Spectroscopy of Single Molecules

Measuring narrow spectral features over wide frequency ranges

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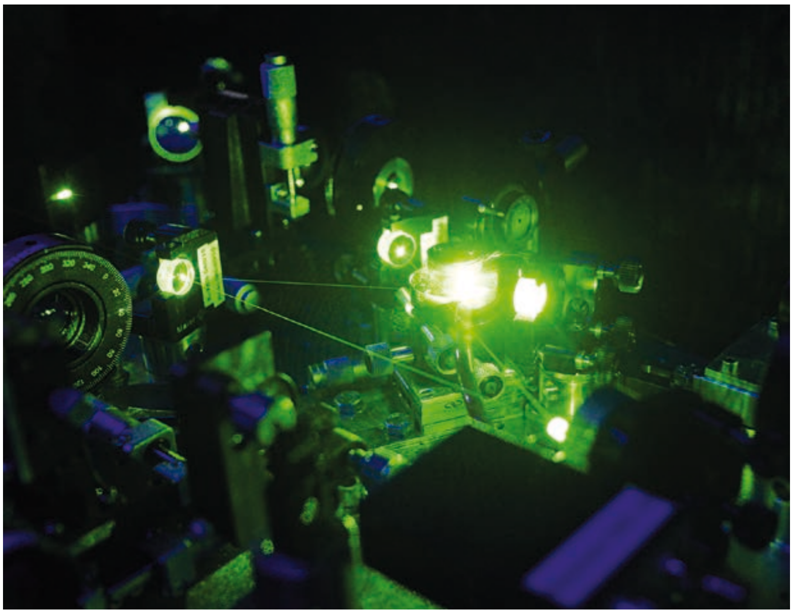
The fluorescence excitation spectra of single organic molecules in a solid-state crystal are measured at cryogenic temperatures. As a tunable laser light source, the optical parametric oscillator C-WAVE is employed, since it exhibits promising features as a laser light source for spectroscopy applications, like a broad tuning range from 450 to 650 nm, a narrow line-width < 1 MHz, and mode-hop-free tuning over > 25 GHz. C-WAVE allows for high-resolution spectroscopy.



Tunable laser light sources exhibit promising features for spectroscopy applications, like a broad tuning range from 450 to 650 nm, a narrow linewidth < 1 MHz, and mode-hop-free tuning over more than 25 GHz.

Investigations of molecular processes and their characteristics play an important role in many scientific disciplines, like medicine, biology, chemistry, and physics. Fluorescence spectroscopy of single molecules gives fundamental insights into their properties and the influence of their surroundings [1, 2]. However, studying single molecules in a host material is a challenging task with high demands on the detectors and on the laser light sources [3]. This report discusses the applicability of a new tunable continuous-wave (cw) laser light source for various spectroscopy methods.

The experimental setup is illustrated in **Fig. 1**. A frequency-tunable laser beam is focused onto a sample containing dibenzanthanthrene (DBATT) molecules hosted in a naphthalene crystal. The laser beam is tuned to resonances of the DBATT molecules, leading to their excitation and subsequent fluorescence. The fluorescence light is filtered and measured with a single photon detector, SPCM-AQR from Perkin Elmer. A High-Finesse WS/6-200 wavemeter monitors the frequency of the excitation laser. A more detailed description of the experimental methods is given, e.g., in [3].

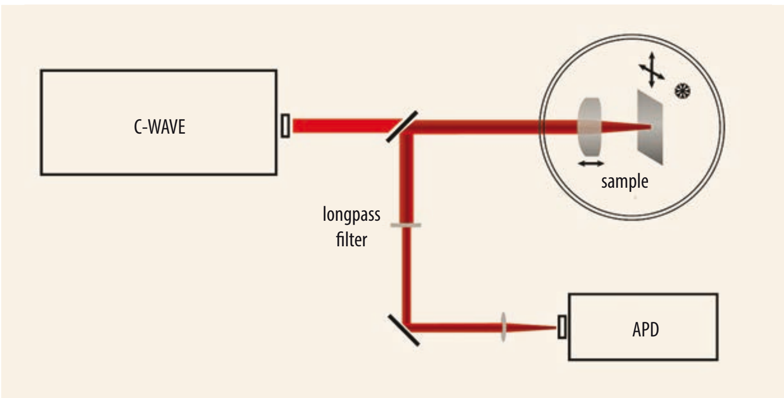


Fig. 1 Experimental setup: confocal microscope including a cryostat. A fiber guides the laser light to the experimental setup where it is cleaned up with filters and focused onto the sample. The red-shifted fluorescence light is collected, filtered, and analyzed by means of an avalanche photodiode (APD).

