Overview of calculations for energy transfer project
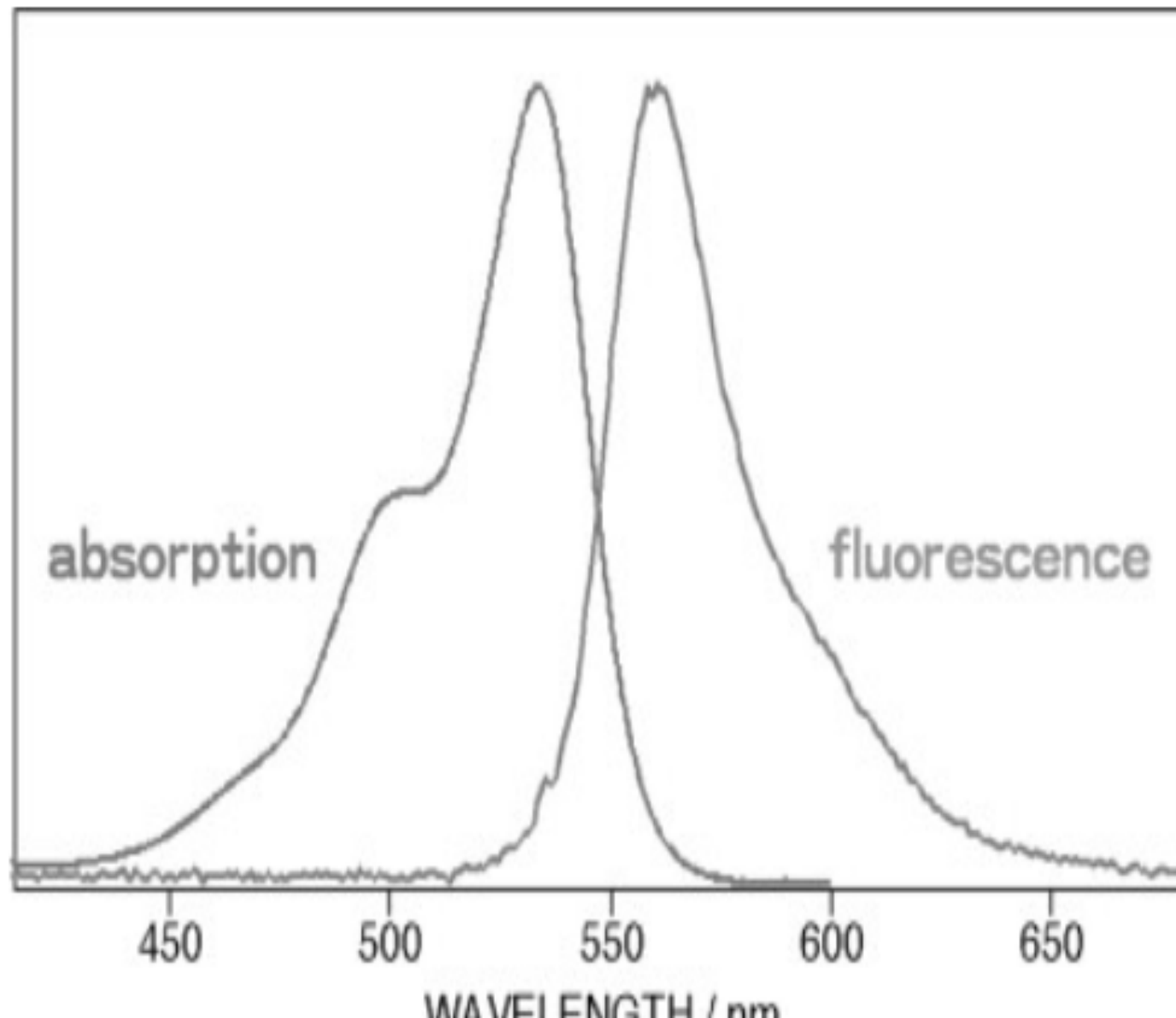
Estimating Franck-Condon factors from Raman spectra

Calculating absorption spectra using the time-correlator

Calculating spectral overlaps

Rhodamine 6G

Rhodamine 6G fluorescence spectra

absorption

fluorescence

WAVELENGTH / nm

Rhodamine 6G Raman

We can use relative Raman cross sections to determine the displacement of modes in the excited state. All the modes in the Raman spectrum are Franck-Condon active. This means that they arise from vertical transitions. To a first approximation their intensity is proportional to Se^{-S}, where S is known as the electron-phonon coupling constant. These data are obtained using 514.5 nm excitation.

Source: Handai Biophotonics (2007)
Hiroshi Masuhara & Fumio Tokunaga, Eds.
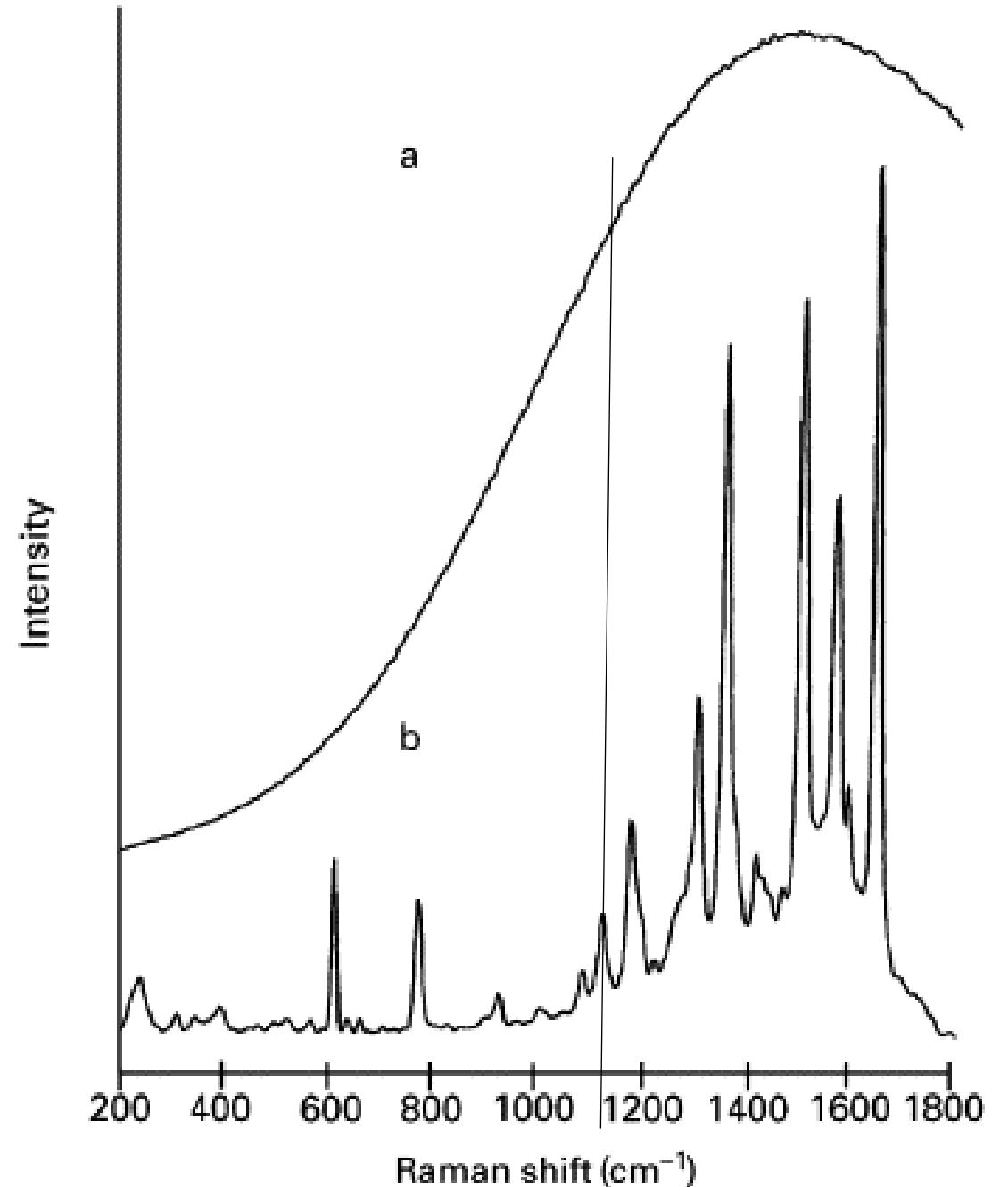
Calculated model of Raman spectrum

