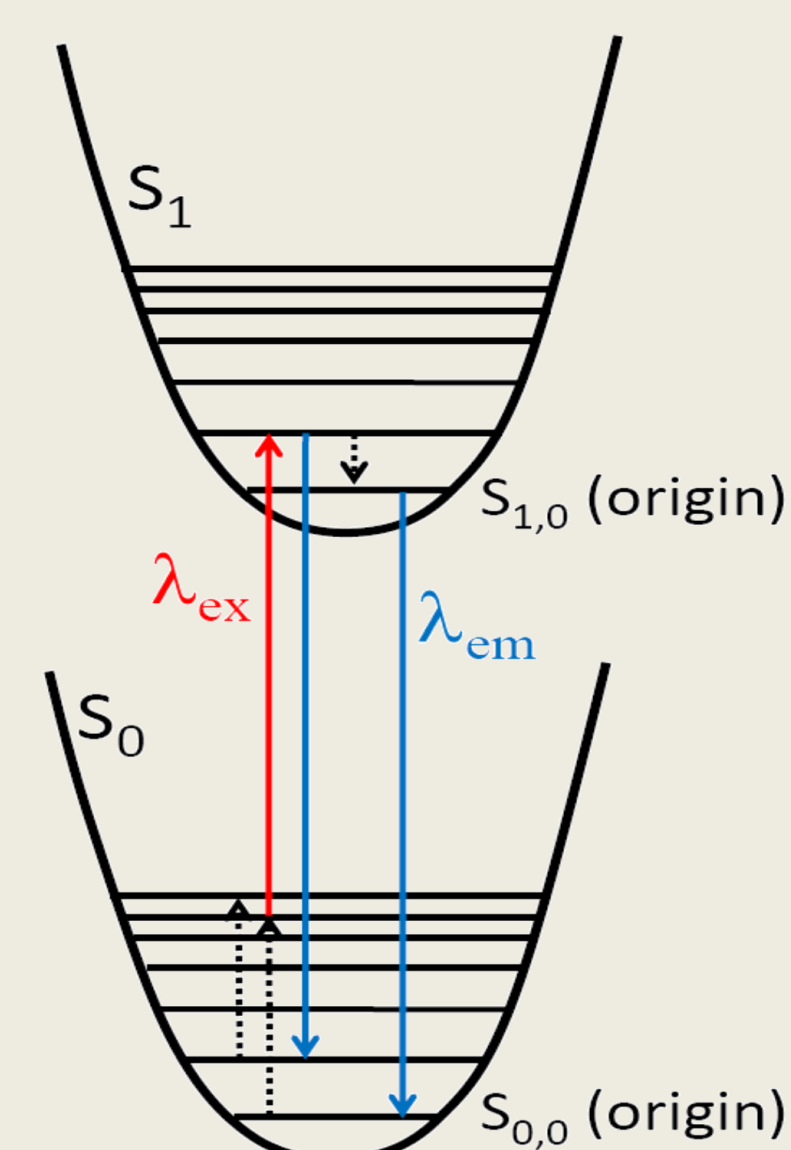


## Introduction

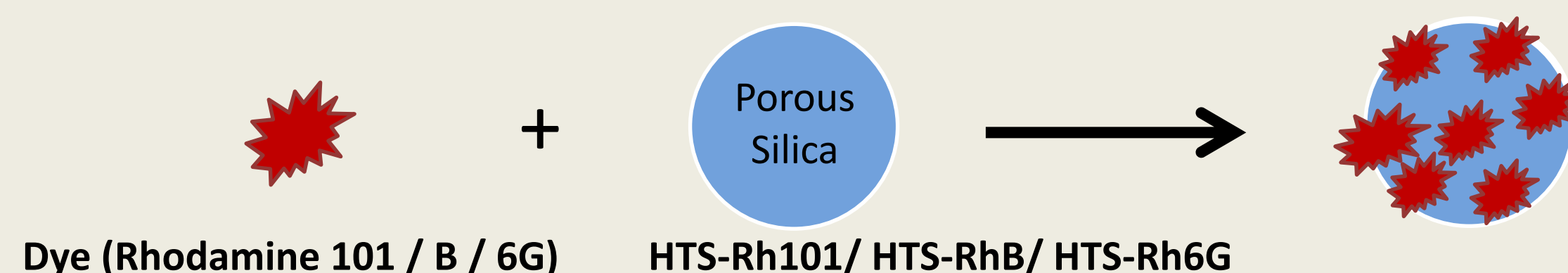


Anti-Stokes fluorescence in organic compounds (*e.g.* laser dyes) in the condensed phase can potentially be observed, if the energy of the excitation photons is smaller than the gap between the origins of the ground state ( $S_0$ ) and first excited electronic state ( $S_1$ ) of the respective dye (see Figure on the left). In this case only molecules can be excited that are "hot", i.e. vibrationally excited. The excited  $S_1$  