

Variation in photon flux during extended photochemical aerosol experiments: Implications for atmospheric laboratory simulations

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ABSTRACT

In order to simulate the interaction of sunlight with planetary atmospheres, including Pluto, Titan and the early Earth, many laboratory studies have used high-power broadband lamps with spectral features that extend into the vacuum-ultraviolet (VUV, < 200 nm) to initiate photochemistry relevant to the atmosphere of interest. In many cases, experiments are run on the order of hundreds of hours with no accounting for how the photon flux within the system may be evolving with lamp age or a possible buildup of films over optical surfaces when working with high-yield photochemical systems. Given that the nature of photochemistry depends on the ratio of photons to reactants, variations in flux must be taken into account if the system is to be fully understood. In this study, standard N₂O actinometry was used to measure the VUV flux of high-intensity deuterium lamps before, during, and after the photochemical synthesis of Titan analog aerosols made from methane or benzene precursors. It was found that VUV photon flux can be decreased by over 50% in under 10 h at higher number densities, with recorded flux losses of over 75% during extended (> 60 h) photochemical experiments. While this is only one model system, it is apparent that changes in photon flux during simulations must be taken into account if adequate comparisons of the photochemical kinetics to their respective planetary environments are to be made.

1. Introduction

Since Urey and Miller carried out the first early Earth experiments [2], many astrobiologists have endeavored to recreate abiotic atmospheric environments in the lab with the hope of producing prebiotic molecules thought to be important in the formation of life. In recent years, these laboratory simulations have expanded to include the atmospheres of other worlds. Most notably, the atmospheres of Titan, Saturn's largest moon, and Pluto have received increased attention due to the wealth of new data from the Cassini and New Horizons missions. Both atmospheres are predominantly nitrogen and methane (CH₄) with additional trace gases [3–7]. One of the most notable features of these atmospheres are the haze layers composed of organic aerosols [3,6].

The haze layers shrouding Titan's surface give the moon its characteristic orange color [8] and have long been of interest because of potential similarities to the hazes hypothesized to be present in Earth's distant past [1,9,10]. The full extent of Pluto's hazes is only now being revealed with the recent flyby of the New Horizons spacecraft. The spacecraft revealed multiple haze layers extending for kilometers above the surface [6]. While the hazes are more disperse than those of Titan, they are initiated by similar atmospheric processes.

In general, one of two energy sources initiates the organic chemistry in atmospheres: energetic particles (cosmic rays and solar wind) or solar photons [11]. While both processes can occur simultaneously, experimentally the two cases are studied separately using plasmas, moderate to high intensity light sources, or other means [3]. The aerosol analogues, often referred to as tholins, that result from these setups are made from a complex mixture of products with variable yields and composition. While plasma generated aerosols made from CH₄ and nitrogen can yield on the order of 10–20 mg/h or more depending on conditions [12,13], photochemical yields are 100–1000 times less [1]. This inherently lower yield of photochemical aerosols imposes minimal time limits for producing an analyzable quantity of material. In some cases, yields are so low as to make some analytical studies impossible [14,15]. While higher photochemical yields have been obtained with the addition of other gas species (e.g. aromatics [16–20], carbon monoxide [13], carbon dioxide [1] and others [15,21,22]) to traditional methane/nitrogen gas mixtures, experimental lengths for single samples can still run to the hundreds of hours to generate sufficient material if ex situ analysis is to be performed [18–20,23]. In some studies, experimental time lengths are not detailed beyond that the experiment was run until enough material was

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generated [24,25].

Multiple high power, VUV light sources have been used to generate aerosol analogues including synchrotron sources [26,27] and mercury lamps [15,21,22]. While sufficient aerosol amounts for ex situ analysis can be generated in under 10 h using high power, high energy (extreme-UV, < 121 nm) synchrotron radiation [26], synchrotrons cannot produce a continuum of wavelengths for more accurately simulating the influx of solar radiation into an atmosphere. In addition, the expense and access involved with synchrotron work limits their potential use. While the use of a low-pressure mercury lamp solves the issues associated with access, the lamp is limited to producing photons of 185 nm and 254 nm, restricting its use to only those systems that absorb those wavelengths. Sample yields are often low enough, that no macroscopic studies are possible under reasonable time constraints [14,15].

Deuterium lamps have received considerable interest in recent years because of their ease of implementation, high power, and spectral overlap with many gas species of interest [10]. The continuum spectral output of many deuterium lamps (115 nm–165 nm) overlap with the strongest absorptions of methane in the range from 115 nm–145 nm [28] making them an ideal photochemical source for methane based aerosols. A study by Trainer et al., [1] determined that their lamp (Hamamatsu, L1835) had an intensity of $(4.4 \pm 0.1) \cdot 10^{15}$ photon/s in the vacuum ultraviolet using standard N₂O actinometry [29]. This lamp model has been used in many subsequent studies [13,16–20,23,24], with several requiring sample generation times (175–200 h) that are significant compared to the expected lifetime of 300 h for this model [18,20,23], yet no accounting for change in photon intensity over time, either from lamp age or cleaning of optics, was included.

As aerosol formation is an inherently “dirty” process, care must be taken to ensure that experimental conditions, particularly photon flux, do not vary significantly over the course of long duration experiments. Aerosols that settle on optical surfaces may decrease the photon flux within a reaction vessel, thus reducing the extent of the chemistry taking place. A sufficient drop in transmission will cause the photochemistry in the chamber to be significantly altered compared to “clean” running conditions. To date, there has been no accounting for how reaction conditions may change over the course of an extended photochemical run.