The model of the Raman spectrum was taken from the reference on the previous slide. There is a rise in the baseline above 1000 cm^{-1} that we did not try to model. The point of such a model is to obtain an estimate for the relative intensities of the Franck-Condon active Raman modes.

We used the program raman_spec.f which can be compiled and used on any unity account.
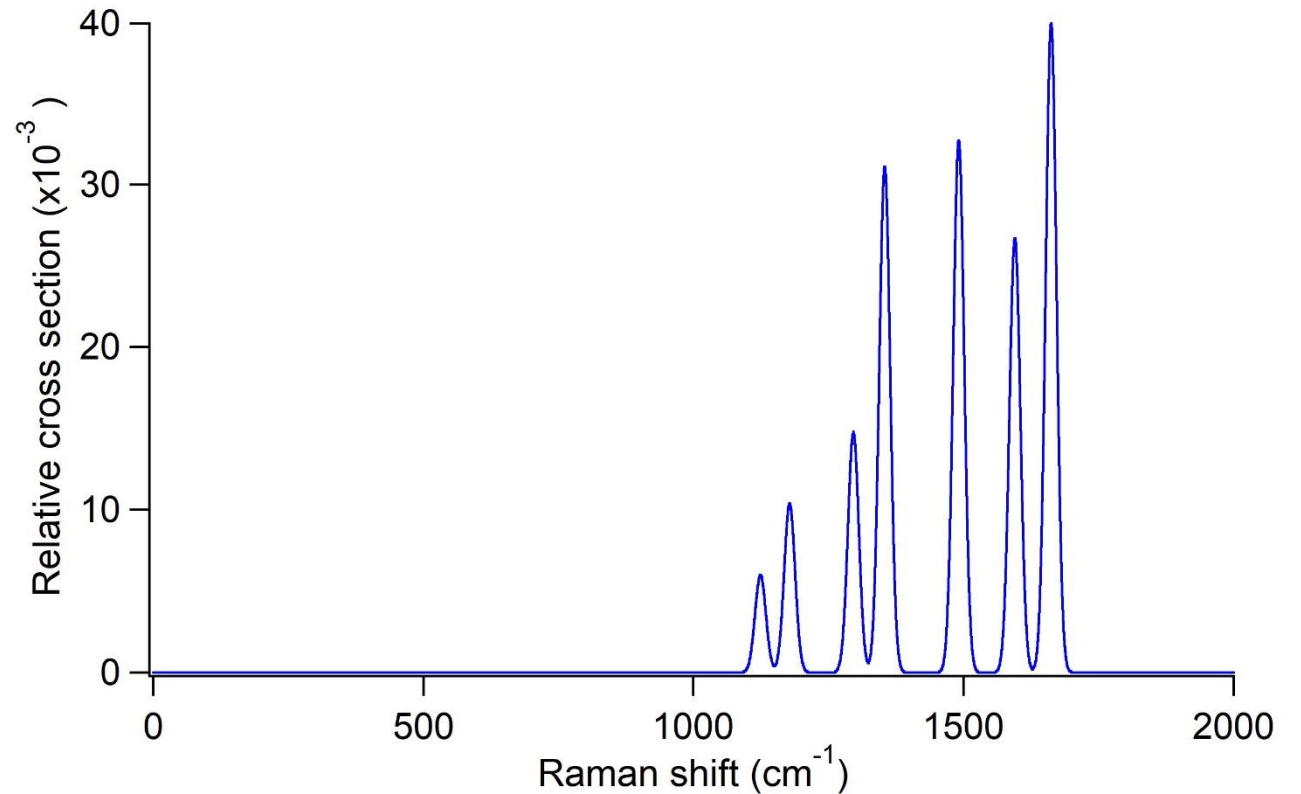
Method for modeling a Raman spectrum

Make a list of wavenumber shifts and relative intensities of the Raman bands. Obtaining absolute intensities would be better, but it is very difficult. The list obtained from the above paper looks like

