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Acrylonitrile characterization and high energetic photochemistry at Titan temperatures

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ABSTRACT

Laboratory infrared spectra of amorphous and crystalline acrylonitrile (C_2H_3CN) ices were recorded between 4000 and 650 cm^{-1}. Heating up the acrylonitrile sample to 160 K shows details on the transition between amorphous and crystalline ice at ∼94 K. This molecule can be used as an indicator of the surface temperature of Titan since it is known also to be ∼94 K. The desorption energy of acrylonitrile was determined using two methods (IRTF and mass spectrometries) to be around 35 kJ mol^{-1}. Solid phase acrylonitrile was irradiated with vacuum ultraviolet (VUV) light at low temperatures (20, 70, 95 and 130 K) using a microwave-discharge hydrogen flow lamp. Isoacrylonitrile, cyanoacetylene (HC_3N), isocyanoacetylene (HC_2NC), acetylene (C_2H_2) and hydrogen cyanide (HCN) were identified as photoproducts by using FTIR spectroscopy. The branching ratio of each pathway has been calculated for the different temperatures. We have estimated the acrylonitrile, HCN and HC_3N $\nu_{C\equiv N}$ stretching band strengths to be respectively $\mathcal{A} = 3.98 \times 10^{-18}$, $\mathcal{A} = 1.38 \times 10^{-18}$ and $\mathcal{A} = 2.92 \times 10^{-18}$ cm molecule^{-1}.

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1. Introduction

During these last 30 years, the chemical atmospheric composition of Titan (the largest satellite of Saturn) has been extensively explored (Liang et al., 2007; Kammer et al., 2013). The different constituents have been identified by infrared spectroscopy during the Voyager and Cassini-Huygens missions (Coustenis et al., 1989, 1991, 2007). A wide variety of organic molecules comes from the coupled photochemistry of CH_4 and N_2, the two most abundant components in the atmosphere. Among the molecules detected, numerous hydrocarbon species have been found in gas phase: acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), methyl-acetylene (CH_3CCH), propane (C_3H_8), diacetylene (C_4H_2) and benzene (C_6H_6) (Coustenis et al., 2007; Hébrard et al., 2007). Other interesting compounds formed in the atmosphere are the nitriles as hydrogen cyanide (HCN), cyanoacetylene (HC_3N), cyanogen (C_2N_2), dicyano-acetylene (C_4N_2) and more recently detected, acrylonitrile (C_2H_3CN) (Cui et al., 2009; Magee et al., 2009; Lellouch et al., 2010). Some of them (HC_3N, C_4N_2, and $CH_3 CH_2CN$) have been observed in solid phase such as C_2H_2 (Khanna, 2005a,b). As stated by Moore et al. (2010), these interpretations of Titan observations depend on the knowledge of the spectra of various molecular solids

suspected to be present. The temperature and physical state (different phases) of the medium are important for the molecular identification since they can induce large frequency shifts in the absorption band position, intensity and width of the absorption (Khanna, 2005a). Spectra have been published concerning crystalline acrylonitrile (or 2-propenenitrile or vinyl cyanide) (Dello Russo and Khanna, 1996), but no data have been found concerning the different phases and complete photochemistry of acrylonitrile. Encouraged by the works of Khanna et al. (Khanna, 2005a,b; Dello Russo and Khanna, 1996; Samuelson et al., 1997) and Kim and Kaiser (2009) who suggested that nitriles could be condensable on Titan, it seems to be interesting to study the acrylonitrile molecule. Since Titan's surface is known to be cold 94 K and lower temperatures around 70 K are present in the low atmosphere or troposphere (50 km), acrylonitrile could also exist in its solid form as either an amorphous or crystalline solid because its freezing point is at ∼190 K in normal conditions (Finke et al., 1972).

