ECE ILLINOIS
Department of Electrical and Computer Engineering

MOLECULAR SPECTROSCOPY OF RARE EARTH AND METAL-HALIDE MOLECULES

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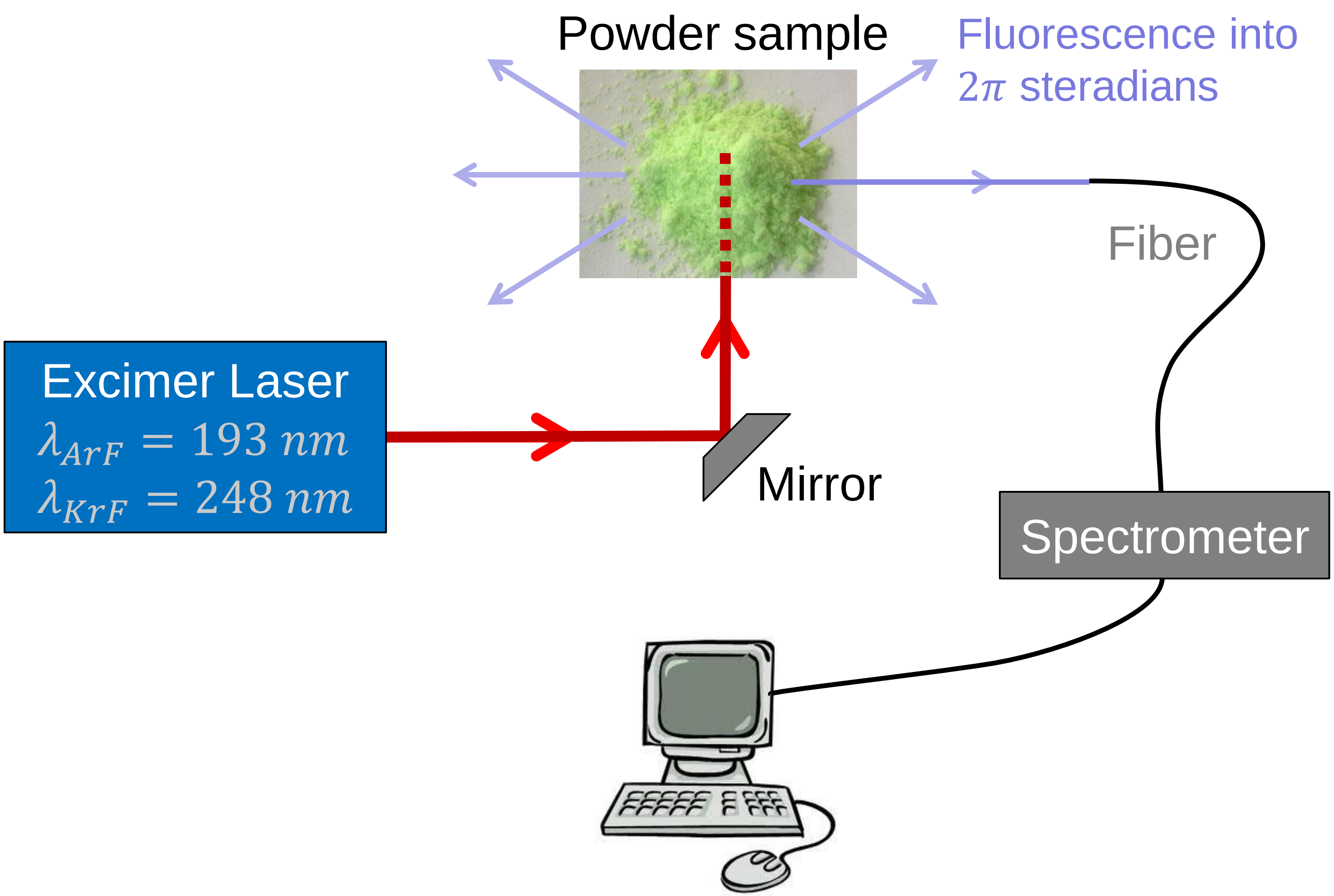
Motivation