1662.0, 1.0

1595.0, 0.67

1491.0, 0.82

1354.0, 0.78

1296.0, 0.37

1178.0, 0.26

1124.0, 0.15

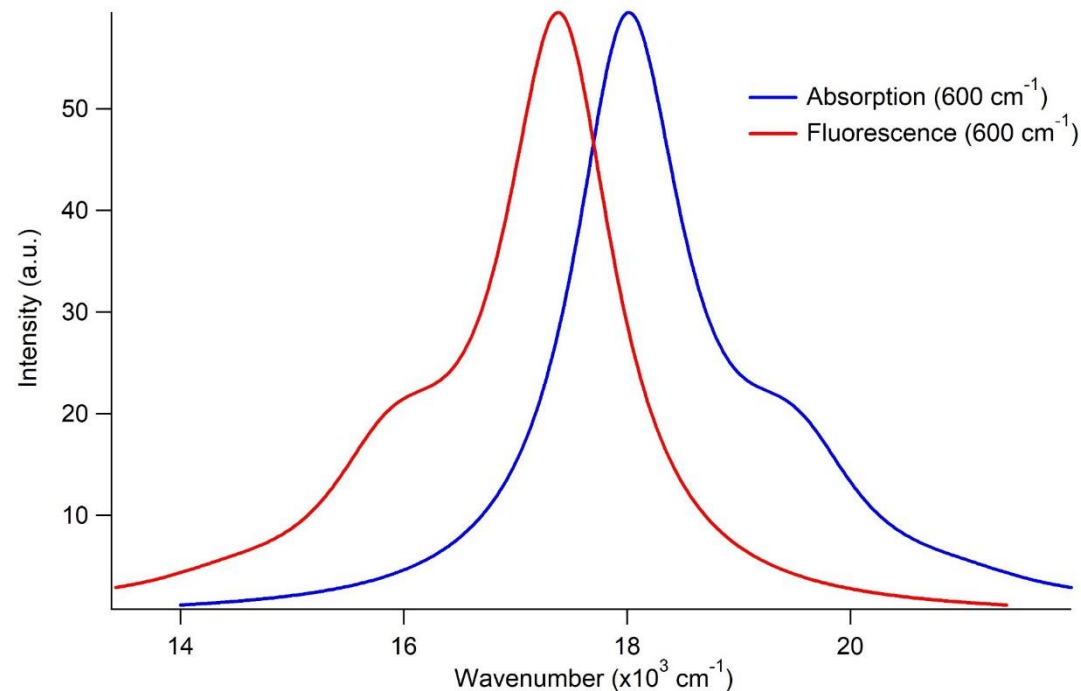Since these are relative values they will need to be scaled. In our example,
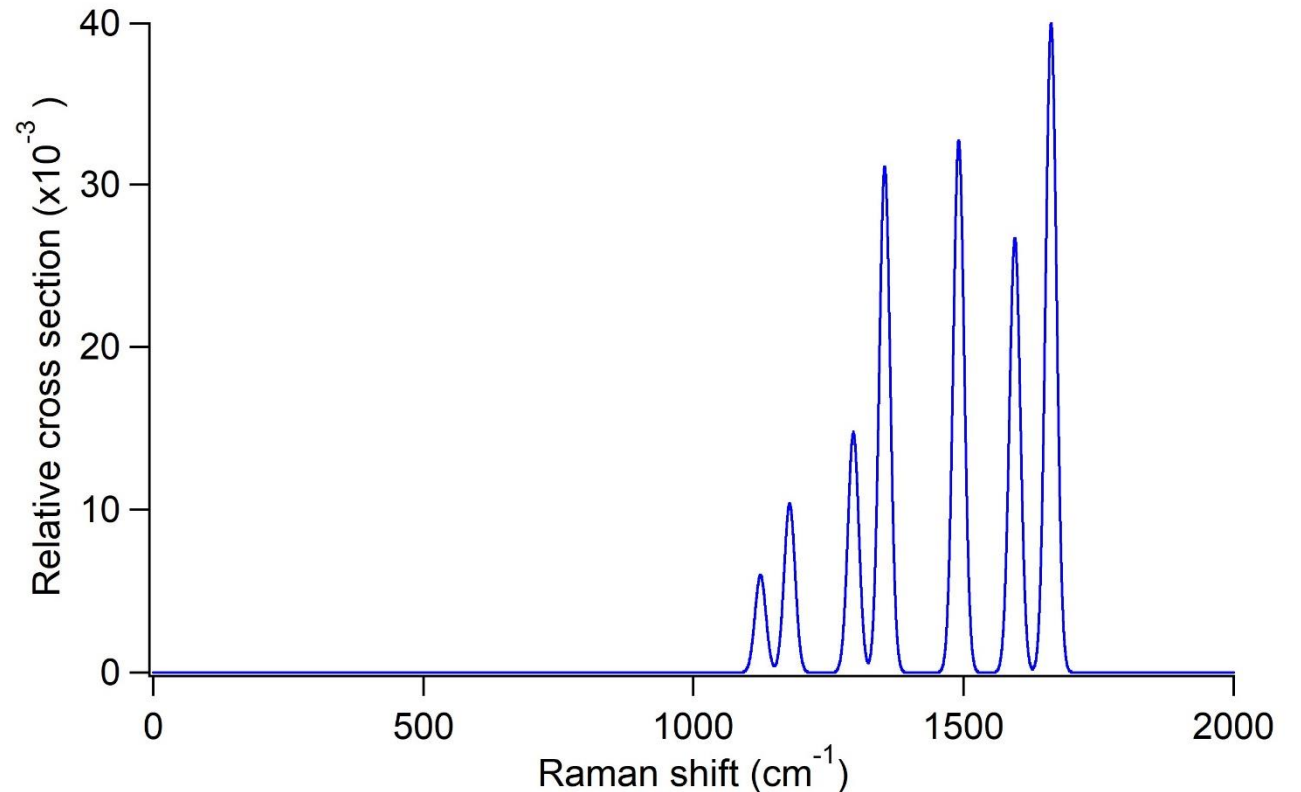
we divided them by a factor 20 to calculate the absorption spectrum.

Method for calculating an absorption spectrum

For this calculation we use the time-correlator formalism for calculating the Franck-Condon factor. The Raman frequencies and relative intensities are an input. We use the approximation that the intensity is approximately equal to S. This is true as long as S << 0.1, which is the case here. For this calculation we Use the program timetherm.

Finally, once we have the absorption spectrum we can calculate the fluorescence spectrum using the mirror image relationship. In our project we wil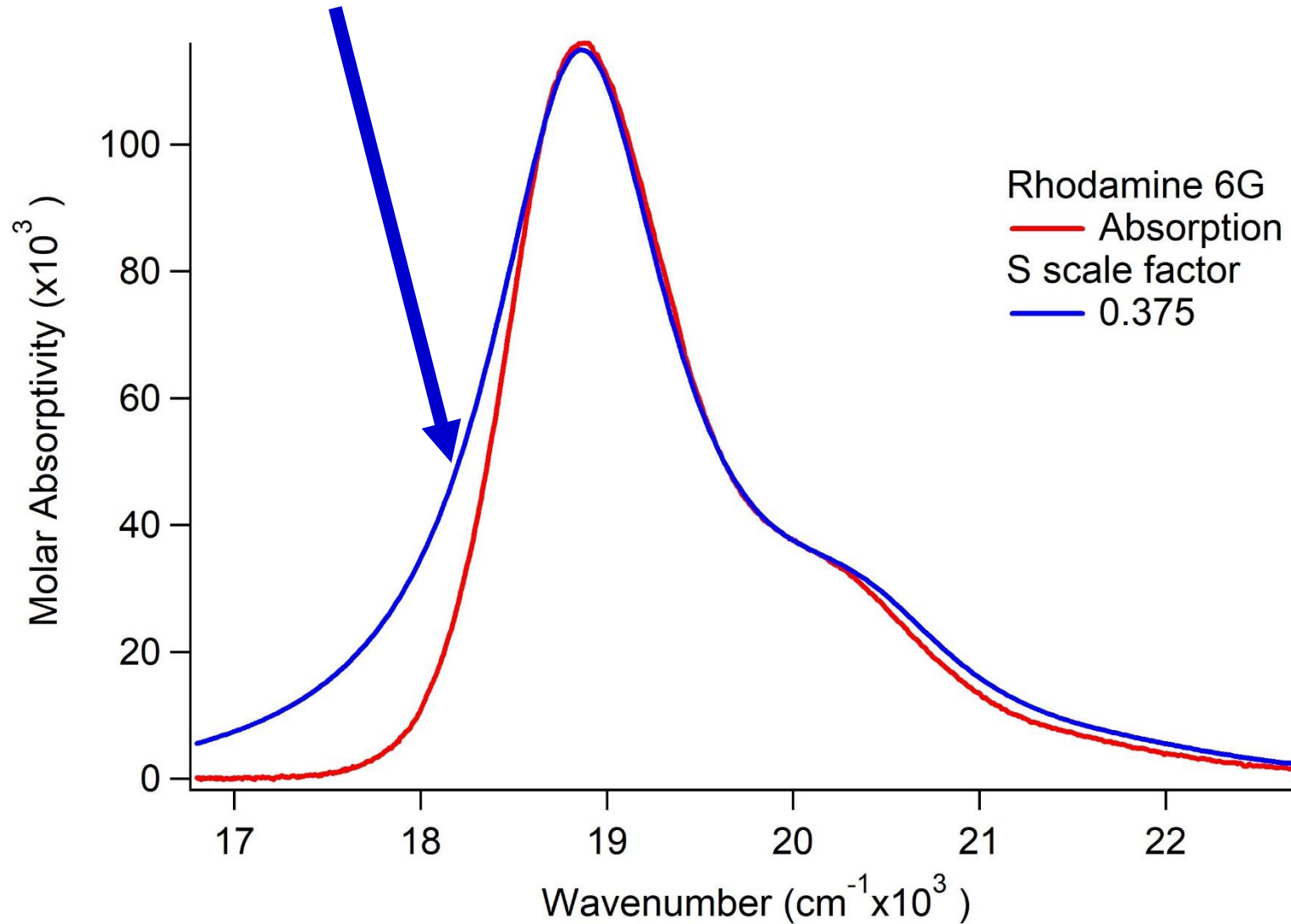l be helped by the fact that rhodamine and fluorescein have quite similar structures and therefore they have similar vibrations and absorption line shapes. You can see this from the available data.

