



# Doppler-free two-photon absorption spectroscopy of rovibronic transition of naphthalene calibrated with an optical frequency comb



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## ABSTRACT

We performed Doppler-free two-photon absorption spectroscopy of naphthalene using an optical frequency comb as a frequency reference. Rotationally resolved rovibronic spectra were observed, and absolute frequencies of the rovibronic transitions were determined with an uncertainty of several tens of kHz. The resolution and precision of our system are finer than the natural width of naphthalene. We assigned 1466 lines of the  $Q(K_a)Q(J)$  transition and calculated molecular constants. We attribute systematic spectral line shifts to the Coriolis interaction, and discuss the origin of the spectral linewidths.

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## 1. Introduction

The dynamics of electronic excited states in polyatomic molecules constitutes one of the most significant topics in molecular science. The dynamics, as a consequence of the interactions between energy levels in the electronic excited states, appears in the form of minute effects such as frequency shifts, line broadening, intensity anomalies, and Zeeman effects in high-resolution spectra. To observe such minute effects, high-resolution spectroscopy has become a powerful tool. Highly resolved spectra of polyatomic molecules such as benzene [1], naphthalene [2,3], and *trans*-glyoxal [4] have been studied by Doppler-free spectroscopy [5], and the dynamics of excited states has been subsequently revealed.

Studies on the dynamical processes of the simple aromatic molecules are key to understanding the chemical reactions of organic molecules, and naphthalene functions as one of the prototypical aromatic molecules. Naphthalene exhibits radiationless relaxation processes such as internal conversion, intersystem crossing, and intra-molecular vibrational energy redistribution, which have been studied according to their fluorescence quantum yield and lifetime [6–8]. In order to investigate these properties, Doppler-free two-photon absorption (DFTPA) spectroscopy of naphthalene was first performed by Chen et al. [9], and higher-resolution DFTPA spectroscopy has been reported by Okubo et al.

[2]. Although Okubo et al. observed almost rotationally resolved DFTPA spectra, the resolution was limited to 5 MHz as a result of the laser linewidth, and the uncertainty of the frequency measurement was limited to 6 MHz because of the etalon marker used for laser frequency calibration. These values of resolution and uncertainty are not sufficient for studying detailed dynamics in excited states because they are several times larger than the natural width of naphthalene: about 1 MHz [7,8]. To study minute effects that reflect the dynamics in excited states, spectroscopy with higher resolution and smaller uncertainty must be achieved.

Precision frequency measurement systems for molecular spectroscopy have been studied [1–4,10–17], and the present state of molecular spectroscopy suggests that wide-frequency applicability is as crucial as precision. In fact, the fringe pattern of an optical resonator has been used in order to achieve a healthy balance between these two factors [1–4,10,11]. However, the attainable precision is several MHz even if the optical resonator is stabilized. As the definitive solution for this problem, optical frequency combs provide precise frequency rulers in wide frequency regions; several spectroscopic systems harnessing fiber optical frequency combs as frequency references in the infrared region have been recently developed [12–15]. More specifically, we have developed two types of spectroscopic systems employing Ti:Sapphire optical frequency combs as frequency references in visible region [16,17]. Each of our systems utilizes a single-mode continuous-wave (CW) dye laser, which allows for a continuous frequency scan across a wide frequency range, and has a large output power that is suitable for nonlinear spectroscopy. One of our systems [17]

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realizes not only precision frequency measurement but also analysis of the frequency characteristics of the scanning dye laser.

In the present study, we develop this frequency measurement scheme [17] and adopt it to the DFTPA spectroscopy of naphthalene in the ultraviolet region. This represents the first application of an optical frequency comb for Doppler-free comb-referenced spectroscopy to study the electronic transitions of a polyatomic molecule in ultraviolet region. The resolution and the precision of our system are finer than the natural width of naphthalene. We observe rovibronic transitions in the  $S_1^1B_{1u}$  ( $v_4 = 1 : b_{1u}$  (C–C stretch))  $\leftarrow S_0^1A_g$  ( $v = 0$ ) band, and determine the assignment for 1466 lines. We discuss interactions in the excited state, and analyze the origins of the observed spectral linewidths.

## 2. Experiment

Our experimental setup is illustrated in Fig. 1. The system is composed of a DFTPA spectroscopic system of naphthalene and a frequency measurement system with an optical frequency comb.

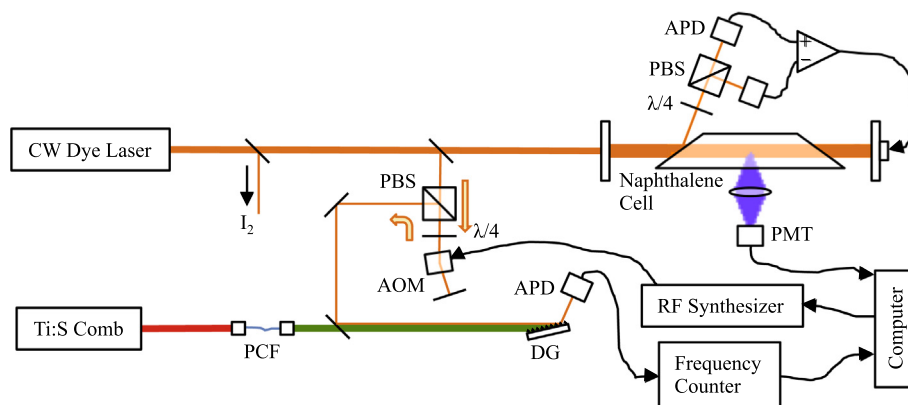
A CW dye laser (Sirah, Matisse DX) was used as a light source for the spectroscopy. We used rhodamine 6G dye to achieve oscillation around 596 nm. The dye laser provided single-mode radiation with a linewidth of 130 kHz in 5 ms. Its output frequency was continuously scanned during measurements by the built-in controller. No external controls were required to scan the dye laser frequency, meaning that the system was stable and easily operated across a wide frequency range. The maximum output power was 2.0 W at about 596 nm.