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Suitable excitation lasers

Single molecules in a solid-state crystal can be regarded as nearly ideal two-level systems with natural linewidths in the range of 10 to 50 MHz. Due to imperfections in the crystal, the transitions of individual molecules are inhomogeneously distributed over more than 1 THz. With a narrow-band laser, tuned to an individual transition, single molecules can be isolated from the ensemble. Therefore, the laser is a crucial component for the excitation of single molecules: It requires a linewidth below the natural linewidth of the molecules and a mode-hop-free tunability over a broad spectral range to address many molecules. Furthermore, the flexibility in choosing the center wavelength for different kinds of molecule-host combinations, an output power well above 200 mW, and low intensity noise are other important parameters.

Commonly, dye lasers, Ti:Sa lasers, or tunable diode lasers are used for such experiments. Ti:Sa lasers are restricted to the wavelength ranges of 700 to 1000 nm or 350 to 500 nm when frequency-doubled. Dye lasers require a change of the dye or even of the used pump laser when switching between wavelength ranges. Diode lasers are typically restricted to small tuning ranges and low output powers in the visible wavelength range. Optical parametric oscillators (OPO) offer an attractive alternative: The wavelength coverage of OPOs can be designed according to the experimental requirements. OPOs are solid-state systems which do not rely on consumables as dyes, and they deliver relatively high output powers.

For this report, the commercially available cw-OPO C-WAVE is employed. This OPO with SHG unit covers the wavelength ranges of 450 to 650 nm and 900 to 1300 nm. The output power is in the range of 500 mW and the linewidth is below 1 MHz. The output frequency can be swept mode-hop free over more than 25 GHz. Changes of the center frequency of several GHz as well as large variations of the wavelength are fully computer controlled. The good beam profile allows high coupling efficiencies into optical fibers and, therefore, a simple integration into existing setups.

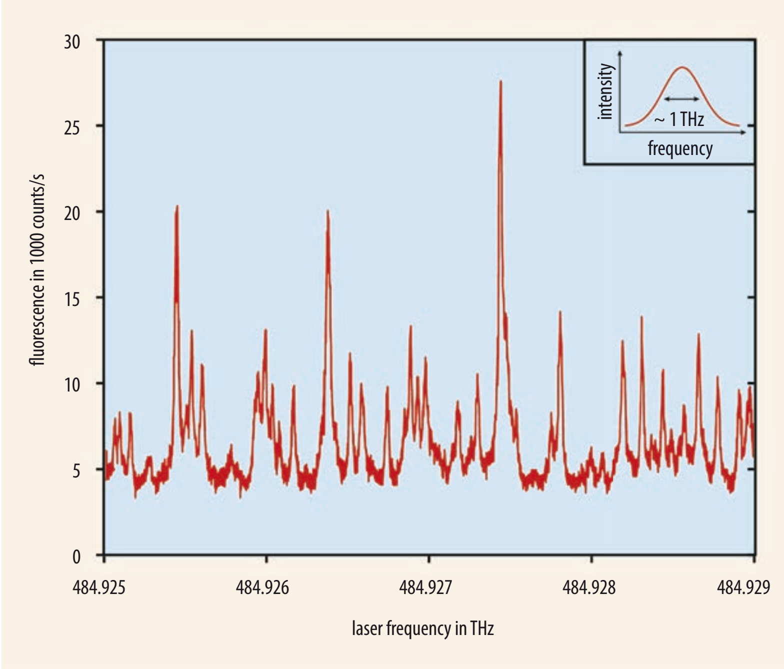

Fig. 2 Fluorescence intensity of DBATT molecules hosted in a naphthalene crystal versus excitation frequency. Inset: Schematics of the inhomogeneous broadening of DBATT molecules with a linewidth of 1 THz.

Results

Fluorescence spectra of DBATT molecules have been measured at a center wavelength of 618 nm and over a range of 1 THz by stitching several mode-hop-free frequency sweeps. **Fig. 2** shows a zoom into one of the mode-hop-free scans. The molecules' redshifted fluorescence signal is measured with the APD while the laser frequency is scanned. The measurement shows several narrow spectral features corresponding to individual DBATT molecules [4]. With C-WAVE, it is also possible to lock the laser frequency with wavemeter-precision to one single molecule resonance in order to study its photo-physics and photon dynamics.

The presented setup enables the measurement of fluorescence excitation spectra of single molecules in transparent host materials. Both laser light sources, Ti:Sa lasers and C-WAVE, are well suited for measuring narrow spectral features over wide frequency ranges. A combination of these laser sources allows a nearly complete wavelength coverage from 450 to 1300 nm with fully automatic wavelength control and no need to change laser media or perform realignments. This makes the presented setup a user friendly, flexible, and sensitive spectrometer for characterizing single molecules, color centers, and semiconductor quantum dots.

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[2] *A. Maser* et al., Nature Photon. **10**, 450 (2016)
[3] G. *Wrigge* et al., Nature Phys. **4**, 60 (2008)
[4] *F. B. Zhelezko* et al., Appl. Spectrosc. **66**, 334 (1999)