states contain mainly electronic but only very little vibrational energy. Therefore Franck-Condon-uninhibited transitions to the ground state will mainly occur at wavelengths that are shorter than the excitation wavelength and hence give rise to so-called anti-Stokes fluorescence (blue-shifted). The energy for this (one-photon) frequency "upconversion" is delivered by the molecular environment of the organic dye. Therefore anti-Stokes fluorescence strongly depends on the temperature of the host matrix and on the (phonon) coupling between the dye and the host material. If the emission quantum yield is very large (>99%) and reabsorption of light can be maximized, anti-Stokes emission can be used to cool systems in the condensed phase. The cooling efficiency,  $\eta_c$ , is given by [1]:

$$\eta_c = \eta_{ext}\eta_{abs} \frac{\nu_{em}}{\nu_{ex}} - 1$$

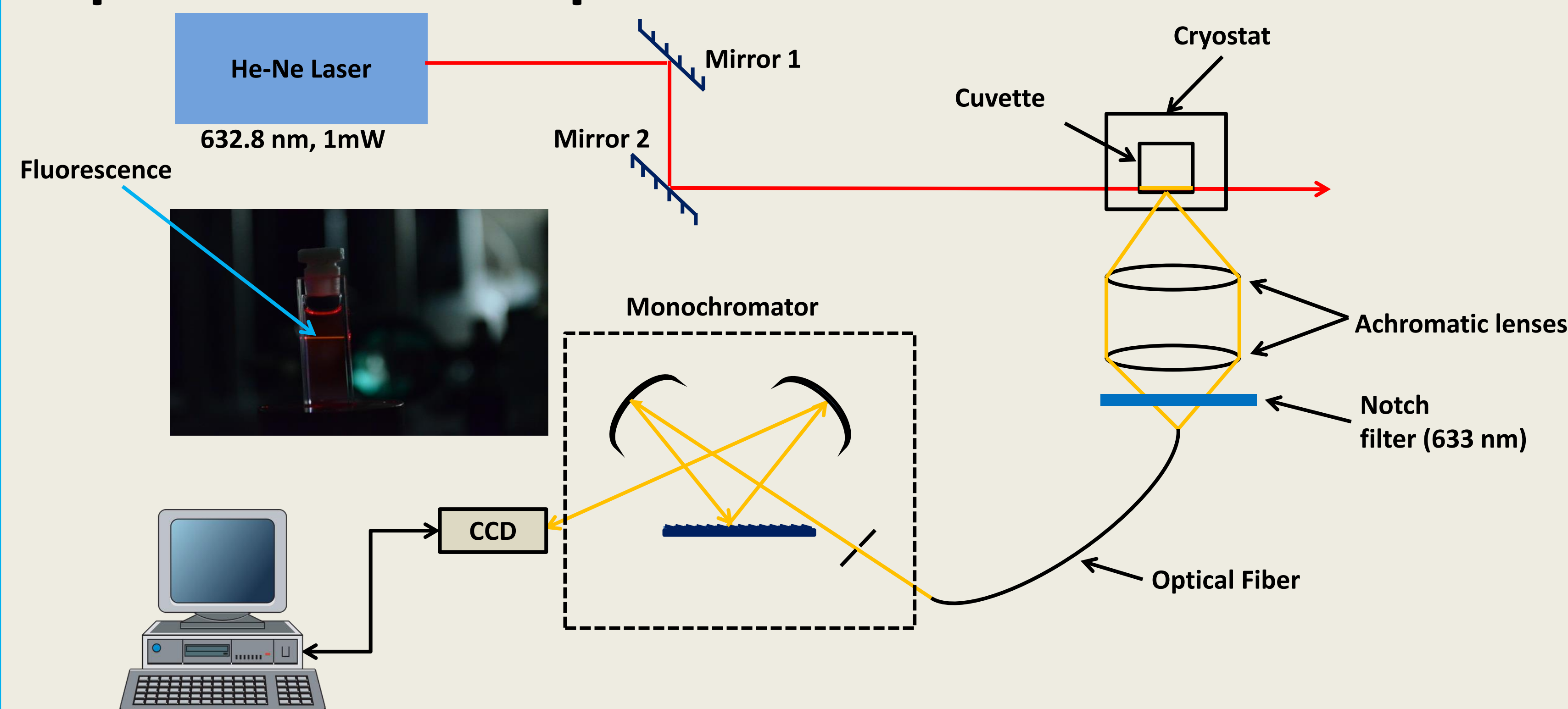
$\eta_{ext}$  : external quantum efficiency  
 $\eta_{abs}$  : absorption efficiency  
 $\nu_{em}$  : mean fluorescence frequency  
 $\nu_{ex}$  : mean fluorescence frequency

