

## VUV Photoabsorption Cross Sections of $^{15}\text{NH}_3$

With radiation from the high-flux beam line at spectral resolution of 0.02 nm, we measured photoabsorption cross sections of gaseous  $^{15}\text{NH}_3$  in the spectral region of 140-226 nm with temperature at about 298 K. The oscillator strengths of  $^{15}\text{NH}_3$  for the transition  $A\leftarrow X$  in the range 165-220 nm and for the transition  $B\leftarrow X$  in the range 144-165 nm are evaluated to be 0.0858 and 0.0124, respectively. Absorption bands in the  $A\leftarrow X$  system of  $^{15}\text{NH}_3$  are red-shifted from those of  $^{14}\text{NH}_3$ , in contrast to blue shifts for four deuterated variants of  $^{14}\text{NH}_3$ .

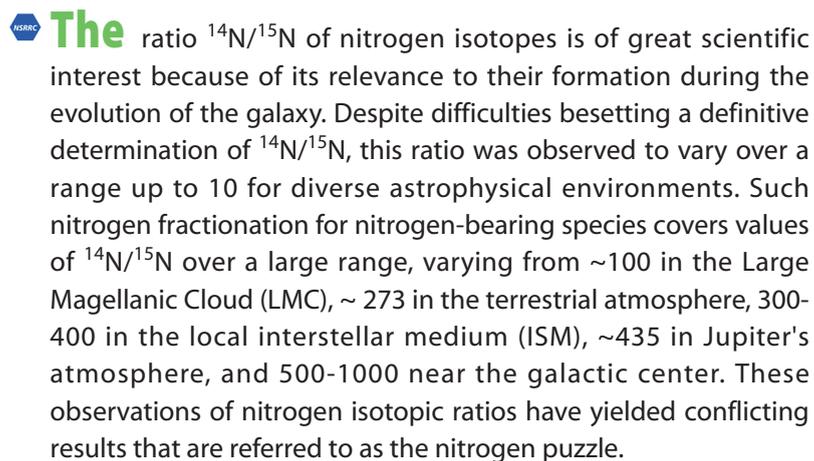
### Beamline

03A High-flux

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The ratio  $^{14}\text{N}/^{15}\text{N}$  of nitrogen isotopes is of great scientific interest because of its relevance to their formation during the evolution of the galaxy. Despite difficulties besetting a definitive determination of  $^{14}\text{N}/^{15}\text{N}$ , this ratio was observed to vary over a range up to 10 for diverse astrophysical environments. Such nitrogen fractionation for nitrogen-bearing species covers values of  $^{14}\text{N}/^{15}\text{N}$  over a large range, varying from  $\sim 100$  in the Large Magellanic Cloud (LMC),  $\sim 273$  in the terrestrial atmosphere, 300-400 in the local interstellar medium (ISM),  $\sim 435$  in Jupiter's atmosphere, and 500-1000 near the galactic center. These observations of nitrogen isotopic ratios have yielded conflicting results that are referred to as the nitrogen puzzle.

To explain the gradient of the  $^{14}\text{N}/^{15}\text{N}$  ratio from a large value 1000 near the galactic center to 300-400 near the position of the Sun, it has been suggested that nitrogen was formed through nuclear synthesis in the interior of stars via CNO cycles in  $p$  and  $\alpha$  capture reactions. This interpretation is generally consistent with the tendency of  $^{14}\text{N}/^{15}\text{N}$  values observed in the galaxy, but such a scenario requires further evaluation. The argument of the  $^{14}\text{N}/^{15}\text{N}$  ratio is based mostly on the determination of nitrogen isotopic species in the gaseous phase. For instance, the composite infrared spectrometer (CIRS) on the *Cassini* spacecraft remotely measured unique global infrared spectral maps of  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$  in the atmosphere of Jupiter and evaluated the ratio  $^{14}\text{N}/^{15}\text{N}$  to be  $448 \pm 62$ . This determination is definitive and conclusive for the present nitrogen isotopic ratio, but an interpretation to achieve the present value from the past should include the photochemical model of ammonia in these planets. As is well known, because of photo-induced fractionation (PHIFE) by the sun, the variation in rates of dissociation for isotopic variants is significant in Mars (Cheng et al. 1999), Jupiter (Lee et al. 2001), Venus (Bahou et al. 2001), and comets (Cheng et al. 2002). We accordingly expect this PHIFE to be a common process in planetary atmospheres throughout the solar system and PHIFE is expected to provide the key to understand the history and evolution of the planets. A similar scheme should be applicable to interpret distributions of  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$  in Jupiter. The differences in VUV absorption cross sections

between  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$  would imply disparate rates of photodissociation for these isotopic species, consequently major differences in the abundance of these isotopic species through the history of evolution.

