INFRARED SPECTROSCOPY OF THE PHOTOLYSIS AND SUBLIMATION OF ACETONITRILE (CH_3CN) ICE WITH SUBLIME. S. Cuevas-Quiñones[1, 2], O. H. Wilkins[3, 4], K. M. Yocum[3, 4], and S. N. Milam[3], [1]Purdue University (cuevas26@purdue.edu), [2]Lunar and Planetary Institute (USRA), Houston, TX. [3]NASA Goddard Space Flight Center, [4]NASA Postdoctoral Fellow Program.

SubLIME: The Sublimation of Laboratory Ices Millimeter/submillimeter Experiment (SubLIME) investigates the relationship between ice and gas composition in the interstellar medium and planetary/cometary surfaces. Through the use of multiple experimental techniques, presented in Fig. 1, measurements taken are directly comparable to observational telescopes such as ALMA and SOFIA.

Introduction: Nitrile chemistry is relevant throughout the cosmos. Acetonitrile (CH_3CN) is of special interest in astrobiology since it is able to produce prebiotic molecules, including aminoacetonitrile when mixed with ammonia, upon hydrolysis [1,2]. CH_3CN has been observed throughout different regions of the interstellar medium (ISM), in nebulae, and in protoplanetary and circumstellar disks. Additionally, CH_3CN is relevant within solar system environments and has been detected in several icy worlds and comets with ground-based telescopes and orbital instruments [3]. For example, the IRAM 30 m radio telescope observed CH_3CN in Titan's atmosphere [4]. Further away in the solar system, observations of Pluto by Voyager II found rich chemistry based on nitrogen (N_2), methane (CH_4), and carbon monoxide (CO), which can form larger molecules such as CH_3CN upon energetic processing [5]. The same chemistry can be observed in Triton, a satellite of Neptune.

For these reasons, investigating CH_3CN chemistry in the laboratory is required for a deeper understanding of nitriles in astrophysical environments and direct comparison to observational data. In this work, Fourier-transform infrared spectroscopy (FTIR) was used to monitor the UV photolysis, simulating solar UV radiation, of CH_3CN ice at 10 K, 40 K, and 50 K followed by warm-up to 300 K to study the sublimated photoproducts and how they are affected by photolysis temperature. The photolysis temperatures were chosen to simulate planetary and cometary conditions. Temperatures of 10 K applies to cometary formation temperature, while 50 K pertains to planetary and satellite surfaces such as Pluto or Triton. The aim is to eventually perform these experiments using the gas-phase sensitive technique, submillimeter/far-IR spectroscopy, which can unambiguously identify and quantify structural isomers [6].

Methods: The experiments were performed in the SubLIME Labat NASA Goddard Space Flight Center. For each experiment, the ice sample was vapor deposited at 9 K onto a gold substrate attached to a closed-cycle helium cryostat in a stainless-steel ultrahigh vacuum (UHV) chamber with a base pressure of $\sim 10^{-9}$ Torr. The ice sample was then exposed to UV photons from a microwave-discharge hydrogen-flow lamp (MDHL) for an hour-long photolysis after which the lamp was turned off.

The ice sample was photolyzed at different temperatures (10 K, 40 K, 50 K) depending on the experiment. It was then heated from the respective photolysis temperature to 300 K at a rate of 1 K min^{-1}. IR spectra were taken at 10-minute intervals during photolysis and every 5 K during warm-up using a Thermo Scientific Nicolet™ iS50 FTIR spectrometer. New IR features appeared during photolysis and were assigned to low-temperature photoproducts.