Since the dominant energy source available to dissociate N_2 and CH_4 in the upper atmosphere is solar radiation (Lavvas et al., 2011), the neutral species present in Titan's atmosphere can undergo dissociation. So after providing measurements of amorphous and crystalline condensed solid acrylonitrile at different temperatures in this work, we will present the results of photolysis experiments on acrylonitrile. These experiments have been conducted in order to understand the behavior of the molecules when they are formed and submitted to UV radiation in Titan's atmosphere. The

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quantification of gas-phase acrylonitrile photochemistry has already been studied at 213.9 nm by Gandini and Hackett (1978). Two primary processes have been identified in the gas phase with the main one corresponding to the C—H and C—C bonds cleavage yielding to C_2H_2 and HCN formation. The branching ratio of this process was estimated to be 50%. The pathway leading to HC_3N (with the loss of molecular hydrogen) yields 31%. Wilhelm et al. (2009), using time-resolved Fourier transform infrared emission spectroscopy, studied the photodissociation of acrylonitrile and its isotopologue ($CD_2=CDCN$) at 193 nm. The presence of HCN and its isomer HNC with C_2H_2 has been revealed during these experiments. Recently we reported (Toumi et al., 2014) that the photochemistry of acrylonitrile in argon matrix induces the formation of C_2H_2:HCN, C_2H_2:HNC complexes, HC_3N (with three other isomers) and isoacrylonitrile. The purpose of this work is to present the first experimental approach for the photochemistry of acrylonitrile in simulated atmospheric conditions of Titan (Couturier-Tamburelli et al., 2014). Herein we report temperature-dependent infrared spectra of amorphous and crystalline ices of acrylonitrile. We present the results obtained after temperature-dependent photolysis of solid acrylonitrile. Using FTIR, mass spectrometry and previous experiments, we characterized the different products obtained in solid phase and compared the results with similar processes measured in the gas phase. We give a rough approximation of the branching ratios obtained for each product identified during photolysis experiment at different temperatures. Since all the identified compounds have a $\nu_{C\equiv N}$ or $\nu_{N\equiv C}$ stretching band, we used these modes to determine the branching ratio. We also discuss the consequence of this study on the understanding of acrylonitrile photochemical behavior in titanian conditions.

2. Experimental section

Acrylonitrile (from Aldrich, with a purity ⩾99%) was used after purification by vacuum distillation. Acrylonitrile was vapor deposited at a rate of 6×10^{-1} mol min^{-1} on a gold-plated copper surface kept at different temperatures between 20 and 300 K with the help of a cold head cryostat (CTI, model 21) within a high vacuum chamber (ca 10^{-7} mbar). The warming up of the samples was performed at a heating rate between 0.8 and 5 K min^{-1} using a resistive heater along with a Lakeshore model 331 temperature controller. The spectra were recorded in reflection–absorption (doubled absorption) using a Fourier Transform Infrared Spectrometer (Nicolet serie II Magna System 750) from 4000 to 650 cm^{-1}. Each spectrum was averaged over one hundred scans with 1 cm^{-1} resolution. Mass spectra of the samples were recorded up to 130 amu with a resolution of 1 amu during precisely controlled warm-up sessions using a quadrupole mass spectrometer (MKS Microvision-IP plus), with a 70 eV electron impact ionization source. A microwave-discharge hydrogen flow lamp (Opthos Instruments, operating pressure 0.4 mbar, MgF$_2$ window) was used as the far-UV source; its flux, confined to the range of 3–10 eV, is dominated by two broad bands, centered around 120 (Lyman-α) and 160 nm, with a continuum in the visible. We estimated the Lyman-α photons flux using the actinometric method (Gerakines et al., 2000) in which we photolyzed a pure O_2 solid deposition with the hydrogen flow lamp and measured the photolysis rate when O_2 turned into O_3. The Lyman-α photons flux was calculated to be $4.02\,(\pm1.15) \times 10^{12}$ photons cm^{-2} s^{-1} with a forward power of 70 W and a reflected part less than 2 W. Quantitatively, a difference is observed with the solar flux Lyman-α photons penetrating the high atmosphere of Titan and which is known to be 4.12×10^{11} photons cm^{-2} s^{-1} (Toublanc et al., 1995; Lean, 1991). A recent work performed by Chen et al. (2014) permits us to calculate the total flux of the lamp from the Lyman-α photons one. With a F-Type microwave McCarroll cavity and with a MgF$_2$ window, the

proportion of Lyman-α is 8.4%. So, in our case, we have a total flux of $4.79\,(\pm1.37) \times 10^{13}$ photons cm^{-2} s^{-1}. Irradiation of solid acrylonitrile was also carried out using an Osram 200 W high-pressure mercury lamp equipped with a quartz envelope ($\lambda > 230$ nm). The photon flux of this last lamp is estimated to be 2.75×10^{16} photons cm^{-2} s^{-1} (Gudipati et al., 2013; Couturier-Tamburelli et al., 2014).