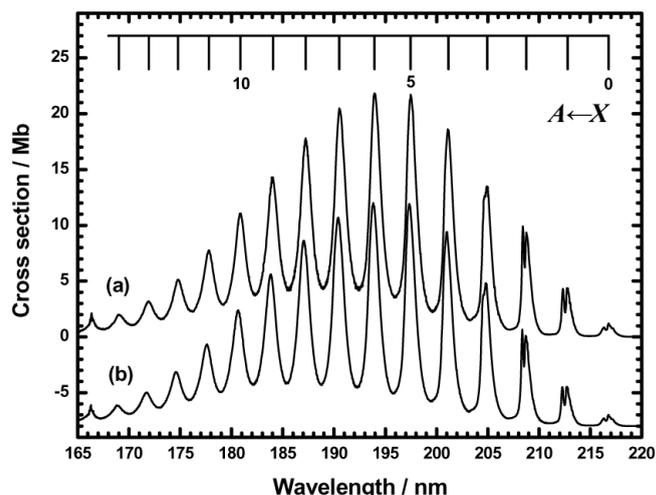
To understand the isotopic fractionation of  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$  in outer space, especially in Jupiter and Saturn, we must know absolute absorption cross sections of  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$  in the VUV range. Although absorption cross sections of  $^{14}\text{NH}_3$  have been extensively measured in the VUV range (Cheng *et al.* 2006), such data for  $^{15}\text{NH}_3$  are lacking. In this work, we have measured the absorption cross sections of  $^{15}\text{NH}_3$  in the range 140-226 nm and applied the results to photochemical models of Jupiter for understanding its nitrogen isotopic ratio.

We measured absorption cross sections in the VUV region with a double-beam apparatus. The experimental setup has been described in detail (Cheng *et al.* 1999; Lu *et al.* 2004). Vacuum ultraviolet radiation from Taiwan's synchrotron is dispersed with a cylindrical-grating monochromator (focal length 6 m). With a grating having 600 grooves  $\text{mm}^{-1}$  and a slit width 0.050 mm, a resolution 0.02 nm was achieved. The VUV light intensity before entering the gas cell was monitored by reflecting light from a  $\text{CaF}_2$  plate placed at  $45^\circ$  from the beam line; the reflected light passed one additional  $\text{CaF}_2$  window before impinging on a glass window coated with sodium salicylate for detection. The  $\text{CaF}_2$  plate also served to eliminate the second-order light from the synchrotron radiation. The transmitted light passed through the absorption cell before being detected similarly. Fluorescence of sodium salicylate induced with VUV light in both reflected and transmitted beams was detected with photomultiplier tubes in a photon-counting mode. The wavelengths were calibrated with absorption lines of Xe, CO,  $\text{O}_2$  and NO. The accuracy in measurements of wavelength is limited by the scan step, typically 0.02 nm.

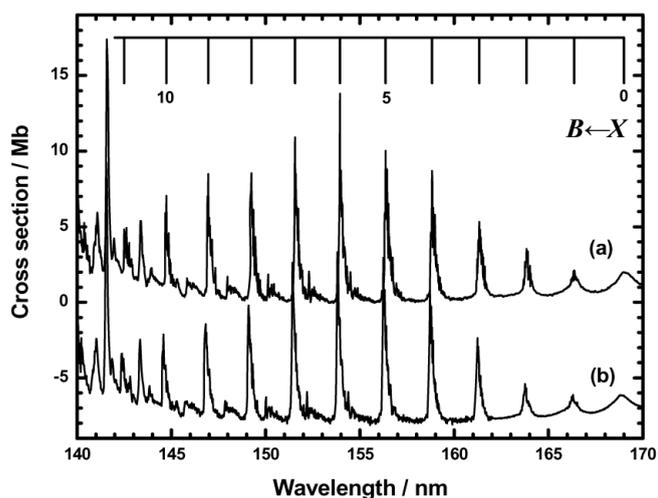
The absorption cross section is determined from the absorbance  $A$ ,  $A = \ln(I_0/I) = n \sigma l$ , in which  $I_0$  is the intensity of reflected light,  $I$  is the intensity of transmitted light,  $n$  is the gas density,  $\sigma$  is the absorption cross section, and  $l = 89$  mm is the length of absorbing path through the gaseous sample. A reservoir of volume  $620$   $\text{cm}^3$  was connected to the sample cell to suppress possible interference resulting from variation in gas pressure caused by surface adsorption, photofragments, and fluctuation of temperature. The absorbance was adjusted to zero when the gas cell was evacuated. The density of a gaseous sample was determined from its pressure monitored with