**Scope of study:** Anti-Stokes fluorescence from Rhodamine dye molecules attached to porous hydro-thermally prepared silica nano particles (HTS):



Suspensions of HTS-Rh101, HTS-Rh B and HTS-Rh6G in ethanol were prepared and excited using a He-Ne laser at 632.8 nm. (a) The absorption spectra (recorded using lambda 1050 UV-Vis spectrometer) and anti-Stokes spectra for all three samples were recorded over 150 nm around the excitation wavelength. (b) Variation of the spectral intensity at 590 nm along with temperature proved to be a good way of calibrating the local temperature for HTS Rh 101. (c) The emission from HTS-Rh101 at two different excitation wavelengths (532 nm and 632.8 nm) were compared.

## Experimental Setup

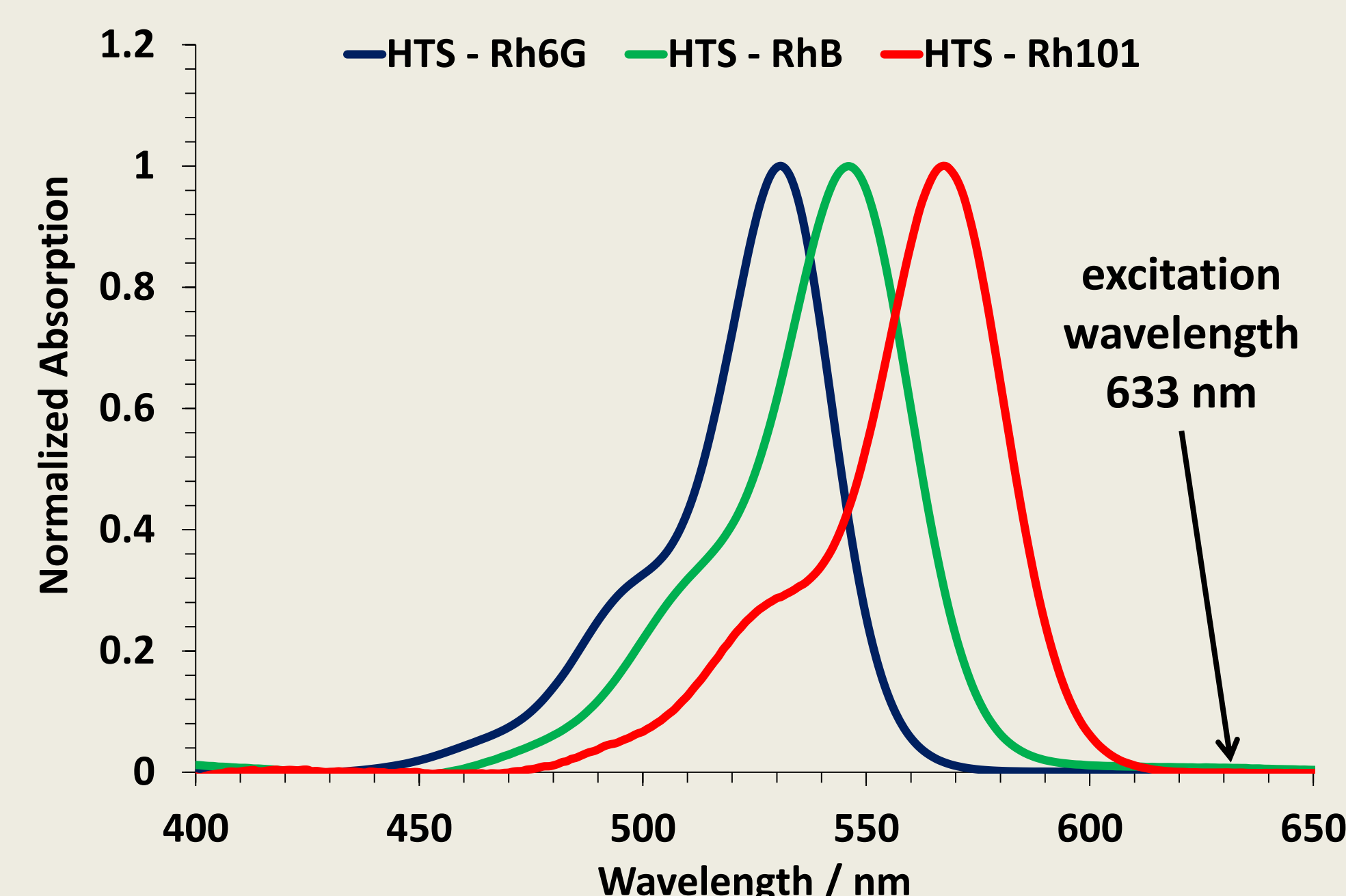


## Reference

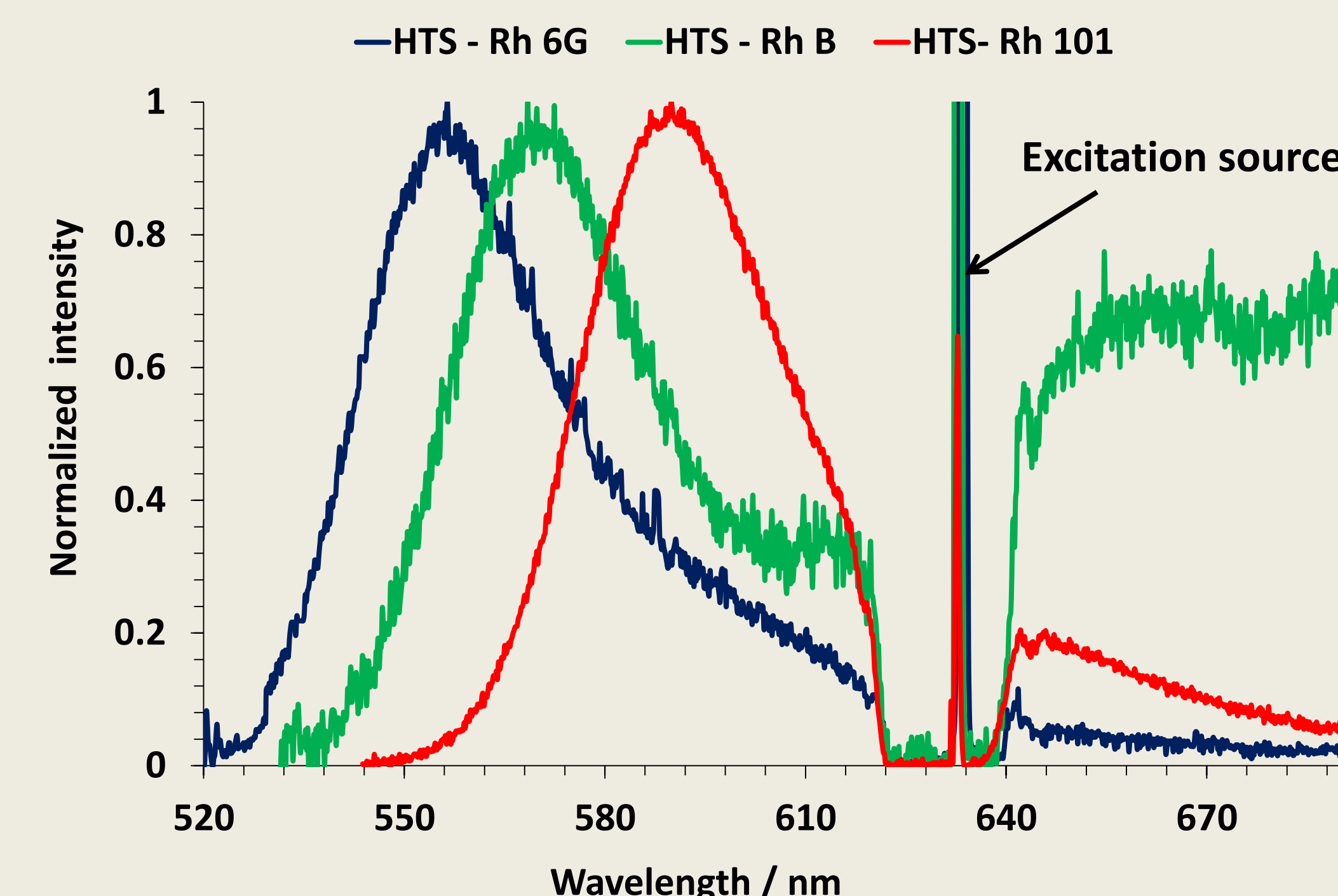
[1] J. L. Clark, P. F. Miller, and G. Rumbles, J. Phys. Chem. A 102, 4428-4437 (1998).