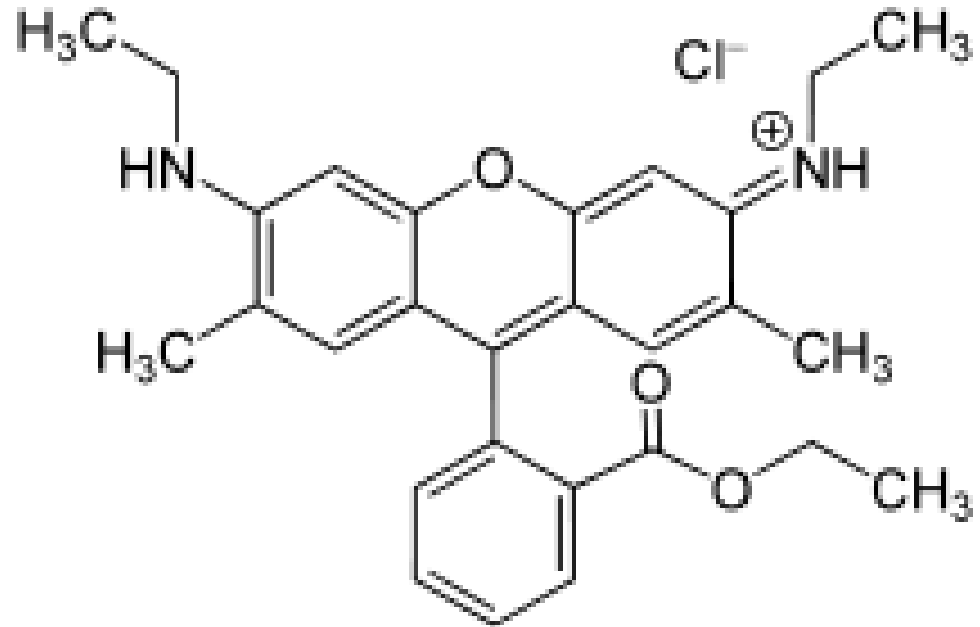# Using timetherm calculate absorption spectra
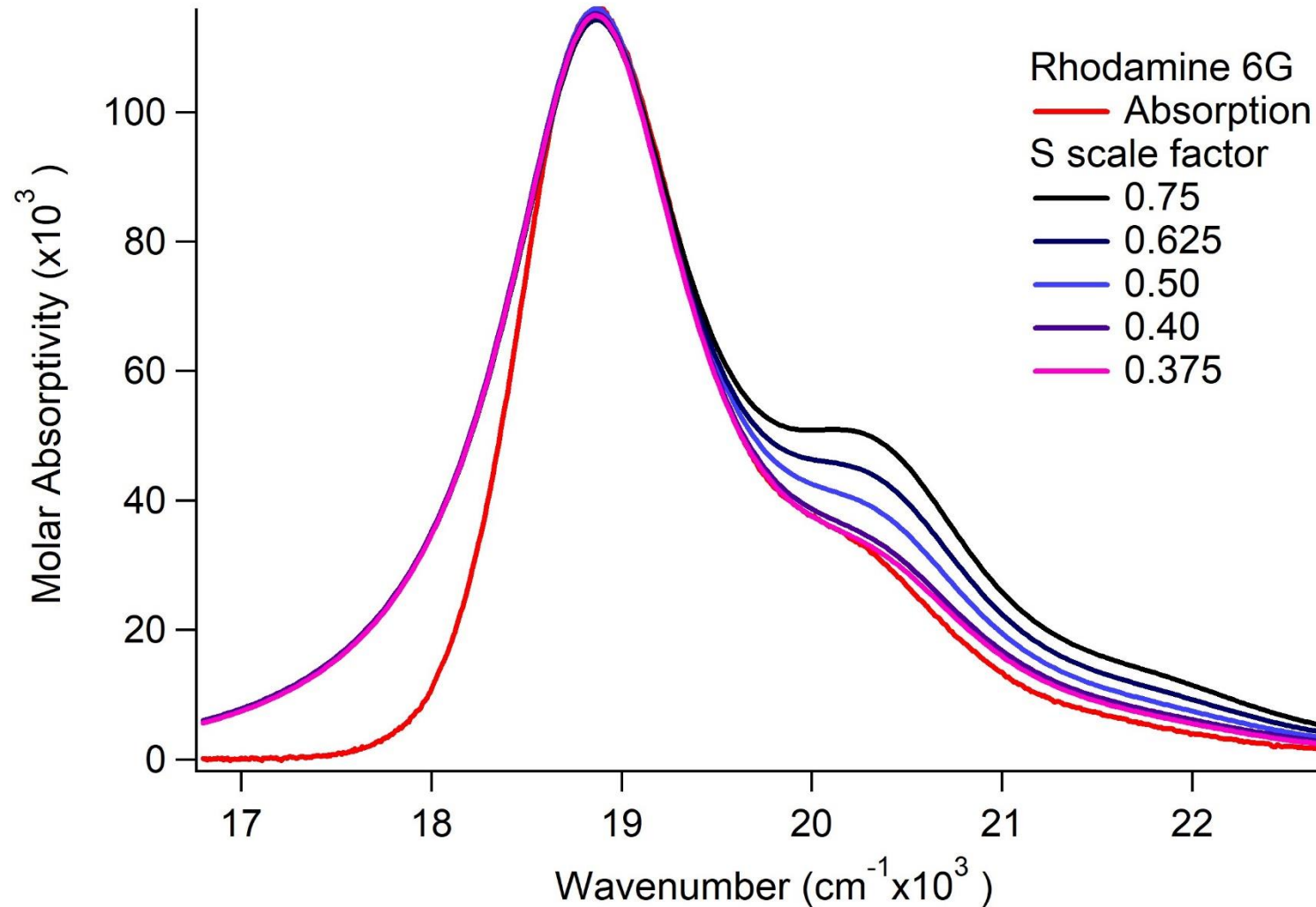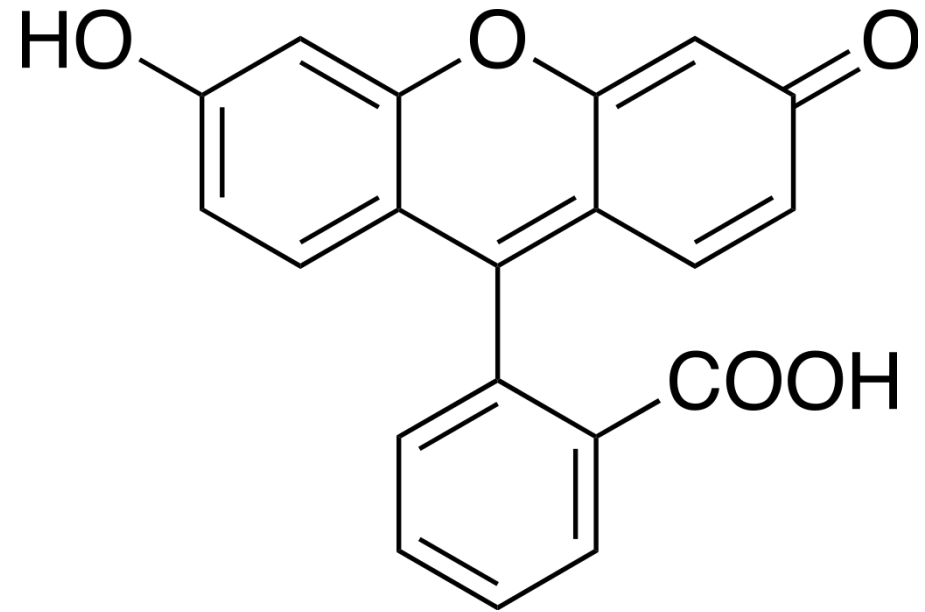
Satisfactory, but not excellent model…

