , and ^{18}O isotopic variants of the peaks assigned to HMT-methanol in the GC-MS chromatograms of several residues produced from the UV irradiation of H_2O : $CH_3OH:NH_3:CH_4:$ purine ice mixtures at < 20 K [6].

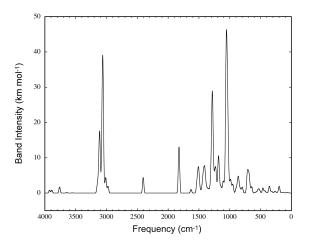


Fig. 3. Composite spectrum consisting of the coaddition of the computed spectra of HMT, HMT-CH₂OH, HMT-OH, HMT-NH₂, HMT-CH₃, HMT-CN, HMT-OCN, HMT-OCH₃, HMT-CH(OH)CHO, and HMT-NHCHO, in which the bands have been smoothed to have a FWHM of 25 cm⁻¹ to better simulate solid-state bands in grain mantles [6,7].