## Results

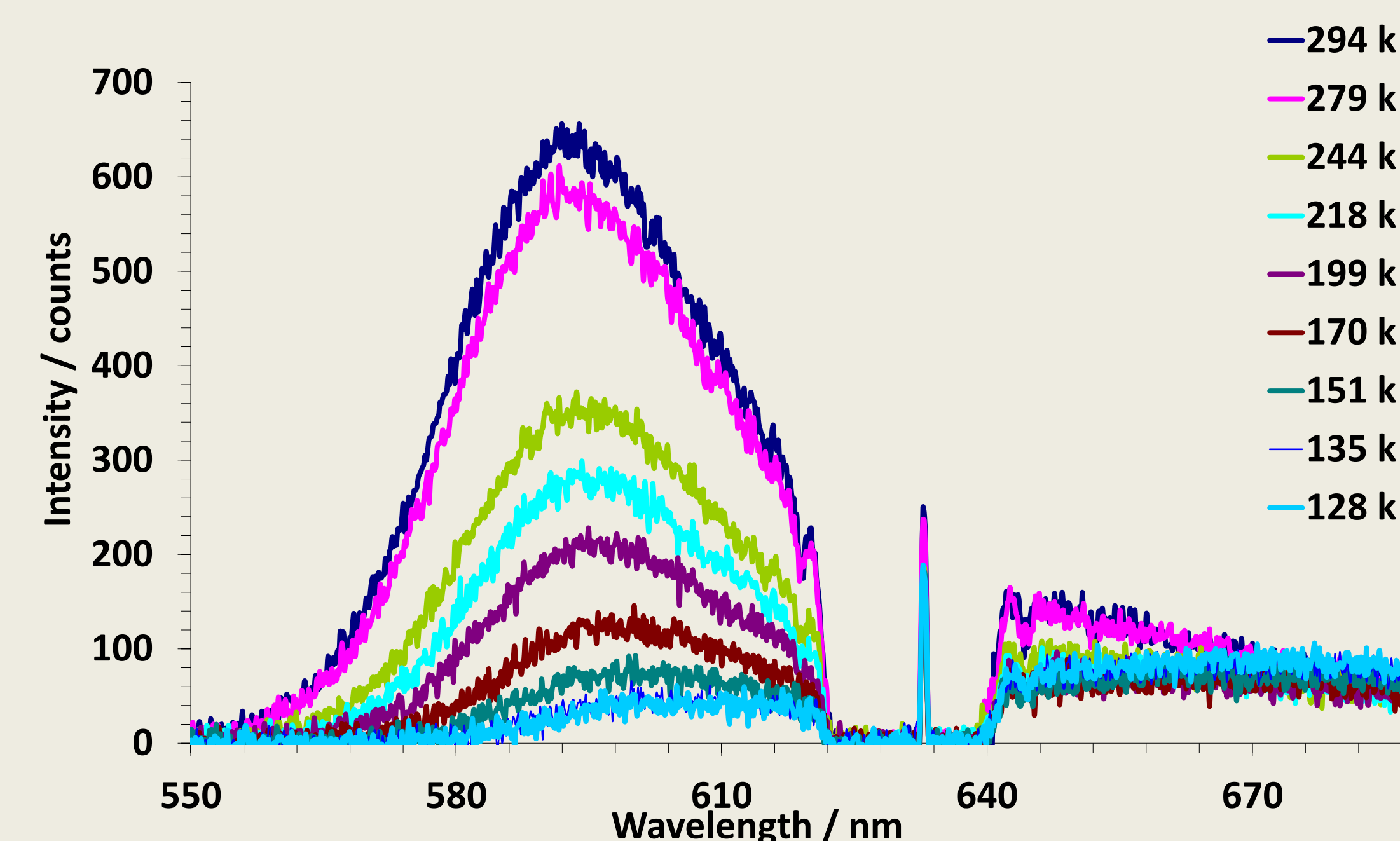
(a. 1) Absorption spectra



(a. 2) Anti-Stokes emission spectra



