Doppler-free two-photon absorption spectroscopy of vibronic excited states of naphthalene with reference to an optical frequency comb

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1. INTRODUCTION

In the excited states of polyatomic molecules, there are some interesting phenomena such as, internal conversion (IC), intersystem crossing (ISC), and intramolecular vibrational energy redistribution (IVR). In the first electronic excited state of naphthalene, it was reported that IVR become dominant for the excess energy (E_x) larger than about 2000 cm^{-1}.

In this study, we observed Doppler-free two-photon absorption (DFTPA) spectra of three transitions, A^1B_{1u} ($v_4 = 1$, $E_x = 1560$ cm^{-1}) <- X^1A_g ($v = 0$), A^1B_{1u} ($v_4 = 1$, $v_8 = 1$, $E_x = 2260$ cm^{-1}) <- X^1A_g ($v = 0$) , and A^1B_{1u} ($v_4 = 1$, $v_7 = 1$, $E_x = 2545$ cm^{-1}) <- X^1A_g ($v = 0$), in the following, we call "orange band," "yellow band," and "lemon band," respectively. Then, we analyze the linewidth of rovibronic lines in each band.

2. EXPERIMENT

Figure 1 shows our experimental setup. This system consists of DFTPA system for naphthalene and frequency measurement system [1]. The light source for DFTPA system is a single mode CW dye laser. Its output power is about 1.8W, and the linewidth is about 130 kHz. Most part of the dye laser output is used to observe DFTPA spectra of naphthalene. The resonance frequency of the Fabry-Perot interferometer is locked to the dye laser frequency by Pound-Drever-Hall method. The frequency of the dye laser is scanned and the fluorescence intensity is observed by the photon counting system.

We use a GPS-disciplined Ti:Sapphire optical frequency comb as a frequency measure. The spectral range of the Ti:Sapphire comb is broadened by a photonic crystal fiber. A part of the dye laser output is split to measure its frequency. An acousto-optic frequency shifter in double pass configuration shifts the dye laser frequency to realize wide range continuous frequency measurements [2].

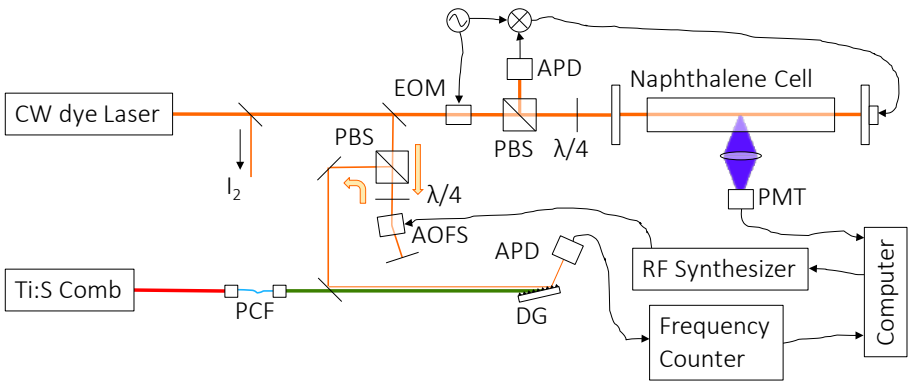

Figure 1. Experimental setup. PCF, photonic crystal fiber; PBS, polarizing beam splitter; EOM, electro-optic modulator; AOFS, acousto-optic frequency shifter; APD, avalanche photodiode; DG, diffraction grating; PMT, photomultiplier tube.

3. RESULTS AND DISCUSSION

The observed spectra are shown in the figure 2. They are a part of spectra of the lemon band, the yellow band, and the orange band from top to bottom. For the orange and yellow bands, linewidths are about 2.5 MHz, and they show small dependences on the rotational quantum numbers. On the other hand, the linewidths in the lemon band spectra become broad, and depend on the rotational quantum numbers. This means that the IVR become dominant in the upper state of the lemon band transition.

[1] A. Nishiyama, K. Nakashima, A. Matsuba, and M. Misono, J. Mol. Spectrosc., 318, 40 (2015).
[2] A. Nishiyama, A. Matsuba, and M. Misono, Opt. Lett., 39, 4923 (2014).

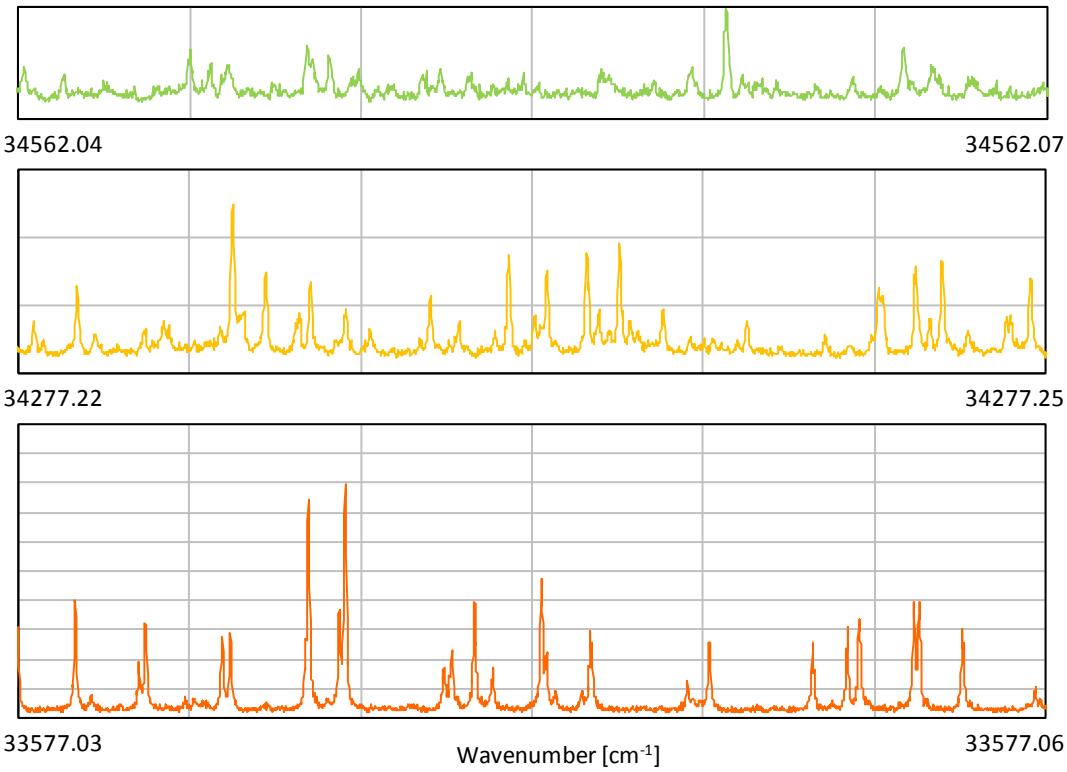

Figure 2. Observed spectra.