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Rotationally resolved fluorescence excitation spectrum produced through photoexcitation of the coupled $c'_4(0)$ and $b'(1)$ states of N_2

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ABSTRACT

Employing a high-resolution spectrometer in a synchrotron radiation facility we have demonstrated the feasibility of studying rotationally resolved fluorescence excitation spectra (FES) in the extreme ultraviolet region. Specifically, we have obtained FES spectrum of the (1,0) band of the $b'\ ^1\Sigma_u^+$–$X\ ^1\Sigma_g^+$ transition using a resolution of 0.0024 nm and the resonance FES of the (0,0) band of the $c'_4\ ^1\Sigma_u^+$–$X\ ^1\Sigma_g^+$ transition using a resolution of 0.0048 nm produced through photoexcitation of N_2 in the spectral region between 95.75 and 96.00 nm. Strong local rotational perturbation between the $c'_4(0)$ and the $b'(1)$ states occurring at excited rotational levels $J' = 10$ and 11 has been confirmed in the FES of the $b'\ ^1\Sigma_u^+$–$X\ ^1\Sigma_g^+$ transition, in excellent agreement with early absorption spectroscopic study. From the observed relative fluorescence intensities we conclude that the production of the intense emission of the (1,0) b'–X transition is at the expense of the (0,0) c'_4–X emission of N_2. The $c'_4(0)$ state apparently prefers to radiate back to the ground electronic state while the $b'(1)$ state appears to favor branching to the $a\ ^1\Pi_g$ state and the subsequent $a\ ^1\Pi_g \rightarrow X\ ^1\Sigma_g^+$ transition.

1. Introduction

It is well known that strong couplings exist among the Rydberg and valence states in N_2 [1–9]. In addition to the global interactions there are local rotational perturbations [2,4,7–11]. Both experimental investigations [4,12–15] and theoretical and model calculations [2,3,16–20] have shown that many band oscillator strengths of these transitions strongly depend on the rotational quantum number J. Furthermore, the distributions of the P-, Q-, and R-branch oscillator strengths for many bands significantly deviate from the well-known Hönl–London formulae [12–14,16,18]. Therefore, neither the excitation rates nor spontaneous emission rates can be reliably estimated from calculations based on rovibronic band oscillator strength partitioned by the Hönl–London formulae. Another complication of the strong coupling is the rotational J-dependent predissociation rates (yields), as demonstrated in many experimental lifetime and bandwidth measurements [6,19,21–30], fluorescence excitation spectra [31–34], and theoretical studies [2,3,16]. Therefore, high resolution absorption and fluorescence studies are required to determine the emission rates (fluorescence production cross-sections) and predissociation yields for each J-level of the relevant transitions, and are required for accurate quantitative analysis and evaluation of the nitrogen airglow in the N_2-rich planetary atmospheres. In this work we investigate the strongly coupled $c'_4(0)$ and $b'(1)$ states of N_2 using the fluorescence spectrometry technique.

The bandheads of the $c'_4\ ^1\Sigma_u^+$–$X\ ^1\Sigma_g^+$ (0,0) band and the $b'\ ^1\Sigma_u^+$–$X\ ^1\Sigma_g^+$ (1,0) band are only separated by 0.0505 nm [7–9]. The c'_4–$X(0, 0)$ absorption transition is known to show predissociation at rotational levels $J \geq 5$ [7–9,25]. Yoshino and Tanaka [8] have shown that the local rotational perturbations take place at excited rotational levels $J' = 10$ and 11 for the mutually perturbed $c'_4(0)$ and $b'(1)$ states. Thus, the perturbed R(9), R(10), P(11), and P(12) rotational lines were observed and identified in the high resolution absorption spectrum of the (0,0) band of the $c'_4\ ^1\Sigma_u^+$–$X\ ^1\Sigma_g^+$ transition in N_2. In other words, the decay channels resulting from absorption from the rotational levels $J''(=J) = 9$, 10, 11, and 12 of the $v'' = 0$ level of the ground electronic state will be significantly affected [8,32]. This has very important implication in modeling the c'_4–$X(0, 0)$ emission rates in the N_2 airglow because the absorption band oscillator strength of the c'_4–$X(0, 0)$ is much larger than that of the b'–X (1,0) transition [14]. The band f-values (extrapolated to $J = 0$) are 0.138 and 0.00045 for the c'_4–$X(0, 0)$ and the b'–X (1,0) band, respectively, resulting in a ratio of about 300:1. Through perturbation the $b'(1)$ state borrows intensity from the $c'_4(0)$ state, a loss mechanism for absorption to the $c'_4(0)$ state, and hence the

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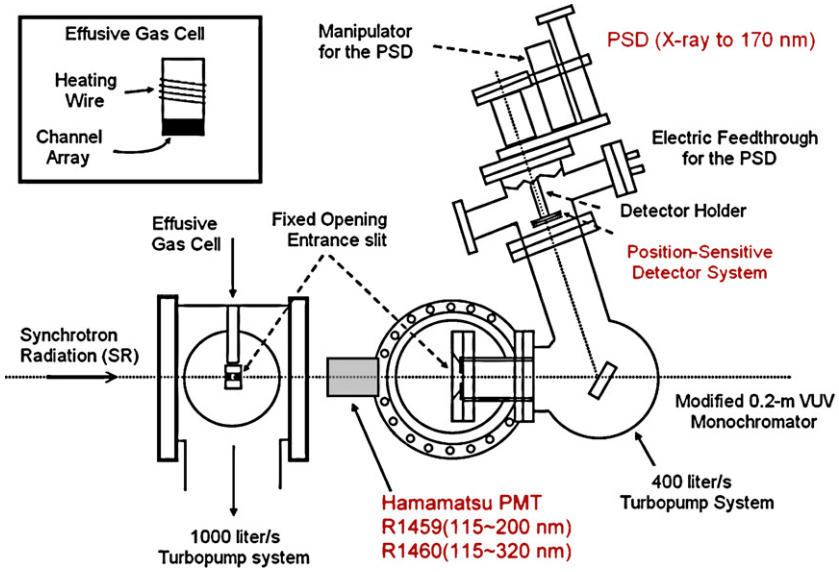