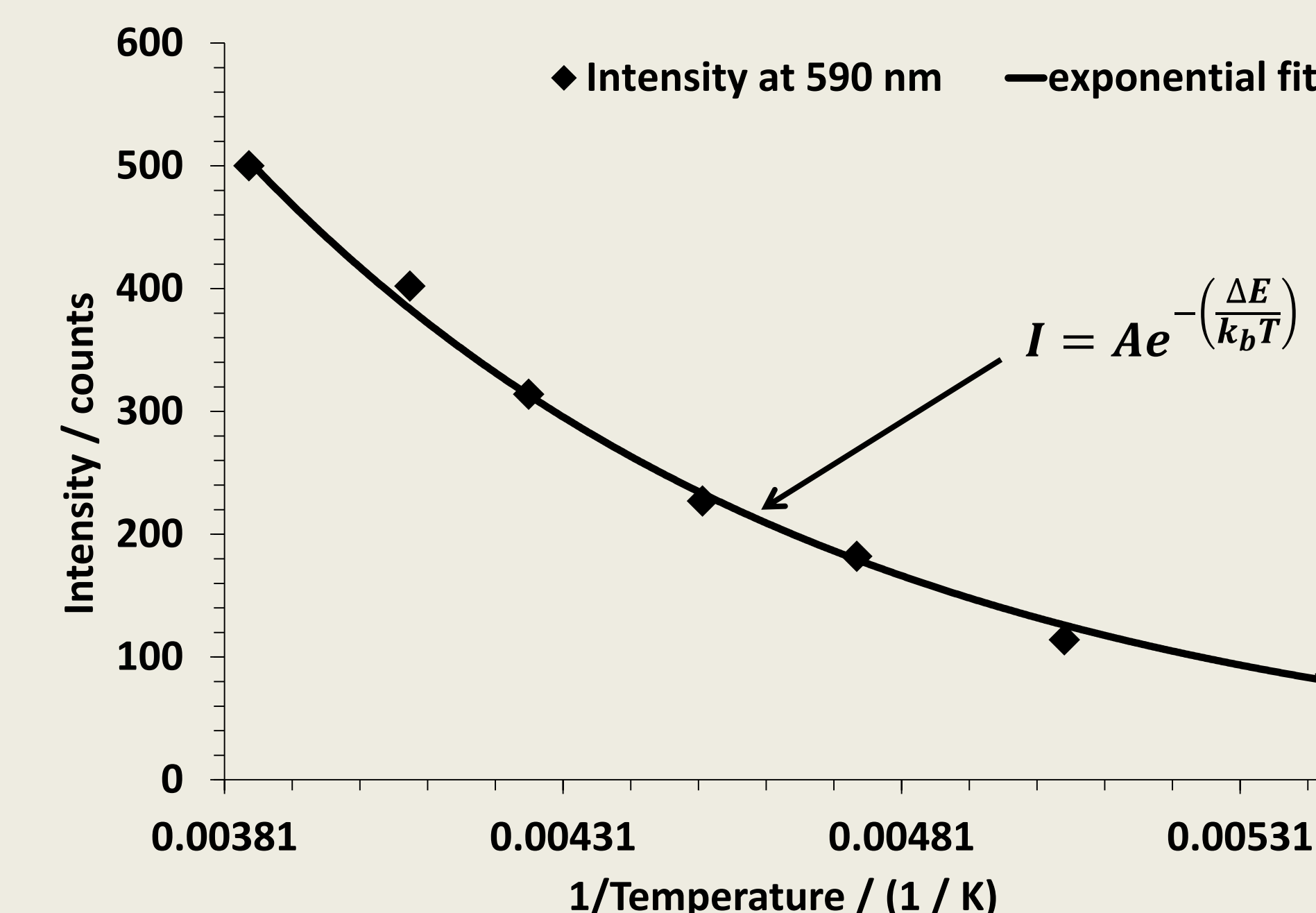
(b.1) Anti- Stokes emission spectra from HTS - Rh101 at different temperatures