Lorentzian tail

Rhodamine 6G
Fluorescein

Fluorescein

Fluorescein absorption and fluorescence spectra
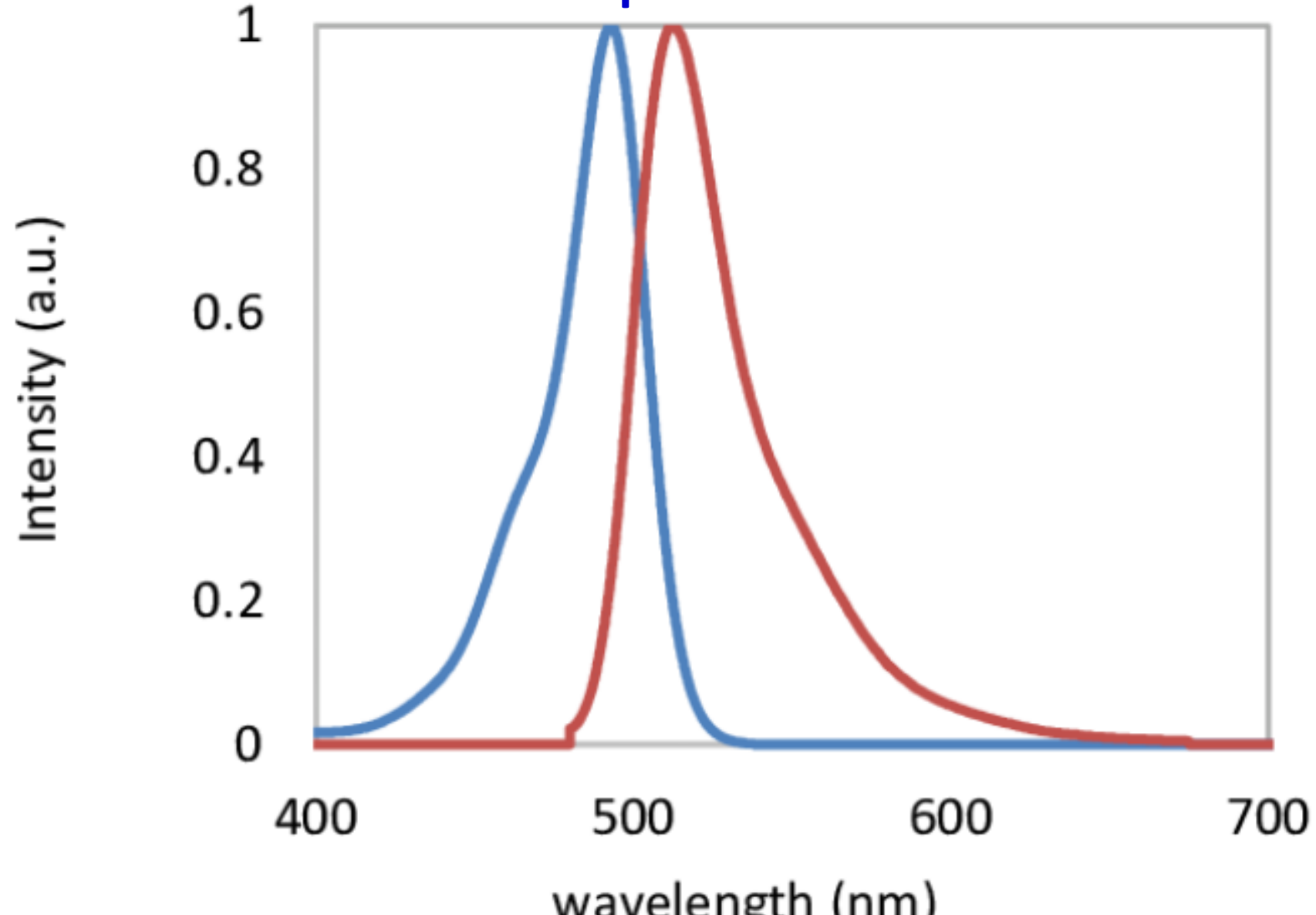
Fluorescein Raman spectra

As for rhodamine 6G, fluorescein spectra can be observed when the molecule is bound to a gold nanoparticle. The fluorescence is quenched and the Raman can be observed.

