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VUV and mid-UV photoabsorption cross sections of thin films of adenine: Application on its photochemistry in the solar system

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ABSTRACT

The photochemistry of an organic compound in extraterrestrial environments is related to its photoabsorption cross sections in the VUV/UV range (<300 nm). Such data, especially in the VUV range (<200 nm) are quite scarce in the literature. This paper presents an experimental setup and associated methodology to measure VUV/UV spectra of thin films of organic molecules. The case of adenine is extensively discussed as an example study. The absorption cross sections spectrum of adenine between 115 and 300 nm is measured from transmission measurements and accurate calculation of the thickness of our samples set thanks to interferometry techniques and infrared spectrometry. From these data, the infrared integrated band strength of solid adenine between 3600 and 1970 cm^{-1} has also been measured and is equal to $7.9\times10^{-16}\pm4\%$ cm molecule^{-1}. The use of the VUV/UV spectrum to estimate the photolysis rate constant is discussed and compared to direct kinetic measurements available in the literature for low Earth orbit experiments. However the lack of measurements of the photodissociation quantum yield as a function of the wavelength prevents a precise calculation. VUV/UV cross section spectrum is yet a necessity to conduct either proper kinetic studies on optically thin samples (less than 2 nm in the VUV for adenine) or an appropriate modeling for optically thick samples.

1. Introduction

The emergence of life is the final stage of complex processes involving liquid water and organic matter. The transition between no-life and life occurred when genetic material began to accumulate and replicate in the Earth's primitive environment. Nitrogen bases, composing RNA and DNA, constitute fundamental building blocks of life and have probably played an essential role in prebiotic chemistry. Thus, many studies concentrate on their origin.

Hydrogen acid (HCN) is a key molecule amongst the different mechanisms proposed that lead to the formation of nulceobases. HCN is a major product of spark discharge (Schlesinger and Miller, 1983), UV radiation (Scattergood et al., 1989) and high-energy laser shocks experiments (McKay and Borucki, 1997) on various gas mixtures. This molecule's key role in prebiotic chemistry has been first identified in Miller experiments (Miller, 1957). During the 1960s, works conducted by Oro and Kimbal showed that polymerization of concentrated HCN solutions heated to 80–90 °C can lead to adenine synthesis in yields up to 0.5% (Oro, 1960; Oro and Kimball, 1961, 1962). Since then, many researches are devoted to the abiotic synthesis of adenine from HCN polymerization in different primitive earth conditions. In 1966, adenine has been produced in 15% yield, so far the highest one, by heating a solution of hydrogen cyanide and liquid ammonia at 120 °C (Wakamatsu et al., 1966). In 1978, Ferris et al. (1978) detected 0.04% adenine from NH_4CN stored in dark at room temperatures for 4–12 months. However, these syntheses require a high ammonia concentration (above 1.0 M), which is not relevant to earth primitive environment (Summers and Chang, 1993). Furthermore, such reactions need high concentration of HCN (above 0.1 M) to compete with hydrolysis to formamide ($HCONH_2$) and formate ion ($HCOO^{2-}$) (Sanchez et al., 1967). It is difficult to reach such concentrations in prebiotic oceans. Stribling and Miller (1987) evaluated HCN concentration in prebiotic oceans as 3.5×10^{-5} M in the most favorable condition of pH and temperature (8 and 0 °C). One way to obtain higher HCN concentration is the eutectic freezing of dilute solutions of HCN (Sanchez et al., 1966). In 1982, adenine has been synthesized by freezing 0.01 M HCN at −2 °C, but at very low yields (0.004%) (Schwartz et al., 1982). Ten times more adenine has been observed from dilute solution of 0.1 M ammoniacal HCN, frozen for 25 years at −20 °C and −70 °C (Levy et al., 2000). Not to mention the limitation of adenine synthesis to restricted locations, it is difficult to believe that such small quantities produced by these methods are significant and sufficient for the formation of the first nucleic acid.

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Alternative prebiotic processes not based on HCN chemistry have been proposed for instance, adenine formation may derive from formamide catalyzed by $CaCO_3$ and other inorganic minerals (Saladino et al., 2001). Nevertheless, hydrolysis rates of formamide have been calculated for a wide range of temperatures (30–150 °C) and pH (0–14). Under these conditions steady state concentrations of formamide are very low and do not seem to have a significant role in prebiotic chemistry (Miyakawa et al., 2002).

Thus, the paths toward synthesis of adenine on primitive Earth is still debated and is far from being a consensus in the prebiotic chemistry science community.

An extraterrestrial origin of adenine or at least a contribution is also proposed. Organic material can be delivered to Earth by meteorites, comets and interplanetary dust particles (IDPs) (Chyba and Sagan, 1992).