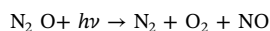
As the behavior of any photochemical system depends on the relative amounts of photons to reactants, it is vitally important to keep track of the relative amounts of each during a given experiment. While many past studies have been done at a convenient partial pressure of reactants in terms of generating significant amounts of product [13,18,19], there are very few aerosol studies directly addressing the question of photon flux versus number density [1,23]. While it is possible the chemistry that occurs within a given domain does not significantly change across a range of photon to reactant ratios, there is evidence to suggest that photon-dominated aerosol chemistry is significantly different from reactant-dominated aerosol formation [23]. The difference in chemistry is thought to be correlated to the optical depth of the reactant species. As reactant concentration increases, the depth at which the photons permeate the photochemistry chamber decreases. At lower optical depths, the deeper penetrating photons can cause secondary or tertiary reactions, whereby the initial products are pushed further down the reaction pathway. Higher optical depths limit photons to primary chemical reactions only, thus changing the nature of the chemical reaction system as a whole.

The effect of photon flux in atmospheric experiments and simulations are vital to understand if accurate comparisons between experiments and planetary systems are to be maintained and modeled. In this study, we characterize the photon intensity of a similar high intensity deuterium lamp (Hamamatsu, L11798) both with respect to the lifetime of the lamp, and its in situ performance when used to initiate photochemistry of a moderate-yield benzene based aerosol similar to those studied previously [16,18,23]. The rate of transmission degradation with respect to benzene number density is also investigated and

comparisons are made to the more traditional methane-based aerosol studies [1] carried out at the dawn of the Cassini era.

2. Experimental details

The total vacuum-ultraviolet flux of several deuterium lamps (Hamamatsu, L11798) with MgF₂ windows were measured using standard N₂O actinometry [29] at varying points in their lifetime. In order to evaluate the flux of the lamps across the largest lifespan possible, a total of six lamps of varying ages were used. An evacuated photolysis chamber was filled with N₂O and the initial pressures from 5 to 10 Torr were measured with a Baratron gauge. The range of pressures was chosen to minimize the effects of surface interactions of the gas products with the walls of the vessel as demonstrated by Rajappan et al [30]. The lamp irradiated the gas for 10–15 min (Δt), while the pressure increased over time according to the mechanism:



From the change in pressure, the volume of the chamber, and the measurements of the temperature from a Type T thermocouple (± 0.1 K), the change in gas moles, Δn , was determined. Using the literature quantum yield ($\Phi_{\Delta n} = 1.00 \pm 0.05$) for the reaction under these conditions [29], it was possible to determine the total VUV flux intensity, I (photon s⁻¹), of the lamp using the equation:

$$I = \frac{\Delta n}{\Phi_{\Delta n} \cdot \Delta t} \quad (1)$$

Each actinometry measurement was repeated a minimum of five times for statistical purposes.

In order to study the effects of film deposition on the total VUV flux of the lamp, a photochemical aerosol chamber similar to those used previously [17,18], was utilized. In order to examine the best-case scenario for photochemistry (minimal film thickness), the lamp was mounted vertically in a continuous flow setup (Fig. 1). Gas mixtures were created from with benzene (Sigma Aldrich, $\geq 99.9\%$) or methane (Airgas, 99.99%) in nitrogen (Airgas, 99.999%).

The benzene was put through several freeze-pump-thaw cycles prior to mixing to increase its purity. Gas mixtures were allowed to mix for a minimum of eight hours to ensure homogeneity before flowing through the reaction vessel at 20 sccm at total pressures of 20 Torr, 100 Torr, or 500 Torr. This range was chosen as 20 Torr is the lowest stable running pressure of the chamber while 500 Torr is similar to the highest atmospheric pressure where far-UV photolysis takes place at Titan [31]. The pressure of 100 Torr was selected as it is both five times higher and five times lower in number density than 20 Torr and 500 Torr respectively. The combined effects of the vertical geometry, continuous gas flow, and gravity minimizes the dwell time of larger chemical products near the lamp surface. A mixture of 50 ppmv benzene was selected as a medium yield aerosol based on the previous studies showing the aerosol mixture to be more productive than methane, but less productive than other species [17]. In addition, benzene has been confirmed to be present in the atmosphere of Titan at tens of ppm in the upper atmosphere (> 700 km) and has been postulated to play an important role in that atmosphere's photochemistry as its mixing ratio drops to a few parts per billion near the surface, where the aerosol concentration is highest [16,17]. For comparison to previous work on methane aerosols [1,3], mixtures composed of 0.1% methane, a recipe with high aerosol yields for ex situ work [1], and 1.5% methane, a less productive recipe that is more Titan-like, in nitrogen were run at 500 Torr.

The performance of the Hamamatsu L11798 deuterium lamps are shown in Fig. 2. A new lamp (0–250 h) has a flux of $(9.0 \pm 0.2) \cdot 10^{15}$ photons/s. This is well above the flux reported for the L1835 in previous studies [1] (Fig. 2, red dashed line). In the age window from 250 to 350 h, the lamps show a steep decline in flux leveling off at $(7.2 \pm 0.1) \cdot 10^{15}$ photons/s. This flux is maintained beyond the lifetime of 1000 h guaranteed by Hamamatsu. As the lamps are pushed beyond

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