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# Ultraviolet photolysis of amino acids on the surface of icy Solar System bodies

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ABSTRACT

The icy worlds of the outer Solar System are of significant astrobiological interests due, in large part, to the evidence of liquid water beneath the surfaces of a number of jovian and saturnian satellites. Many of these surfaces are subject to various levels of particle and photon radiation. If molecular compounds of biological origin are present in the surface ice layer (originating either *in situ* or delivered from a subsurface aqueous environment), can they be detected as evidence of biological activity, or do they decompose too rapidly in the surface radiation environment? We present a wavelength resolved study of the ultraviolet photolysis of glycine and phenylalanine to address this question. Studying these reactions at multiple discreet wavelengths distinguishes the present work from previous matrix isolation studies using hydrogen flow lamps and continuum sources by resolving the important contribution of photons with energies much lower than Lyman-α (121.6 nm). We find that although the half-lives of glycine and phenylalanine are essentially identical at 147 nm, they diverge at 206 nm and diverge significantly at 254 nm with glycine having longer half-lives at these longer wavelengths. Scaling the results to account for the wavelength dependent variation in solar irradiance shows that despite the reduction of photon energies in the 200–250 nm range, versus 147 nm, it is the longer wavelengths that will dominate the destruction of amino acids in icy surfaces. It seems unlikely that organics can survive long enough on the surface of an icy planetary body to be detected without being frequently replenished from a shielded source such as a subsurface ocean.



## 1. Introduction

The Solar System contains a rich population of objects that are either partially, or entirely covered in water ice. Significant evidence exists that liquid water is present on at least five of these, namely Europa, Titan, Ganymede, Callisto, and Enceladus (Collins and Goodman, 2007; Khurana et al., 1998; Kivelson et al., 2002; Lorenz et al., 2008), leading to considerable interest in the potential habitability of environments on these bodies. For example, Russell and Kanik (2010) speculated that organic chemical synthesis could be occurring around hypothesized hydrothermal vents on the floor of the subsurface Europan ocean. One must also consider the possibility of exogenic sources of organic material on the icy surfaces of the outer Solar System such as impacts of carbonaceous chondrites, which have been shown to contain organics (Cronin et al., 1993; Huang et al., 2005). Further, Elsila et al. (2009) recently identified glycine of extraterrestrial origin in samples returned from Comet 81P/Wild 2 by NASA's Stardust spacecraft suggesting that comet dust may be another possible source of organic material. Regardless of the origin and nature of any biotic or prebiotic chemistry in/on icy worlds, it is the surface and near surface regions of these bodies that are the most accessible to investigation.

The surfaces of icy planetary bodies are subject to a variety of particle and photon bombardment, which can chemically alter any chemical signatures of life. Within the upper layers of these icy surfaces, photolysis, radiolysis and reactions involving secondary radical species are expected to limit the survivability of chemical biomarkers as well as the reaction products that may be signatures of biologically important parent molecules. To define search strategies and develop mission scenarios to look for evidence of extant or extinct life on these bodies, we need a detailed understanding of the physical chemistry within these icy environments.

Solar photons, energetic protons and electrons from the solar wind and planetary magnetospheres are all commonly invoked external energy sources that impact/penetrate an airless body's surface and can contribute to the chemistry of the surface material. Of these energy sources, ultraviolet (UV) solar photons are ubiquitous. They are not severely attenuated by the presence of a thin atmosphere, and they are expected to play an important role in environments such as the polar caps on Mars. A detailed

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understanding of photolysis over the complete range of chemically significant wavelengths is crucial.

There is a large body of work on photolysis of organic molecules under cryogenic conditions. Previous photolysis studies of amino acids related to their survivability in space environments include Ehrenfreund et al. (2001) and Bernstein et al. (2004) who performed matrix isolation studies using microwave excited hydrogen flow lamps. These lamps primarily provide an intense source of photons from Lyman-α emission (121.6 nm). Studies of photolytic destruction of amino acids have also been conducted using continuum UV sources. For example ten Kate et al. (2006) used a deuterium lamp to investigate the photochemistry of amino acids under conditions relevant to the surface of Mars. Half-lives have also been reported by Orzechowska et al. (2007) for amino acids in 100 K water ice matrices when exposed to continuum UV radiation from an Ar-arc lamp.

In the experiments presented here, photolysis of matrix-isolated amino acids using monochromatic resonance line lamps (5–10 eV) is used to identify direct photolysis products at a discrete set of photon energies. Glycine was chosen for this study, as glycine is the simplest of amino acids, while phenylalanine was chosen as a representative aromatic amino acid (see Fig. 1). Further, both glycine and phenylalanine can be sublimed without decomposition. By performing experiments in a chemically inert Ar matrix, any decomposition of amino acids can be directly attributed to photolysis, avoiding the complications due to chemical reactions with radicals, e.g., OH, that can occur in a water–ice matrix. Determining the decomposition due to direct photolysis is an important first step in understanding the destruction of amino acids in water ice matrices on icy bodies in the Solar System. Studying these reactions at multiple discreet wavelengths distinguishes the present work from previous matrix isolation studies using hydrogen flow lamps and continuum sources by elucidating the effect of lower energy photons.