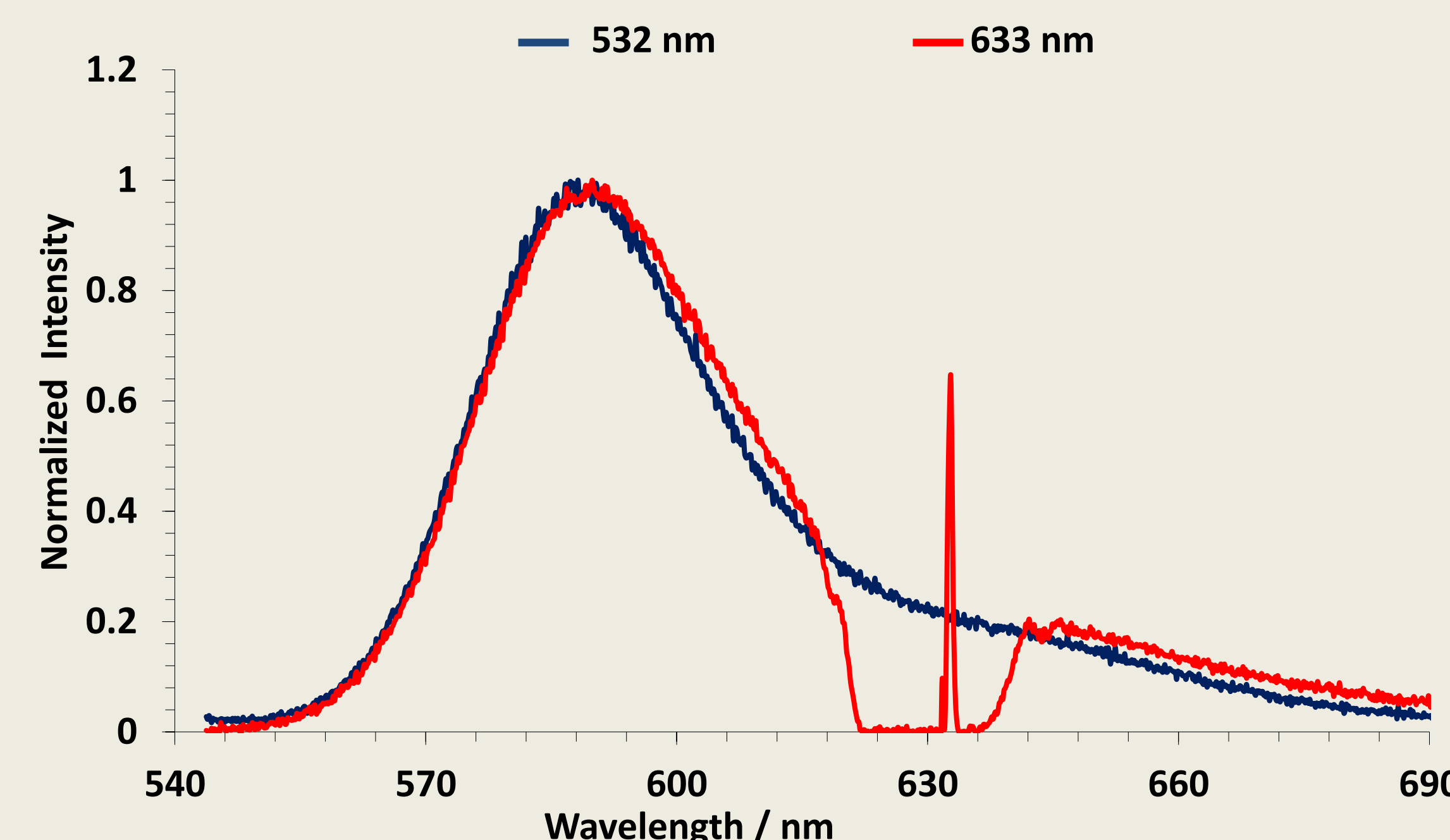
(b. 2) Calculation of  $\Delta E$  from temperature dependent spectra

$$\Delta E = 2.402 \times 10^{-20} \text{ J} = hc \cdot 1212.2 \text{ cm}^{-1}$$

<sup>1</sup>Energy difference reported = 1262  $\text{cm}^{-1}$



(c) Emission spectra obtained from HTS - Rh101 at excitation wavelengths 532 nm (Stokes) and 633 nm (anti-Stokes)



## Summary

- Anti-Stokes fluorescence from HTS-Rh101, HTS-RhB, HTS-Rh6G have been recorded and evaluated.
- Emission spectra of HTS-Rh101 at two different excitation wavelengths 532 nm and 633 nm have been compared.
- Temperature dependent spectra of HTS-Rh101 have shown that the attachment of the dye to the silica nanoparticles does not involve any modification of energy levels.

## Acknowledgement

Financial support from SFI (11/RFP1/PHY/3233) is gratefully acknowledged.