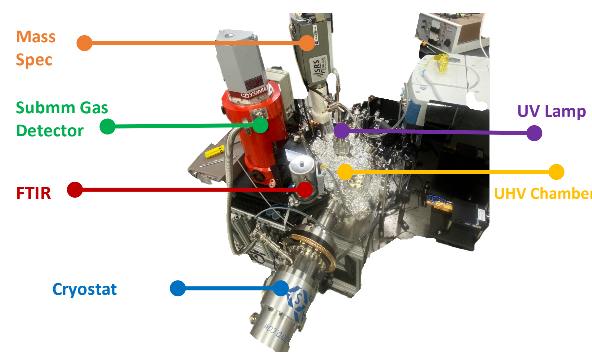

Figure 1. SubLIME UHV setup

Results: IR spectra of the CH_3CN ice sample were taken throughout photolysis and subsequent warm-up. Fig. 2 shows the IR spectra of the sample between 2500 and 1900 cm^{-1} in 10 minute intervals during photolysis at 10 K, with pure acetonitrile ice at 0 minutes (in black). Four distinct photoproducts were identified within this region: methyl isocyanide (CH_3NC), tert-Butyl isocyanide ($(CH_3)_3CNC$), hydrogen cyanide (HCN), and ketenimine (CH_2CNH). Methane (CH_4) was also detected at 1302 cm^{-1}. Fig. 3 shows the spectra at intervals of 20 K (up to 200 K) as the photolyzed ice sample was heated. The sublimated products are labeled following Abdulgalil et al. [7] and Hudson and Moore [8]. A notable product is hydrogen cyanide (HCN, 2090 cm^{-1}), a prebiotic molecule which contains the necessary components for the synthesis of the RNA backbone and has been detected on Pluto [9]. While only simple nitrogen-bearing species have been observed (so far) on planetary bodies in the solar system, laboratory experiments such as those presented and those performed by Hudson and Moore [8] have recorded relatively complex nitroge chemistry resulting from HCN ice photolysis. CH_3CN has been detected in comets [10], and can serve as a building block for more complex chemistry, but further studies are necessary to assess whether larger molecules are produced in high enough abundance to be detected with remote observations. Furthermore, we saw preliminary evidence of temperature affecting our UV-photolyzed samples (Fig. 4). Specifically, we see a feature assigned to isocyanides (specifically, $(CH_3)_3CNC$ and CH_2CHNC) between 2150 and 2125 cm^{-1} that is stronger in the sample photolyzed at 10 K versus at 50 K. We also see, during warmup, a stronger NCCN feature is present at 100 K in the sample photolyzed at 10 K.

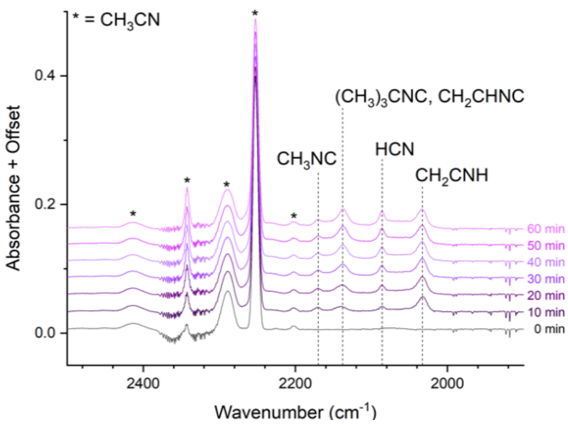

Figure 3. IR spectra of CH_3CN ice between 2500 and 1900 cm-1 at 10-minute intervals during UV photolysis at 10 K. Asterisks (*) label CH_3CN peaks.

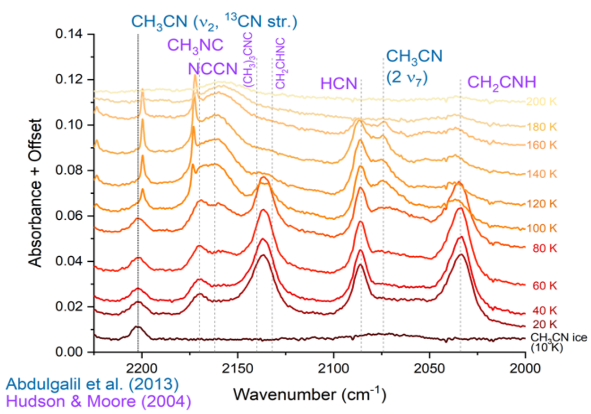

Figure 2. IR spectra of CH_3CN ice during warm-up following UV photolysis at 10 K. The spectrum of CH_3CN ice before photolysis is shown at the bottom in black. The IR assignments are shown in blue [7] and purple [8].

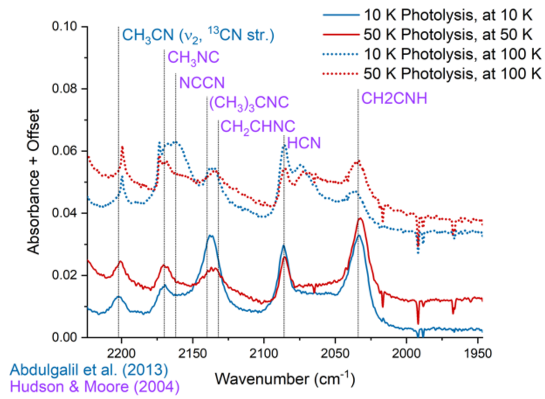

Figure 4. IR spectra of CH_3CN ice provides evidence of temperature affecting photoproducts.

Future Work: The purpose of these experiments was to lay the groundwork for eventual analysis using submillimeter spectroscopy with SubLIME. Submillimeter/far-IR spectroscopy is a gas-phase analytical technique that can distinguish between isomers of desorbed photoproducts that may be indistinguishable in FTIR spectra. Rotational spectroscopy, when used alongside IR spectroscopy, is a powerful tool for the analysis of complex mixtures due to the unique nature of rotational transitions. When this technique was applied to the photolysis of methanol ice, SubLIME detected three new photoproducts—ketene, ethylene oxide, and vinyl alcohol—for the first time in a cosmic ice experiment [6]. Using the rotational spectroscopic capabilities of SubLIME, we can address the following question: What additional UV-photoproducts of CH_3CN ice will we find? How does photolysis temperature affect what CH_3CN UV-photoproducts form in the ice? We also plan to photolyze CH_3CN + H_2O ice samples and measure sublimated volatiles with submillimeter/far-IR spectroscopy to be compared to previous observations of comets.

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