Carbonaceous chondrites contain up to 3 wt % of organic carbon (for reviews see (Botta and Bada, 2002; Pizzarello and Shock, 2010; Sephton, 2002; Sephton and Botta, 2005). The search of nucleobases content in these meteorites has begun in early 1960s. In 1964, 15 ppm of adenine was detected by Hayatsu et al. in an acetylated HCl-hydrosylate (3 M HCl, 120 °C) of the Orgueil sample using paper chromatography. Since some of the organic compounds could have been altered or destroyed during the acetylation step, the same group analyzed another HCl-hydrolyzed sample of Orgueil in 1968 using the same procedure with no acetylation: 20 ppm of adenine was identified (Hayatsu et al., 1968). Later, the same amount of adenine was found in the Murchison meteorite using mass spectrometry (MS) with more drastic extraction conditions applied (3–6 M HCl or trifluoroacetic acid, $\geq$ 120 °C) (Hayatsu et al., 1975). In 1981, Stoks and Schwartz analyzed water and formic acid extracts of the Murchison, Murray and Orgueil meteorites using gas chromatography, high performance liquid chromatography and mass spectrometry: adenine was respectively identified at concentrations of about 267, 236 and 114 ppb. These concentrations are approximately 100 times greater than the ones reported by Hayatsu (1964) and Hayatsu et al. (1975, 1968). These great discrepancies can be explained in part by the compositional heterogeneity of the meteorite samples: for example, Stoks and Schwartz (1981) have observed large differences between purines concentrations of two samples from the same meteorite. Furthermore, the analytical methods used by Hayatsu (1964) and Hayatsu et al. (1975, 1968), paper chromatography and mass spectrometry are not the most appropriate for a quantitative study in contrast to those used in Stoks and Schwartz (1981) (liquid chromatography). More recently, formic acid extracts of 12 carbonaceous chondrites have been analyzed by liquid chromatography–high resolution mass spectrometry which reflected the wide distribution of adenine in these meteorites: Eleven of them contained this purine in range from 5 to 25 ppb (Callahan et al., 2011).

During the comet Halley flyby missions in 1986, in situ analyses of grains ejected from the nucleus have been done by the VEGA space craft mass spectrometer: PUMA. These measurements might indicate presence of adenine (Kissel and Krueger, 1987) but this detection is highly speculative because of the limited resolution of the spectrometer. Rosetta, a European Space Agency (ESA) mission, will reach and study comet 67P/Churyumov–Gerasimenko in 2014 and will provide more information about the chemical composition of comets and IDPs generated by them.

Micrometeorites (i.e. IDPs fallen on the Earth) are considered as the present day dominant source of extraterrestrial material accreted by the Earth (Love and Brownlee, 1993; Maurette et al., 1995); Bland et al., (1996) estimated the current meteorites flux as $\approx$ 10 t/year whereas dust flux have been estimated as 40,000 $\pm$ 20,000 t/year (Love and Brownlee, 1993). In liquid water, they might have acted as a micro-reactor for prebiotic synthesis (Heidmann et al., 1991). Furthermore, a particular class of them, ultracarbonaceous micrometeorites, contain up to 50% of organic matter (Dobrică et al., 2009).

With respect to meteorites and comets, it is within micrometeorites that organic matter is less protected from solar radiation. The importance of their contribution in organic matter's delivery to Earth is then notably linked to the photochemical stability of organic molecules. In the solar system conditions, the energy essential to chemical evolution is brought by mid-UV and Vacuum UltraViolet (VUV, $\lambda < 200$ nm) radiation. Photochemical studies in the VUV domain and the determination of photolysis constants (J) are then crucial to know the extent of the extraterrestrial contribution of micrometeorites to the origin of life. Nevertheless, some approximations have to be done for the calculation of kinetic data. One of these approximations is the absorption of solid state molecules in the VUV domain. Such absorption spectra are very scarce for organic compounds in the solid state in current literature.

This work presents a methodology to measure VUV cross section absorption spectra of thin organic films. It is developed in the frame of experiments conducted in laboratory and in low earth orbit (LEO) to measure the photostability of organic matter in the VUV (Cottin et al., 2008, 2012; Guan et al., 2010).

How VUV cross section spectrum can be used to derive actual photolysis rate in space is also discussed. Application to adenine is presented in this paper.

2. Material and methods

This section presents the procedure to measure the absorption cross section spectrum of adenine in the VUV domain. Solid organic films are prepared and analyzed using infrared and VUV spectroscopy. From VUV transmission data, the absorption cross section spectra is deduced. Calculation requires an accurate value of the sample's thickness, which has been measured by two independent methods: laser interference technique and interferometric microscopy, both using sample's IR spectra.

2.1. Sample preparation

Samples of adenine are prepared on magnesium fluoride (MgF_2) windows, chosen for their optical transmission properties – they transmit UV down to 115 nm and their cut-off in the infrared domain is at 1000 cm^{-1}. They are inserted in an aluminum cell in order to manipulate them without deteriorating the organic film.

Adenine was purchased from Sigma-Aldrich (purity>99%) and MgF_2 windows were provided by Crystran (thickness: 1 mm, diameter: 9 mm).

The method consists of sublimating molecules and recondensing them on MgF_2 windows. For this, a sublimation reactor has been developed (built by Meca 2000 company, France) (Guan et al., 2010), based on the same concept as the one presented in (Ten Kate et al., 2005).

This system (Fig. 1) is composed by the reactor connected to a pumping system (primary and turbo pump) able to create a vacuum as low as 10^{-4} mbar. The reactor, a cylindrical housing ($\sim$0.1 m^3), contains an oven whose temperature can be set up to 800 °C. A ceramic melting pot containing adenine molecules is placed in this oven above which a carrousel accommodating up to nine cells is hung. Only one of the cells is exposed to the molecules that are sublimated while the others are hidden behind a blinder. Once the organic film deposed reaches the thickness desired, the carrousel can be turned thanks to a handlever situated at the bottom of the reactor and the deposit on the next window begins. The thickness