Hildebrandt,
J. Raman Spec. 1986

Figure 2. SERR spectra of (A) FS⁻, (B) FSA⁻ and (C) DIFIA⁻ adsorbed on Ag sol ($c_0 = 5 \times 10^{-7}$ M; pH = 6.5; $\lambda_0 = 514$ nm).

Figure 3. SERR spectra of (A) FS⁰ and (B) FSA⁰ on Ag sol ($c_0 = 10^{-7}$ M; pH = 3.5; $\lambda_0 = 514$ nm).

Rhodamine B and 123

Absorption spectra of three rhodamines

Absorption spectra of three rhodamines overlapped with fluorescein

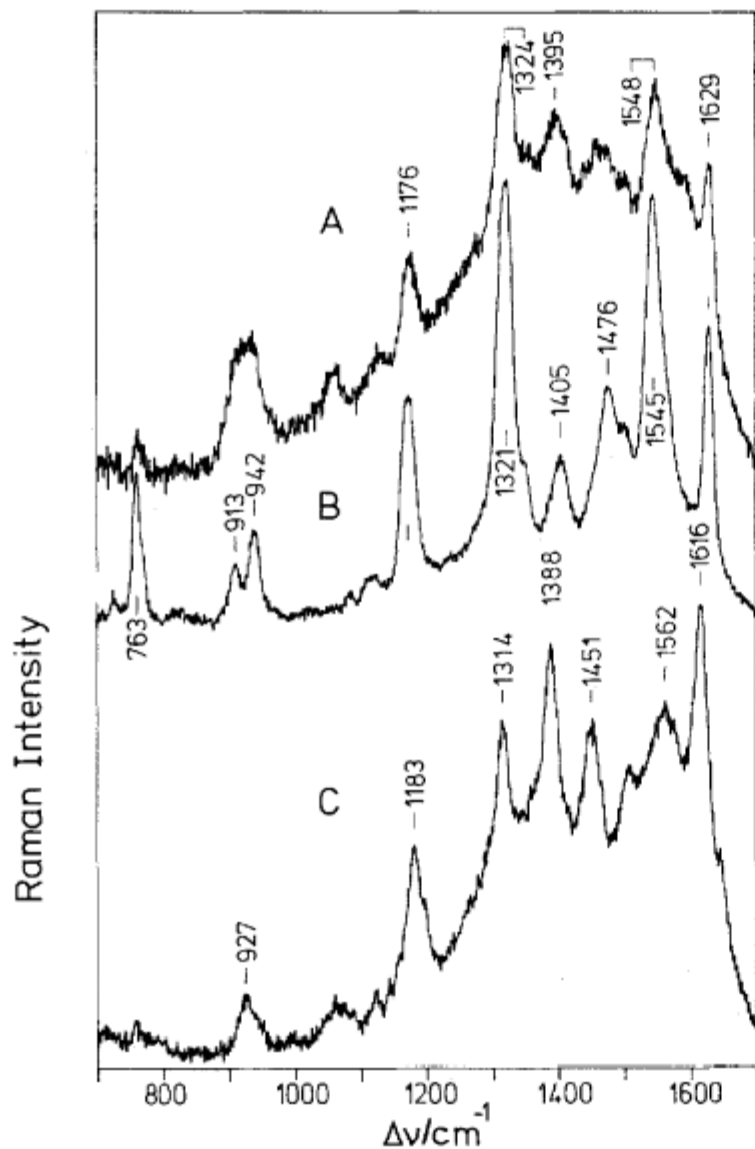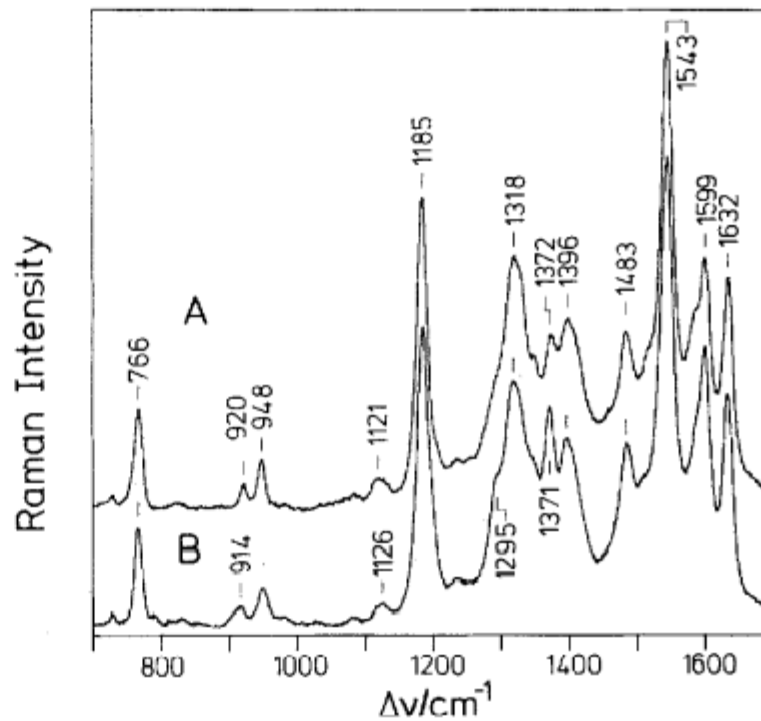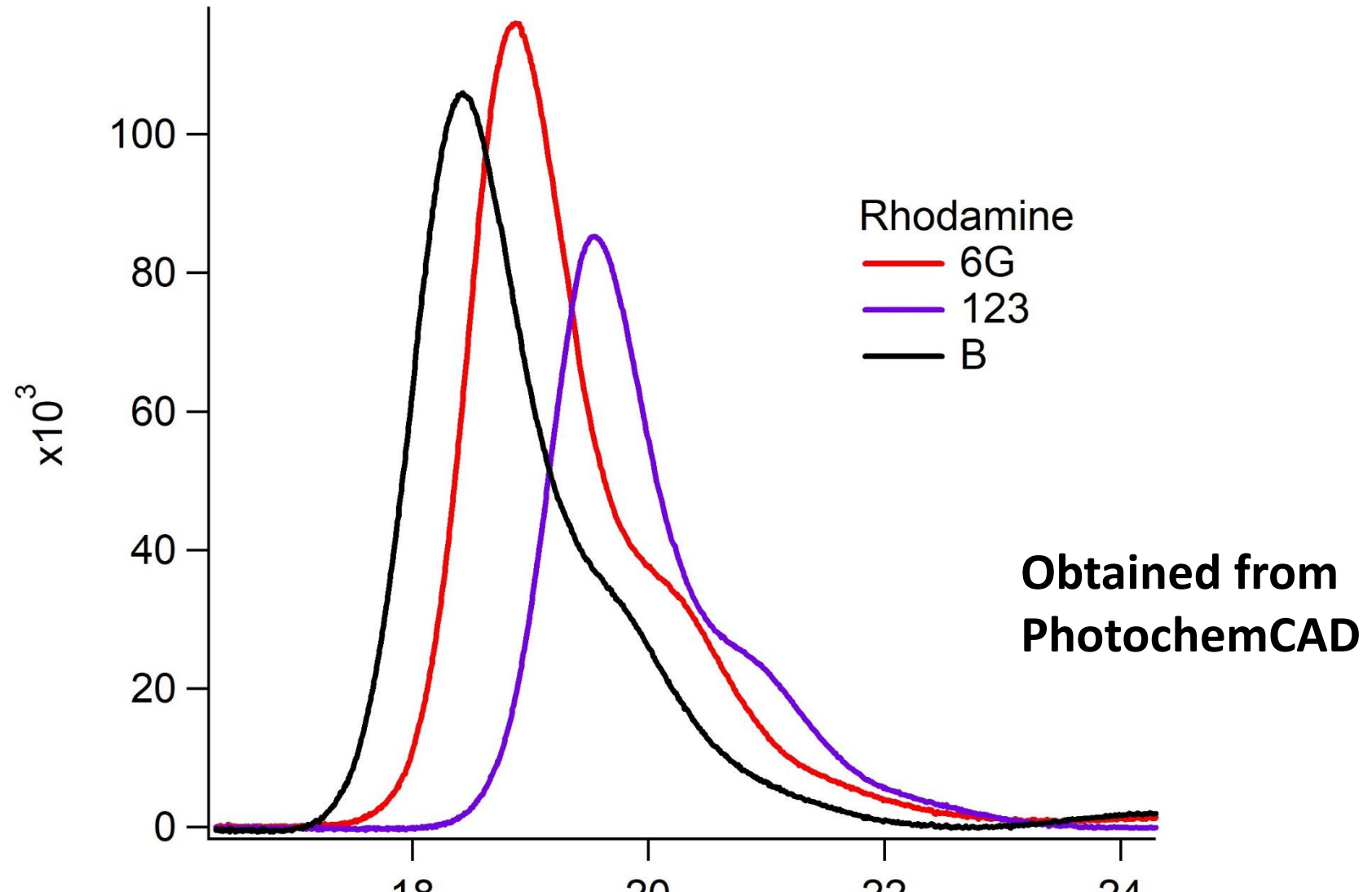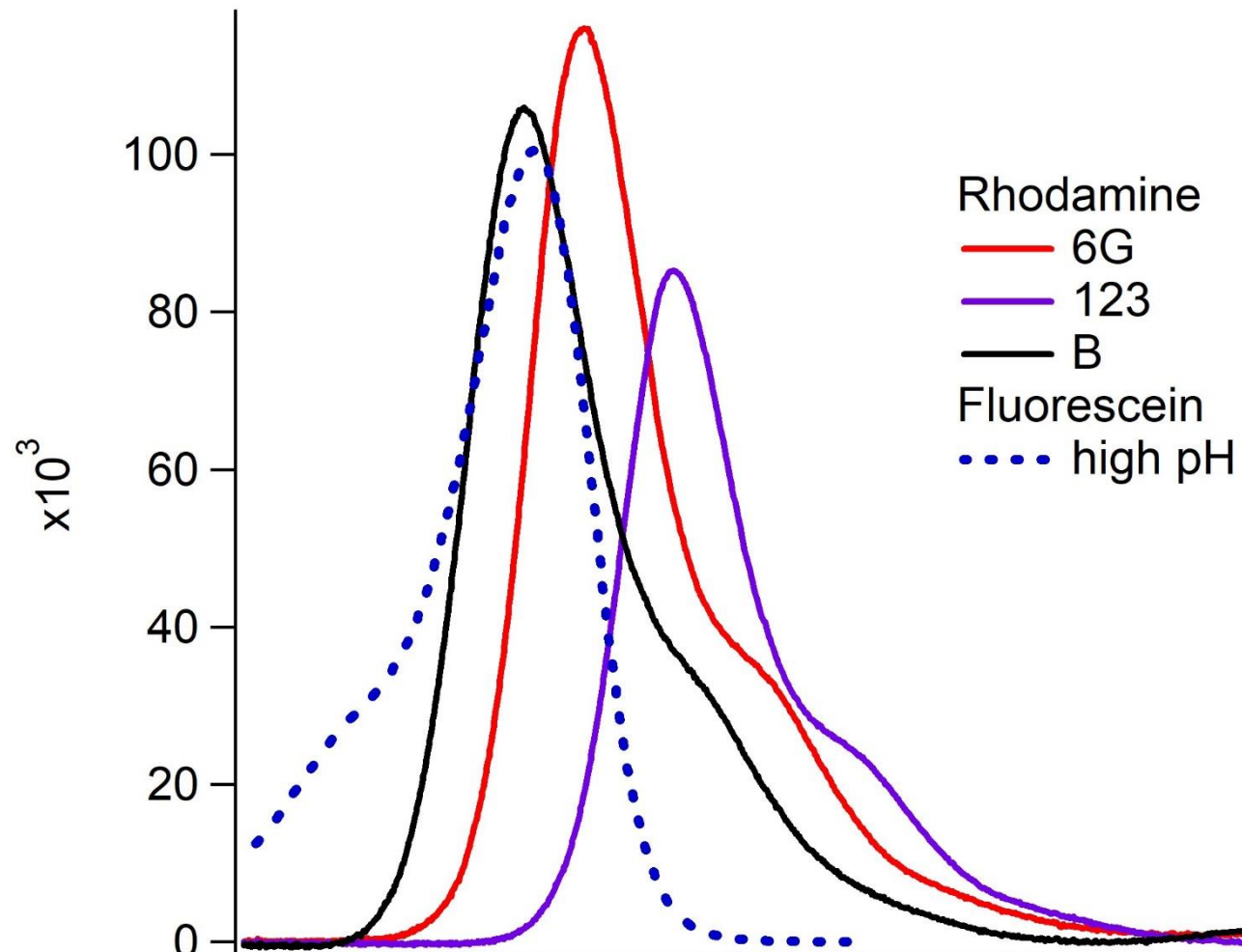# Surface-Enhanced Raman Scattering of Rhodamine 123 in Silver Hydrosols and in Langmuir–Blodgett Films on Silver Islands