Fig. 1. A schematic diagram of the fluorescence apparatus. The side-view of the interaction region is displayed to the left. The inset shows the side view of a diffusive high temperature cell.

subsequent loss of c'_4–$X(0, v'')$ emissions. We have observed these perturbed rotational levels in a recent preliminary fluorescence experiment on N_2 at room temperature [32]. The present paper presents the detailed description of the study.

Prior to the present work, using EUV + UV two-photon ionization laser spectroscopy analysis, Ubachs et al. [25] have reported a strong J-dependent lifetime of the c'_4–$X(0, 0)$ band of $^{14}N_2$, namely, from 740 ± 50 picosecond (ps) for $J = 0$–5 to 495 ± 50 ps for $J = 13$–16. Utilizing a synchrotron radiation source with a spectral resolution of 0.1 nm. Oertel et al. [31] have measured a lifetime of 1130 ± 170 ps for the combined $c'_4(0)$ and $b'(1)$ states, which are not resolved in their experiment. Hesser and Dressler [35] reported a lifetime of 900 ± 200 ps from a linewidth analysis of the c'_4–$X(0, 0)$ absorption transition. These results obtained by the various experimental techniques point to the fact that strong and complex predissociation effects in N_2 are J-dependent. Using an advanced coupled-channel Schrodinger-equation (CSE) model Lewis and his colleagues [2,3,16,26] have considered interactions of the $^1\Sigma$ state with $^1\Pi$ and $^3\Pi$ states, including molecular motion, and have successfully explained the predissociation mechanisms and quantitative predissociation yields. Liu et al. [17–20] have made use of the existing data to model oscillator strengths and predissociation rates for several important transitions of N_2. They have recently applied the modeled values to calculate the column emission rates for the c'_4–$X(0, v'')$ and b'–$X(1, v'')$ transitions [17,20], which can be compared with dayglow data from Far Ultraviolet Spectroscopic Explorer (FUSE) observations [36–38].

We have recently obtained a fluorescence excitation spectrum (FES) of N_2 in the 80–100 nm region with a resolution of 0.06 nm at room temperature. The prominent emission features have been identified to correlate with the b, b', c_n (with $n = 4$–8), $c_{n'}$ (with $n = 5$–9), and $c'_4(v')$ (with $v' = 0$–8) states of N_2 [30]. The relative fluorescence production yields for the observed fluorescence features have also been reported. In the present work we focus on studying FES of the strongly coupled c'_4–$X(0, 0) + b'$–$X(1, 0)$ transitions of N_2 with a resolution of 0.0024 mm, which is twenty-five times better than before. As a result, we are able to achieve rotationally resolved FES. The preliminary results of this work have previously been presented [32]. The goal of our high-resolution fluorescence research is to provide the constraints needed in theoretical and model calculations and to provide accurate temperature-dependent, high-resolution cross-section data that are required for the interpretation and modeling of atomic N and molecular N_2 airglow emissions in the N_2-rich planetary atmospheres. The present work reports our effort toward achieving this goal.

2. Experimental setup and experimental procedures

The experimental apparatus and the experimental procedures used in the present work have recently been described [32–34]. A schematic diagram of the apparatus is shown in Fig. 1. Briefly, the experimental setup allows us to obtain (1) fluorescence spectra (FS) using a 0.2-m VUV monochromator and a Position-Sensitive-Detector (PSD) system and (2) the fluorescence excitation spectrum (FES) by using a PMT or the combination of a monochromator and the PSD system. A solar blind photomultiplier (Hamamatsu R1459 PMT with a CsI coated photocathode) was used to monitor VUV fluorescence in the spectral region between 115 and 200 nm.

The high-resolution, high-brightness U9 Undulator Beamline available at the 1.5 GeV electron storage ring of the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, was employed in the present work. Its typical brilliance is 6×10^{15} photons/s mrad^2/0.1%BW/300 mA. The high order of the high energy synchrotron light has been filtered out by a rare gas cell installed in the Beamline [39]. It may be worthwhile mentioning that the NSRRC facility has been operated in the TOP-UP Operation, in which the electron beam current in the storage ring is maintained at a constant level, e.g., 300 mA, by injecting a few electrons into the ring in a two-second period every minute. The TOP-UP operation thus gives a constant current in the storage ring to better than 0.5% fluctuation, and hence is able to provide a constant photon radiance to better than 99% stability. Thus the photon intensity correction as a function of varying beam current becomes a relatively easy, simple, and straightforward procedure.

The U9 Undulator Beamline is equipped with a 6-m CGM (cylindrical grating monochromator) high-resolution spectrometer, which has a resolving power of about 10^5 at 16 eV using a 1600 l/mm grating. In the present work we used an entrance/exit slit width = 10 μm/20 μm to provide a resolving power of 4×10^4, which corresponds to a spectral width (fwhm) of 0.0024 nm in the 98.5 nm region. We found that it is quite sufficient to obtain excellent FES spectra, see Fig. 2 using 60 s counting time and a scan rate of 0.1 meV (0.00079 nm) per minute. However, using the combination of the 0.2-m monochromator and the PSD system as a fluorescence