Since the reactants are consumed during the photoreaction, the band integration strengths are used to monitor the increase of the products infrared band intensities and to estimate how much of each product is formed. The amount of initial acrylonitrile molecules was obtained with the $\nu_{C\equiv N}$ stretching mode at 2229 cm^{-1}. Since the band strength of $\nu_{C\equiv N}$ of pure acrylonitrile is unknown, it was necessary to determine this value. To do so, we deposited different mixtures of acrylonitrile and CO_2 (Gerakines, 1995). The absorption strength of the $\nu_{C\equiv N}$ stretching mode of pure acrylonitrile at 20 K was calculated from the data experiment to be $\mathcal{A} = 3.98 \times 10^{-18}$ cm molecule^{-1} using the areas under the $C\equiv N$ stretching mode peak and the absorption of the ν_{CO} mode of CO_2 (Gerakines, 1995). This value is of the same order of magnitude as the one published by Bernstein et al. for acrylonitrile in H_2O which is $\mathcal{A} = 7.7 \times 10^{-18}$ cm molecule^{-1} (Bernstein et al., 1997). We used the same procedure to determine the band strengths of HCN and HC_3N which are listed in Table 1.

Based on the work of Hudson and Moore, 2004, the band strength used for CN stretching of nitriles and isonitriles are assumed to be equivalent. For example, the value used in our experiments for the isoacrylonitrile is the one that we have calculated for the acrylonitrile molecule (3.98×10^{-18} cm molecule^{-1}). An infrared band's integrated intensity $\int \tau(\tilde{v})d\tilde{v}$ in cm^{-1} could be converted to a molecular column density N, in molecule cm^{-2}, through $\int \frac{\tau(\tilde{v})d\tilde{v}}{A}$ provided that the band's intrinsic strength, $\mathcal{A}$ in cm molecule^{-1}, was known.

2.1. Infrared spectra of solid acrylonitrile

2.1.1. Amorphous ices formed at 20 K
Vibrational spectroscopy of acrylonitrile in rare-gas matrices has been studied earlier (Toumi et al., 2014). Here we present full infrared spectrum of pure solid acrylonitrile at different temperatures (20, 95, 130 K) along with the vibrational assignment by comparing with earlier studies (Dello Russo and Khanna, 1996; Khlifi et al., 1999). These comparisons are summarized in Table 2. In our experiment, the spectrum of solid amorphous acrylonitrile is obtained at 20 K in the 4000–650 cm^{-1} range and shows fundamental and combination modes (Table 2). The most intense bands are observed at 970 and 2229 cm^{-1} and have been assigned, respectively to wagging modes noted ν_{12}, ν_{13} and $\nu_{C\equiv N}$ stretching mode noted ν_4. In all the spectral regions, the absorptions of amorphous ice are broad and clumpy.

2.1.2. Annealing and phase transition to crystalline ice
The pure acrylonitrile ice is heated from 20 to 180 K with different heating rates (from 0.8 to 2 K min^{-1} when followed by IR and

Table 1
Band strengths of CN stretching mode for different nitriles related to our experiments.

	Band strength ($\times 10^{-18}$ cm molecule^{-1})
$\mathcal{A}$ (acrylonitrile, pure)	3.98
$\mathcal{A}$ (acrylonitrile, water) (Bernstein et al., 1997)	7.7
$\mathcal{A}$ (HC_3N, pure)	2.92
$\mathcal{A}$ (HCN, pure)	1.38
$\mathcal{A}$ (HCN, water) (Bernstein et al., 1997)	5.1