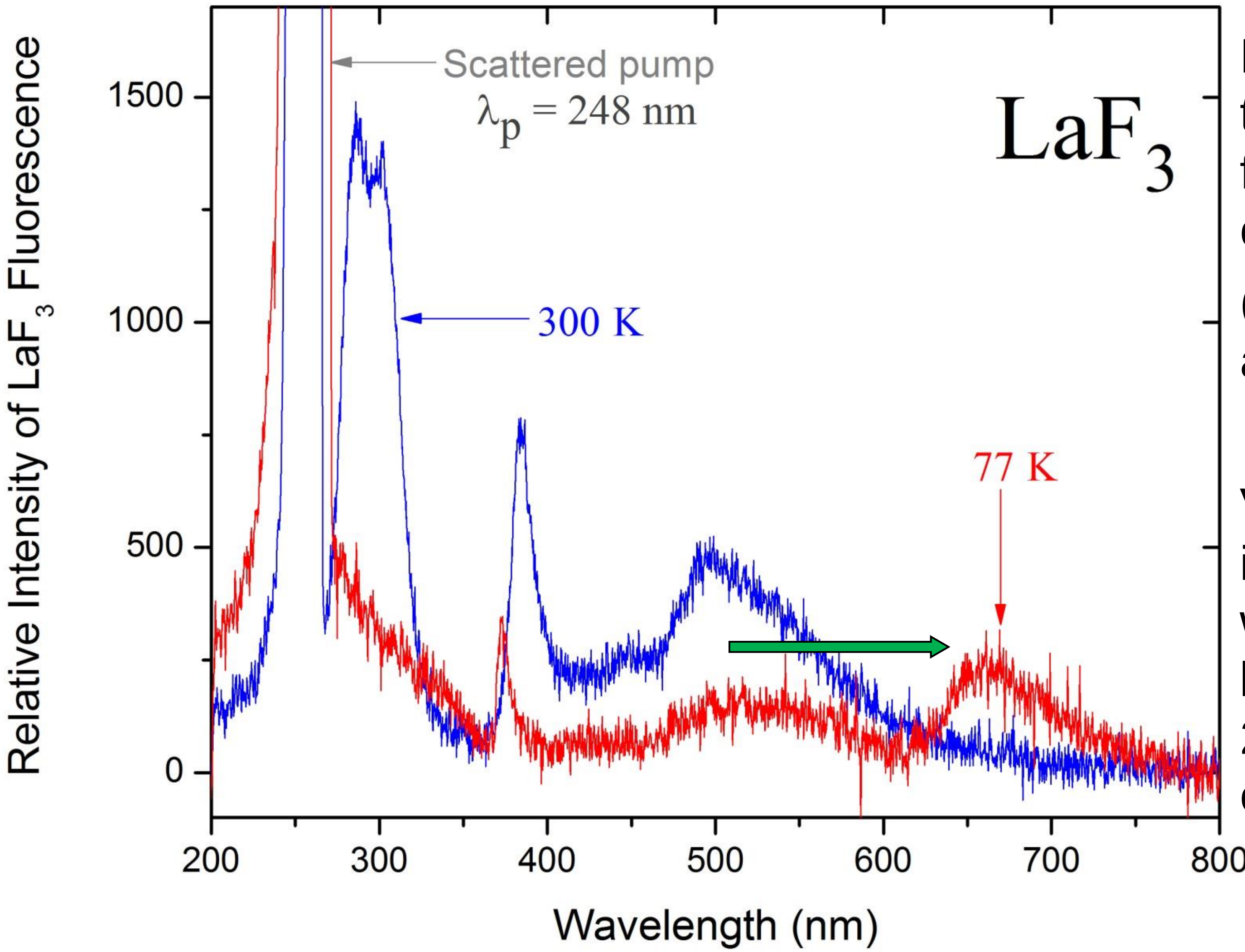
1. Investigating visible and ultraviolet emission spectra of selected rare-earth halides (LaF_3, PrF_3, $PrCl_3$)
   - Potential laser application
   - Phonon – La^{3+} interactions

2. Observation of ScI_3 and DyI_3 photodissociation fragments
   - Detection of MI and MI_2 fragments (M = Dy or Sc) of MI_3 parent molecule (common constituents of arc lamps)
   - Identify fragmentation channels