capacitance manometers and the temperature monitored with a thermocouple. Absorption spectra of gaseous samples were recorded at pressures/Pa in a range 8.9-89860 at 298 K. The absorption cell was evacuated below  $7 \times 10^{-5}$  Pa before being filled with a fresh sample to a specific pressure for each measurement. At each wavelength, the absorption cross section was evaluated from a linear fit of five to ten absorbance values measured at varied pressures. To avoid saturation effects, we limited the maximum absorbance to 0.4 for the region 140-165 nm and 1.4 for the region 165-220 nm. We purified  $^{15}\text{NH}_3$  (issued isotopic purity 99%, Cambridge Isotope Laboratories) further with a freeze-pump-thaw procedure at 77 K, followed by vacuum distillation from 206 K to 77 K.

The absorption cross sections of  $^{15}\text{NH}_3$  are determined at a spectral resolution 0.02 nm in the spectral range 140-226 nm; which includes two transitions. We show the  $A \leftarrow X$  transition in the spectral region 165-220 nm in Figure 1 and the  $B \leftarrow X$  transition in the spectral region 140-170 nm in Figure 2; the cross section has unit megabarn (Mb,  $10^{-18}$   $\text{cm}^2$ ). For comparison, the absorption cross sections of  $^{14}\text{NH}_3$  obtained in our previous work (Cheng *et al.* 2006) are also displayed in both figures, with offsets -8 Mb. Because the isotope shifts of  $^{15}\text{NH}_3$  are small, we assign the vibrational quantum numbers of  $^{15}\text{NH}_3$  in the figures in accordance with assignments of  $^{14}\text{NH}_3$  (Cheng *et al.* 2006). Tabulated numerical values of cross sections at intervals of 0.02 nm are available at <http://ams-bmc.nsrrc.org.tw>. Considering all possible systematic errors, we estimate experimental uncertainties of cross sections to be less than 10 % of reported values. To the best of our knowledge, the absorption cross sections of  $^{15}\text{NH}_3$  are unreported.



**Fig. 1:** Absorption cross sections (in unit Mb,  $1 \text{ Mb} = 10^{-18} \text{ cm}^2$ ) in the spectral region 165-220 nm for (a)  $^{15}\text{NH}_3$  and (b)  $^{14}\text{NH}_3$ ; the offset for  $^{14}\text{NH}_3$  is -8 Mb.



**Fig. 2:** Absorption cross sections (in unit Mb,  $1 \text{ Mb} = 10^{-18} \text{ cm}^2$ ) in the spectral region 140-170 nm for (a)  $^{15}\text{NH}_3$  and (b)  $^{14}\text{NH}_3$ ; the offset for  $^{14}\text{NH}_3$  is -8 Mb.

The absorption maxima in the system  $A \leftarrow X$  of  $^{15}\text{NH}_3$  are red-shifted from those of  $^{14}\text{NH}_3$  by  $\sim 0.02 \text{ nm}$  for  $v' = 0$ ; these shifts increase gradually to  $0.24 \text{ nm}$  for  $v' = 13$ . The widths of corresponding vibrational bands of  $^{15}\text{NH}_3$  and  $^{14}\text{NH}_3$  are similar. The maximal absorption cross sections of this system of  $^{15}\text{NH}_3$  are greater than those of  $^{14}\text{NH}_3$  by 15-23 % for the first three bands and by 5-9 % for other bands.

The absorption maxima of bands in the transition  $B \leftarrow X$  of  $^{15}\text{NH}_3$  are likewise red-shifted from those of  $^{14}\text{NH}_3$  by 0.08-0.24 nm; the widths of vibrational bands of  $^{15}\text{NH}_3$  are slightly smaller than of corresponding bands of  $^{14}\text{NH}_3$ , but the behaviour of the maxima for absorption cross sections of  $^{15}\text{NH}_3$  and  $^{14}\text{NH}_3$  in the transition  $B \leftarrow X$  differs from that in the system  $A \leftarrow X$ : those of  $^{15}\text{NH}_3$  increase by 6-40 % for bands  $v' = 0-2$  and 3-29 % for bands  $v' = 6-11$ , but decrease by 3-6 % for bands  $v' = 3-5$ .

