

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. Matereze⁴, 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; C_6H_{12} ; 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- CH_2OH), 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- CH_2OH , 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 H_2O , CH_3OH , CH_4 , NH_3 , 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 microwave-discharge H_2 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, ^{13}C -labeled CH_3OH and CH_4 , ^{15}N -labeled NH_3 , and ^{18}O -labeled H_2O and CH_3OH 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- CH_2OH , HMT-OH, HMT- NH_2 , HMT- CH_3 , HMT-CN, HMT-OCN, HMT-OCH₃, HMT-CH(OH)CHO, and HMT-NHCHO were also performed using density functional theory (DFT) calculations with a $\omega B97X-D$ functional and a cc-pVTZ basis set.

Results: HMT- CH_2OH was tentatively identified in all the residues produced from the UV irradiation of ice mixtures containing H_2O , CH_3OH , CH_4 , and NH_3 [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}C , ^{15}N , and ^{18}O (Fig. 2) allowed us to confirm its mass (242 Da) and chemical formula ($C_7H_{14}N_4O$). The yield of HMT- CH_2OH was found to increase with the concentration of CH_3OH in the starting ice mixtures. In particular, the absence of CH_3OH in the ices led to no HMT-methanol at all. However, its identification cannot be unambiguously proven, as no commercial standard of HMT- CH_2OH is available for direct comparison.

Ab initio computations of the IR spectra of HMT, HMT- CH_2OH , 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 HMT-related 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 [12,13].

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.

References: [1] Bernstein, M. P. et al. (1995) *ApJ*, 454, 327–344. [2] Cottin, H. et al. (2001) *ApJ*, 561, L139–L142. [3] Muñoz Caro, G. M. & Schutte, W. A. (2003), *A&A*, 412, 121–132. [4] Muñoz Caro, G. M. et al. (2004) *A&A*, 413, 209–216. [5] Materese, C.K. et al. (2018) *ApJ*, 864, 44 (6 pp). [6] Materese, C. K. et al. (2018), *ApJ*, submitted. [7] Bera, P. P. et al. (2018), in preparation. [8] Wolman, Y. et al. (1971) *Science*, 174, 1039. [9] Vinogradoff, V. et al. (2018) *Icarus*, 305, 358–370. [10] Bernstein, M. P. et al. (1994) *J Phys Chem*, 98, 12206–12210. [11] Cottin, H. et al. (2002) *Adv Space Res*, 30, 1481–1488. [12] Oró, J. (1961) *Nature*, 190, 389–390. [13] Chyba, C., Sagan, C. (1992) *Nature*, 355, 125–132.

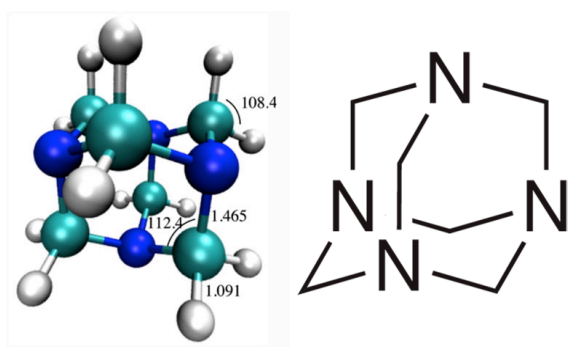


Fig. 1. Molecular structure of hexamethylenetetramine (HMT). (Left) Structural parameters computed using the ω B97X-D/cc-pVTZ method (bond lengths in Å, bond angles in degrees). (Right) Conventional structure of HMT showing its cage-like structure and high symmetry. Variants on this structure can be made by replacing a peripheral H atom with a new chemical side group.

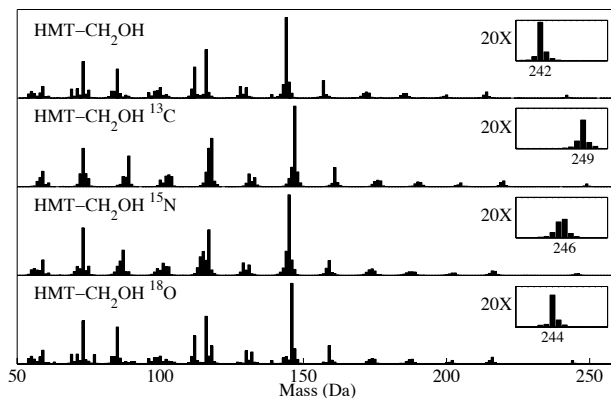


Fig. 2. Mass spectra of the normal, ^{13}C , ^{15}N , and ^{18}O isotopic variants of the peaks assigned to HMT-methanol in the GC-MS chromatograms of several residues produced from the UV irradiation of $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3:\text{CH}_4$:purine ice mixtures at $< 20\text{ K}$ [6].

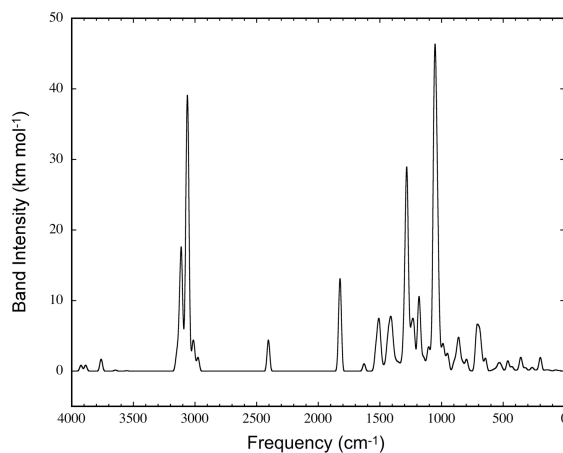


Fig. 3. Composite spectrum consisting of the coaddition of the computed spectra of HMT, HMT- CH_2OH , HMT-OH, HMT- NH_2 , HMT- CH_3 , HMT-CN, HMT-OCN, HMT- OCH_3 , HMT- $\text{CH}(\text{OH})\text{CHO}$, and HMT- NHCHO , in which the bands have been smoothed to have a FWHM of 25 cm^{-1} to better simulate solid-state bands in grain mantles [6,7].