The experimental scheme for DFTPA spectroscopy with a linearly polarized counter-propagating light beam used in the present experiment was reported in Refs. [1,2,4]. A Fabry–Perot optical resonator was composed of two concave mirrors, and a naphthalene cell with Brewster windows was located in the resonator. The radii of curvature were 90 mm, and the mirrors were separated by 165 mm. The reflectances of the concave mirrors were 97%, and the finesse of the resonator was 94. A linearly polarized dye laser output of 480 mW was input to the resonator. The mirror separation of the resonator was controlled to maintain a constant resonance according to the Hänsch–Couillaud scheme [18]. The cell was evacuated and then filled with naphthalene vapor at 20 Pa at room temperature. The fluorescence from naphthalene was collected by a concave mirror and lenses, and was counted with a photon counting system, which was composed of a photomultiplier tube (Hamamatsu, R585), a photon counting unit (Hama-

matsu, C3866), and a frequency counter (Agilent, 53132A). At the same time, the saturated absorption spectra of molecular iodine were recorded. The observed Doppler-free iodine spectra were used to confirm the absolute optical frequency with reference to the Doppler-free atlas [10].

Our frequency calibration setup was based on that of Ref. [17]. The optical frequency comb was a mode-locked Ti:Sapphire laser (Venteon, Pulse One) whose average power was 400 mW. The comb had an octave-spanning spectrum (600–1200 nm). Therefore, a standard  $f$ – $2f$  interferometer was used to detect the carrier-envelope offset frequency ( $f_{\text{CEO}}$ ). The repetition rate ( $f_{\text{rep}}$ ) was about 162.5 MHz. Both  $f_{\text{rep}}$  and  $f_{\text{CEO}}$  were phase-locked to a global positioning system (GPS)-disciplined clock resulting in an relative uncertainty of  $10^{-11}$  in 1 s; these frequencies were monitored by a universal frequency counter (Agilent, 53230A). A photonic crystal fiber (PCF) broadened the short wavelength edge of the comb spectrum to 500 nm to obtain a large spectral intensity at the dye laser's wavelength. The frequency of the scanning dye laser was then shifted by an acousto-optic modulator (AOM, Brimrose, TEF-540-200-633) in a double-pass configuration. Because of the double-pass configuration, the shift frequency was twice the drive frequency from the radio frequency (RF) synthesizer (Agilent, N5181A). The beat frequency between the AOM output of the dye laser light and the PCF output of the comb light was measured by a universal counter (Agilent, 53132A). The gate times of the beat frequency measurement were synchronized with those of the photon counting.

Fig. 2 schematically illustrates changes of the dye laser frequency  $f_{\text{dye}}$ , the shift frequency  $f_{\text{AOM}}$  at the double-pass AOM, the shifted frequency of the dye laser  $f_{\text{dye}} + f_{\text{AOM}}$ , and the beat frequency  $f_{\text{beat}}$ . Suppose  $f_{\text{dye}}$ , which has small fluctuations, is scanned upward as shown in Fig. 2(a). The AOM shift frequency  $f_{\text{AOM}}$  decreases at the opposite rate with  $f_{\text{dye}}$  as shown in Fig. 2(b), so that the shifted frequency  $f_{\text{dye}} + f_{\text{AOM}}$  is held constant with the effect of the fluctuations subtracted as shown in Fig. 2(c). Because the frequency shift  $f_{\text{AOM}}$  of the AOM used in our experiment is limited between 880 and 1280 MHz,  $f_{\text{AOM}}$  has to be reset before it reaches the limitation. If  $f_{\text{AOM}}$  is reset at every  $f_{\text{rep}}$ ,  $f_{\text{dye}} + f_{\text{AOM}}$  increases stepwise with a step of  $f_{\text{rep}}$  as shown in Fig. 2(c). Thus,  $f_{\text{beat}}$  is kept almost constant as shown in Fig. 2(d). We can understand from the above discussion that the fluctuations of  $f_{\text{beat}}$  contain information on the fluctuation of  $f_{\text{dye}}$ . In our experiment, we tuned  $f_{\text{beat}}$  to  $f_{\text{rep}}/4$  (i.e.,  $\sim 40.6$  MHz) for the purpose of convenience.



**Fig. 1.** Schematic diagram of our experimental setup consisting of the frequency calibration system with an optical frequency comb and a Doppler-free spectroscopic system. The frequency calibration system consists of the following components: an acousto-optic modulator (AOM), a photonic crystal fiber (PCF), a diffraction grating (DG), an avalanche photodiode (APD), and a polarizing beam splitter (PBS). We use a Doppler-free two-photon absorption (DFTPA) spectroscopic system for linearly polarized light. Fluorescence from naphthalene is detected by a photomultiplier tube (PMT).

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