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Photochemistry of solid interstellar molecular samples exposed to vacuum-ultraviolet synchrotron radiation

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ABSTRACT

At the vacuum-ultraviolet (VUV) beamline of the Taiwan synchrotron, an end station for photochemistry coupled to instruments to record infrared absorption spectra and ultraviolet and visible emission spectra is used to investigate the photolysis of samples of gases condensed at 3 K. This end station is applicable to explore the VUV photochemistry of interstellar molecules in solid samples. For demonstration, we discuss the response of solid dinitrogen to VUV irradiation. In the future, the upgraded photochemistry end station is applicable to investigate the cometary mixed-ice analogs excited with VUV light from the synchrotron.

1. Introduction

Astronomers believe that vacuum-ultraviolet (VUV) light is an important driving force for the evolution of our solar system. To investigate the VUV spectra and photochemistry of interstellar molecules is intriguing in astroscience, research in this field is currently increasing. For instance, to assess the changes photochemically induced in interstellar media, one must have qualitative or quantitative information about the absorption of molecular species in the VUV range [1–4].

For spectral investigations, the principal sources of excitation have been hydrogen lamps, mercury lamps, xenon lamps, tungsten filaments, tungsten–halogen lamps, and various lasers in the visible and UV ranges. To tune the energy from these conventional and laser sources within the VUV region is difficult. Synchrotron radiation (SR) provides an intense and continuous source of VUV light; a synchrotron hence provides an effective source to explore the spectra and photochemistry of molecules and materials. The great quality of VUV light in SR likewise enables scientists to investigate the VUV spectra and photochemical reactions of interstellar molecules to a far horizon and to explore the VUV astrochemistry in deep space.

For this purpose and with exciting prospects, we have established a few end stations at beamlines of a synchrotron to conduct experiments involving photoabsorption, photodissociation, photodesorption, photoionization and photoluminescence in research related to space [5–8]. To explore new molecular astrophysics and astrochemistry, we continually improve the performance of these end stations. We present here some results from our recently upgraded end station for photochemistry at the VUV beam line from the 1.5-GeV storage ring in Taiwan Light Source (TLS). At this end station we previously detected photoproducts excited with VUV light with only an infrared interferometer; we just added an instrument to record ultraviolet and visible emission at this end station, so that we can now monitor emission simultaneously with absorption. We have in this way expanded the performance of this end station, which will bring new scientific opportunities in the research field of astroscience. In this report, we demonstrate the upgraded performance of this photochemistry end station with an example involving solid dinitrogen.

2. Experiments

The experimental apparatus is displayed schematically in Fig. 1. The VUV radiation is conducted from undulator beamline BL21A2 attached to the 1.5-GeV storage ring at TLS in the National Synchrotron Radiation Research Center (NSRRC), Taiwan. This undulator has periodically spaced permanent magnets (90 mm, U90) to provide pseudo-continuous VUV light with photon flux $\sim 10^{16}$ photons s^{-1} (2% bandwidth). Depending on the desired wavelength, harmonics from the undulator are suppressed through absorption by gaseous Ne, Ar or Kr at pressure 10 torr and a filter window – LiF, MgF_2, CaF_2, sapphire, fused silica or quartz.

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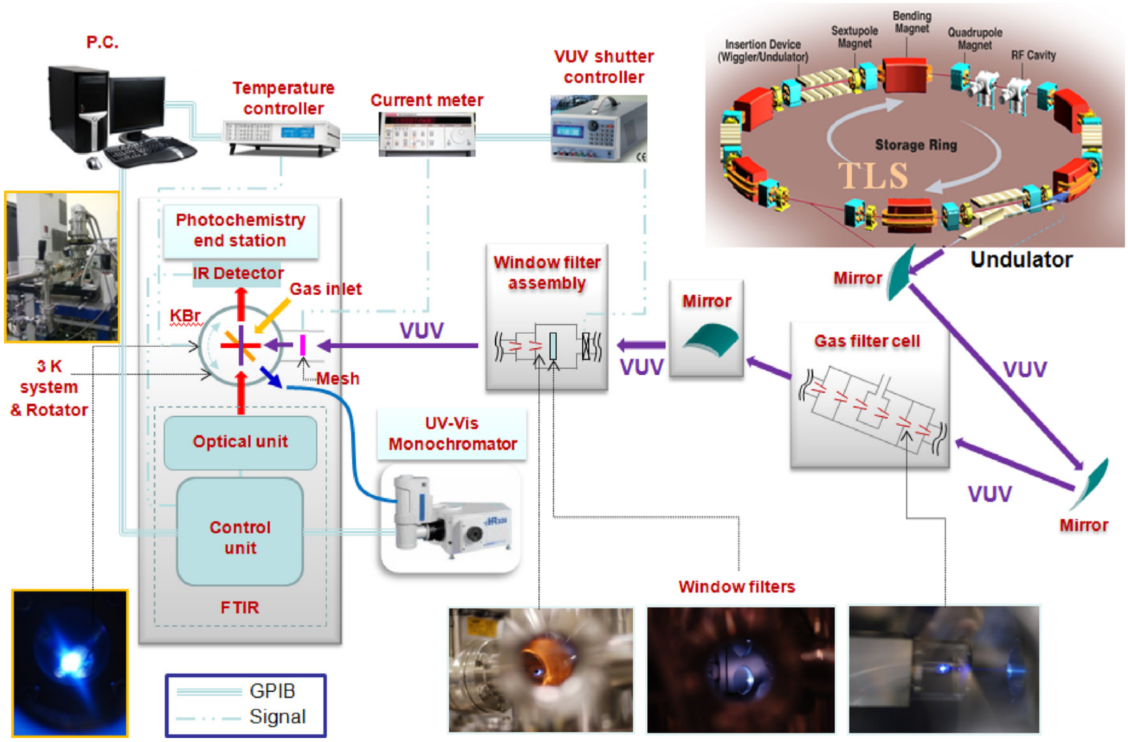