## 2. Experimental section

Experiments were conducted using similar apparatus and methods to that previously described by Hodyss et al. (2008, 2009). Briefly, matrix isolated amino acids were vapor deposited onto a KBr window mounted on a closed-cycle helium refrigerated cryostat within a vacuum chamber with typical base pressures of $1 \times 10^{-9}$ Torr. Ar was introduced into the vacuum chamber through a separate turbo-pumped gas line with a base pressure less than $1 \times 10^{-6}$ Torr. Gas entered the chamber through a 1/16 in. diameter stainless steel tube whose tip was approximately 5 cm from the deposition window resulting in a somewhat collimated jet impinging on the window at ~10° from the normal. Amino acids (either Glycine [Sigma > 99%] or L-phenylalanine [Sigma > 98.5%]) were placed in a quarter inch diameter cylindrical glass Knudsen cell, directed towards the sample window at ~45°. Amino acid–Ar mixtures were co-deposited by simultaneously introducing Ar through a precision leak valve and heating the Knudsen cell to between 125 °C and 158 °C. At these temperatures, the amino acid vapor pressure was sufficient to produce a flow of sublimed vapor phase amino acids onto the sample (Svec and Clyde, 1965) while avoiding heat induced decomposition (Basiuk et al., 1998; Ratcliff et al., 1974; Simmonds et al., 1972).

All mixtures were deposited at the system's minimum achievable window temperature of ~18 K to ensure efficient deposition of Ar. This low temperature also prevented diffusion of the amino acids within the deposited matrix. The cryostat was free to rotate while under vacuum, allowing the sample window to be directed toward the gas inlet and Knudsen cell during deposition and then into position for UV exposures and spectral measurements.

Spectra were recorded in transmission with a Nicolet 6700 FTIR spectrometer from 6500 to 600 $cm^{-1}$ at a resolution of 2 $cm^{-1}$ and were the result of 2000 co-added scans. Following deposition, a spectrum was immediately taken to capture the appearance of amino acids in Ar prior to photolysis. UV photolysis was performed with (near) monochromatic incident light generated by either one of two different microwave excited, resonant gas discharge lamps (a Xe lamp at 147 nm and an $I_2$ lamp at 206 nm) or a Hg pen-ray lamp (at 254 nm). In all cases, UV entered the vacuum chamber through a $MgF_2$ window. In the case of the $I_2$ and Xe lamps the volume between the lamp emission window and the vacuum chamber window was purged with He to minimize atmospheric absorptions. Emission spectra of these three lamps are shown in Fig. 2. The flux of each lamp was measured to be $1.09 \times 10^{19}$ (147 nm), $8.68 \times 10^{18}$ (206 nm), and $3.41 \times 10^{18}$ photons $s^{-1}$ $m^{-2}$ (254 nm) using a calibrated Si photodiode (International Radiation Detectors, Inc.). Spectra were recorded as a function of UV exposure time.

The thicknesses of the ice films were estimated from interference fringes in the infrared spectra as outlined by Roser and Allamandola (2010). By measuring the layer thickness, typically between 2 and 8 μm, and the amino acid carbonyl absorbance (i.e., C=O at ~1780 $cm^{-1}$), assuming an integrated absorbance value of $3 \times 10^{-17}$ cm molecule$^{-1}$ (Ehrenfreund et al., 2001; Wexler, 1967), we were able to estimate the amino acid-to-Ar number density ratio in the deposited ice mixture. Amino acid–Ar mixtures were deposited in proportions that ensured the amino acids were isolated within the Ar matrix, approximately 1:10,000. This condition was met by adjusting flow rates of Ar and the temperature of the Knudsen cell. Although this is a rough estimate of the dilution ratio, it is sufficient to confidently state that the amino acids were well isolated in the matrices. Further, the 2–8 μm sample thickness ensured full UV penetration of these optically thin Ar ice layers (Bernstein et al., 2004; Ehrenfreund et al., 2001).

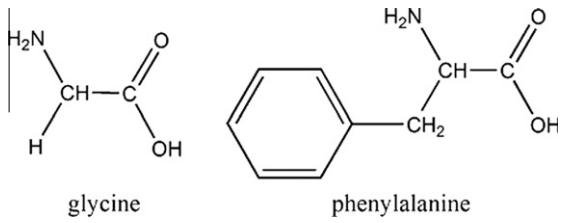


**Fig. 1.** Molecular structure diagrams of the amino acids used in this study.

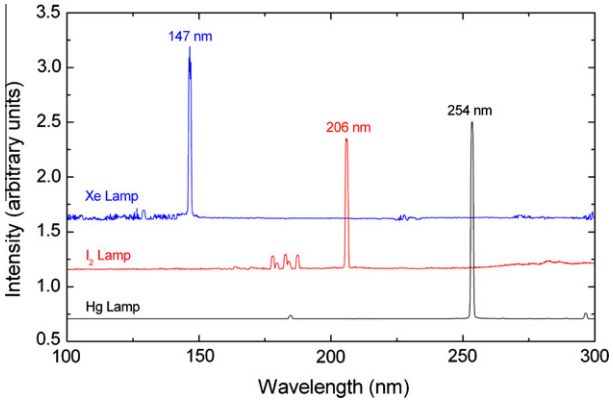


**Fig. 2.** Emission spectra of the discharge lamps used in the current experiments measured with scanning vacuum UV spectrometer and photomultiplier. Each lamp provides nearly monochromatic photons at the labeled emission line wavelength. The spectra have been scaled and offset for clarity of presentation.