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Surface-enhanced Raman scattering(SERS) of the Rhodamine 123 (Rh 123) molecule on ion-induced silver colloids has been studied. A time-dependent study of the SER spectra at a particular pH confirms charge transfer interaction between the probe molecule and the metal. The SER spectra of Rh 123 in Ag sol is compared with that of the molecules organized in a monolayer on silver island films by the Langmuir–Blodgett (LB) technique. The origin of high SERS activity of Rh 123 molecules in a monolayer on a silver island film is shown to be due to physisorption whereas in the ion-induced colloidal SERS both physisorption and chemisorption machanisms are involved. From these results, the contribution of charge transfer interaction to SERS in Ag sol has been estimated. In monolayer SERS, all the in-plane and out-of-plane (of xanthene ring) modes are more or less equally enhanced. This indicates that the xanthene plane of Rh 123 molecule organized in a LB film is oriented neither flat nor perpendicular to the silver island surface but is tilted. © 2001 Academic Press

Key Words: surface-enhanced Raman scattering; Langmuir–Blodgett film; silver colloid; charge transfer.

INTRODUCTION

tronic states of the molecule and the metal (3, 4). An area of contemporary interest in SERS study is to specify the contribution of the charge transfer mechanism to the overall SERS enhancement. As the exact electric potential on the metal surface is not known, it is quite difficult to estimate the contribution of the charge transfer mechanism in colloidal SERS. However, by calculating the adsorption energy between the molecule and the metal surface, Hildebrandt and Stockburger (5) were the first to estimate that for Rhodamine 6G adsorbed on anion-induced silver hydrosols, the enhancement of the Raman signal due to CT interaction is about 2 orders of magnitude. The subsequent work of Grochala *et al.* (6) on SERS of Rhodamine 6G on a silver electrode showed that such an increase in SERS intensity by added anions cannot be exclusively explained in terms of a charge transfer effect. They attributed such an increase to the anion-induced re-orientation of the dye molecules on the silver surface.

Here, we report a comprehensive SERS study of Rhodamine 123 (Rh 123) adsorbed on silver hydrosol prepared by the process of Creighton et al. rather than by the Lie-Miesel method, which has been used for Rhodamine SERS analysis by others

used to adjust the pH value of the mixture, which was measured by a pH meter (Systronics $_{pH}$ system, model 361).

Silver island films were prepared according to Guhathakurta-Ghosh and Aroca (10). The thickness of the island film was monitored with a quartz crystal oscillator (model DTM-101, Hi-tech Instruments Pvt. Ltd., India). The control of the substrate temperature during deposition permitted the growth of a film with a highly homogeneous distribution of particle size and shape.

For LB film deposition, a computer-controlled Joyce-Loebl (U.K) Langmuir trough (model-4) was used. Ultrapure Milli-Q-plus water having resistivity >18 M was used as the subphase.

Surface-enhanced Raman spectra were recorded by a Spex double monochromator (model 1403) fitted with a holographic grating of 1800 grooves/mm and a cooled photomultiplier tube (model no. R928/115) of Hamamatsu Photonics, Japan. The liquid samples were taken in a quartz cell and were excited by 514.5-nm radiation from a Spectra Physics Ar$^+$ ion laser (model 2020-05) at a power of 0.05 W. Raman scattering was collected at the right angle to the excitation. For the monolayer LB-SERS experiment, the Raman excitation was made at 45° to the surface normal at a laser power as low as 0.02 W to avoid sample degradation and carbon contamination. The monochromator control, operation of the photon counter, and data acquisition and analysis were done by Spex Datamate 1B. The acquisition time by the spectral element was 0.5 s. The scattered light was focused onto the entrance slit of width 4 cm^{-1}. All spectral measurements were made at least three times to ensure reproducibility. Normal Raman spectra are recorded with excitation at 609 nm using a dye (Rhodamine 6G) laser (model Spectra Physics: 375B) pumped with the Argon ion laser.

The absorption and the corrected fluorescence spectra were recorded on a Shimadzu 2010 PC UV–vis and Hitachi model

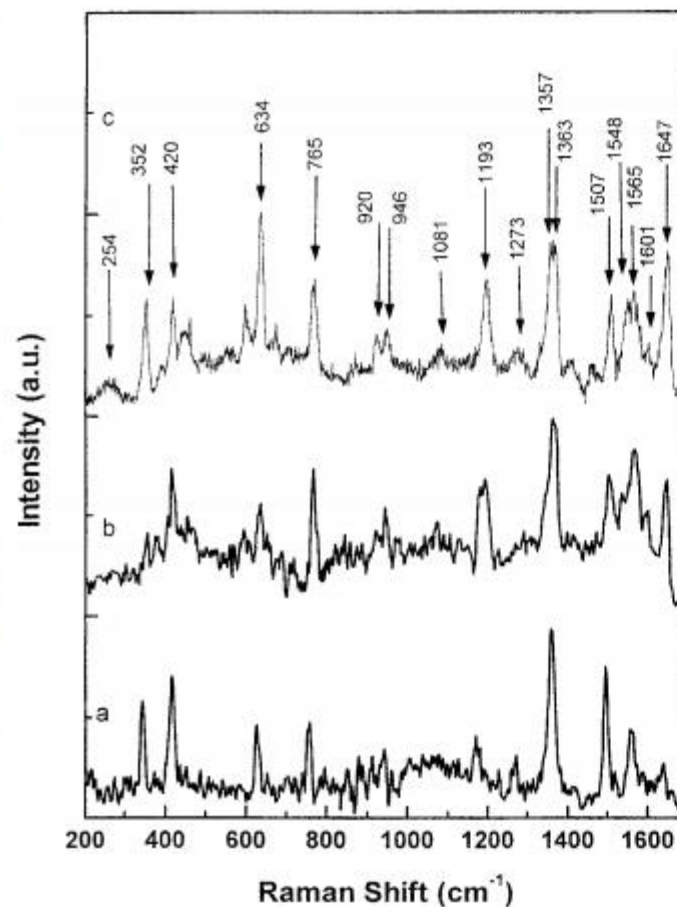**FIG. 2.** Background-corrected (a) Raman spectra of aqueous solution (3.0×10^{-4} M) of Rh 123 at pH ~ 6.5 for $_{exc} = 609$ nm; (b) SER spectrum of monolayer LB film of Rh 123 on silver islands for $_{exc} = 514.5$ nm; (c) SER spectrum of 3.0×10^{-7} M Rh 123 adsorbed in silver hydrosol at pH 2 for $_{exc} = 514.5$ nm. Spectra are plotted with a fixed ordinate-value shift for visual clarity.

TABLE 1
Raman and SER Spectral Data of Rhodamine 123

NRS of solution (cm⁻¹)	SERS on Ag sol (cm⁻¹)	LB SERS (cm⁻¹)	E.F. (for sol)	E.F. (for LB)	Tentative assignment
	254				Ag–Cl str
345	352		9.2×10^5		Torsion of xanthene ring
420	420	417	6.1×10^5	8.0×10^3	Xanthene ring deformation
628	634	631	1.8×10^6	7.9×10^3	C–C–C ring in-plane bend
758	765	764	1.6×10^6	4.8×10^4	C-H out-of-plane bend
914	920	917	9.9×10^5	2.4×10^4	
940	946	942	9.7×10^5	3.1×10^4	
	1081	1076			
1170	1193	1181	2.3×10^6	5.2×10^4	
		1193			
1271	1273		1×10^6		C–O–C stretching
1362	1357	1362	1.5×10^6	3.4×10^4	Xanthene ring stretching
	1363				
1500	1507	1502	1.2×10^6	2.2×10^4	External phenyl ring stretching
1558	1548	1565	2.1×10^6	4.7×10^4	Xanthene ring stretching
	1565				
1592	1601	1600	2.3×10^6	5.2×10^4	External phenyl ring stretching
1642	1647	1646	6.8×10^6	1.1×10^5	Xanthene ring stretching

Raman spectra of Rhodamine B