The oscillator strength ( $f$  value) is calculated according to  $f = 1.13 \times 10^{-6} \int \sigma d\bar{\nu}$ , with  $\sigma/\text{Mb}$  and wavenumber  $\bar{\nu}/\text{cm}^{-1}$ . The value of  $f$  integrated over 165-220 nm for the system  $A \leftarrow X$  of  $^{15}\text{NH}_3$  is 0.0858. Compared to the value 0.0800 of  $^{14}\text{NH}_3$  calculated in the same range, the value of  $^{15}\text{NH}_3$  is only 7.3 % greater than that of  $^{14}\text{NH}_3$  in the transition  $A \leftarrow X$ . In our previous work (Cheng *et al.* 2006), we observed similar small increases of  $f$  values for systems  $A \leftarrow X$  among three deuterated variants of  $^{14}\text{NH}_3$ . As discussed in the previous report, although absorption maxima and bandwidths of the  $A \leftarrow X$  transition for all three deuterated  $^{14}\text{NH}_3$  species varied substantially with the number of D atoms in each species, the  $f$  values of all four isotopologues are almost identical. This condition is applicable also to the  $^{15}\text{NH}_3$  species.

For the system  $B \leftarrow X$  of  $^{15}\text{NH}_3$ , the value of  $f$  integrated over 144-165 nm is 0.0104, 16 % smaller than the value 0.0124 determined for  $^{14}\text{NH}_3$ . We observed similarly large variations of  $f$  values for systems  $B \leftarrow X$  among four deuterated variants of  $^{14}\text{NH}_3$  (Cheng *et al.* 2006). For instance, the  $f$  values of  $^{14}\text{NH}_2\text{D}$  and  $^{14}\text{ND}_3$  are smaller than that of  $^{14}\text{NH}_3$  by 23-27 %. The transition  $B \leftarrow X$  is thus affected by vibrational excitation, presumably due to vibronic coupling. According to calculations (Cheng *et al.* 2006), state A of  $\text{NH}_3$  dissociates into  $\text{NH}_2(^2B_1) + \text{H}$  with a small barrier. The shift of band origin between isotopic variants reflects the difference in zero-point energy of the excited and ground states for these species. The absorption maximum of  $v' = 0$  in system  $A \leftarrow X$  of  $^{15}\text{NH}_3$  is red-shifted from that (216.76 nm) of  $^{14}\text{NH}_3$  by only 0.02 nm, corresponding to a decreased wavenumber difference  $4 \text{ cm}^{-1}$ . In contrast, the corresponding shifts for three deuterated variants of  $\text{NH}_3$  are 0.8, 0.82, and 0.85 nm to the blue for each successive D atom, corresponding to increased wavenumber differences 171, 176 and  $185 \text{ cm}^{-1}$ . Other vibrational bands of  $^{15}\text{NH}_3$  in state A are notably all red-shifted from those of  $^{14}\text{NH}_3$ , whereas those of the three deuterated variants of  $^{14}\text{NH}_3$  are all blue-shifted. As the solar flux decreases rapidly with decreasing wavelength in this spectral region, we expect that an isotopic photo-induced fractionation has opposite effects for  $^2\text{H}$ - and  $^{15}\text{N}$ -variants.

In summary, absorption cross sections and total oscillator strengths for transitions  $A \leftarrow X$  and  $B \leftarrow X$  of  $^{15}\text{NH}_3$  over the spectral range 140-226 nm have been determined for the first time. Wavelengths of absorption bands in the  $A \leftarrow X$  system of  $^{15}\text{NH}_3$  are red-shifted from those of  $^{14}\text{NH}_3$ , whereas those of three deuterated variants of  $\text{NH}_3$  are blue-shifted. The oscillator strengths of  $^{15}\text{NH}_3$  for transition  $A \leftarrow X$  in the range 165-220 nm and for transition  $B \leftarrow X$  in the range 144-165 nm are evaluated to be 0.0858 and 0.0124, 7.3 % greater and 16 % smaller than that of  $^{14}\text{NH}_3$  respectively. The results of these laboratory measurements of cross sections are applicable to the photochemistry of Jupiter's atmosphere (Liang *et al.* 2007).

### Experimental Station

Dual-beam absorption gas-cell end station

### Publications

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