Fig. 1. The layout of the experimental scheme.

A gaseous sample or mixture is deposited on a cold KBr crystal cooled to ~3.0 K with a closed-cycle refrigerator (Janis RDK-415). This cryostat is situated on the plate of a differential rotary-seal stage of which the rotatable angle is 360°. The KBr window can thus be rotated freely to face deposition or photolysis or detection port. The enclosure of the cryostat is evacuated with a turbomolecular pump backed with a scroll pump to less than 1×10^{-8} torr.

IR absorption spectra are recorded in transmission through a sample at various stages of experiments with an interferometric spectrometer (Bomem, DA8) equipped with a KBr beamsplitter and a HgCdTe detector (cooled to 77 K) to cover the spectral range 500–5000 cm^{-1}, typically with 400 scans and resolution 0.5 cm^{-1}.

Visible and ultraviolet light emitted by a sample is focused with a silica lens into an optical fiber to be conducted to an entrance slit of a monochromator (iHR320) that possesses three gratings (600, 1200 and 2400 grooves mm^{-1}). The dispersed emission is detected with photon detector of two types, either a photomultiplier tube (PMT) or a charge-coupled detector (CCD); the PMT (Hamamatsu Model R928) is mounted in a box with water cooling and scanned in a photon-counting mode, whereas the CCD (1024 × 256 pixels, Horiba Symphony II) is cooled with liquid nitrogen and used in an image mode. For the present work, the entrance slit is set at width 0.5 mm and the grating (2400 L/mm) produced resolution about 0.2 nm with CCD detection.

Gaseous dinitrogen ($^{14}N_2$, nominal purity 99.9999%, Matheson; $^{15}N_2$, nominal purity 98%, Cambridge Isotopes) was used without purification other than passage through a U-tube cooled with liquid dinitrogen.

3. Results and discussion

The photolysis of solid samples with VUV radiation has been little investigated because operating in the VUV region with conventional lamps or lasers is difficult. An undulator beam from a synchrotron has an advantage of the wavelength becoming tunable through variation of the gap of the magnets, to deliver intense radiation to explore photolysis. The storage ring of TLS is operated in the 'top-up mode', i.e., maintaining a constant electron beam current, 360 mA, in the storage ring through injection of a few electrons every minute. As the electron current is thus stable to better than 99.5%, the photon flux is essentially constant over time; the photon dose that a sample experiences linearly proportional to the duration of irradiation.

We recorded the infrared absorption spectra of a deposited sample of dinitrogen before and after exposure to radiation at a wavelength selected from our synchrotron source. Before photolysis, the spectrum of solid dinitrogen revealed a doublet at 2349.2 and 2347.7 cm^{-1} due to adventitious CO_2 and weak lines near 3726.8 and 1597.3 cm^{-1} associated with H_2O, both contaminants in vestigial proportions after deposition for 2 h or more. Another weak line at 2328.4 cm^{-1} with full width 0.8 cm^{-1} at half maximum stature was identified as absorption of solid N_2. On subtracting the absorbance spectrum recorded before irradiation with VUV light from that recorded after irradiation, we obtained difference spectra. A feature pointing upward is associated with the absorption of a given product of photolysis, whereas a feature pointing downward pertains to a depleted precursor. Fig. 2 displays a partial IR difference spectrum of pure solid dinitrogen at 3 K after photolysis at 121.6 nm for 30 min. New absorption lines appeared at 1657.6 and 1652.7 cm^{-1}, as shown in Fig. 2(a). The line at 1652.7 cm^{-1} is more intense than that at 1657.6 cm^{-1}; the latter was occasionally accompanied with a small shoulder at 1655.7 cm^{-1}. These features are characteristic of the ν_3 mode of azide radical, N_3, reported by Tian et al. [9] and us [10].

There exist several reports of the production of azide radicals after bombardment of solid N_2 with energetic particles: for example, 4-keV Ne/He^+ [9], 120-eV N atoms [11], 0.8-MeV protons [12], and 5-keV electrons [13]. Tian et al. [9] reported three lines at 1657.5, 1654.5 and 1652.6 cm^{-1} associated with mode ν_3 of N_3 in solid dinitrogen at 20 K. After VUV photolysis of solid dinitrogen at 20 K, we recorded lines also at 1657.8 and 1652.6 cm^{-1} [10]. In both cases at 20 K, the intensity of the line at 1657.8 cm^{-1} is three

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