Experimental Setup : Excitation of Powders



Lanthanum Tri-Fluoride Fluorescence

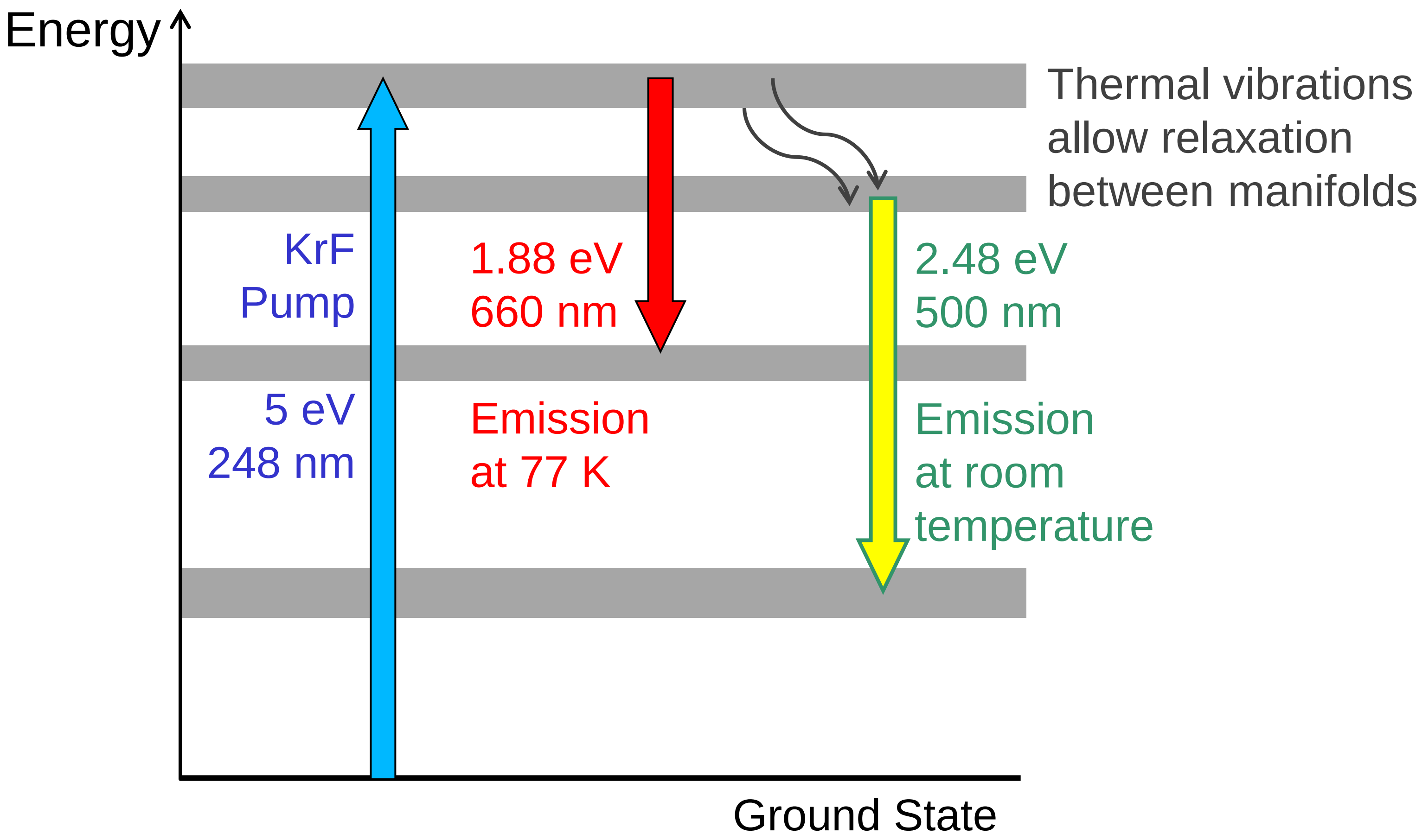


Blue shift of the 380 nm feature with cooling

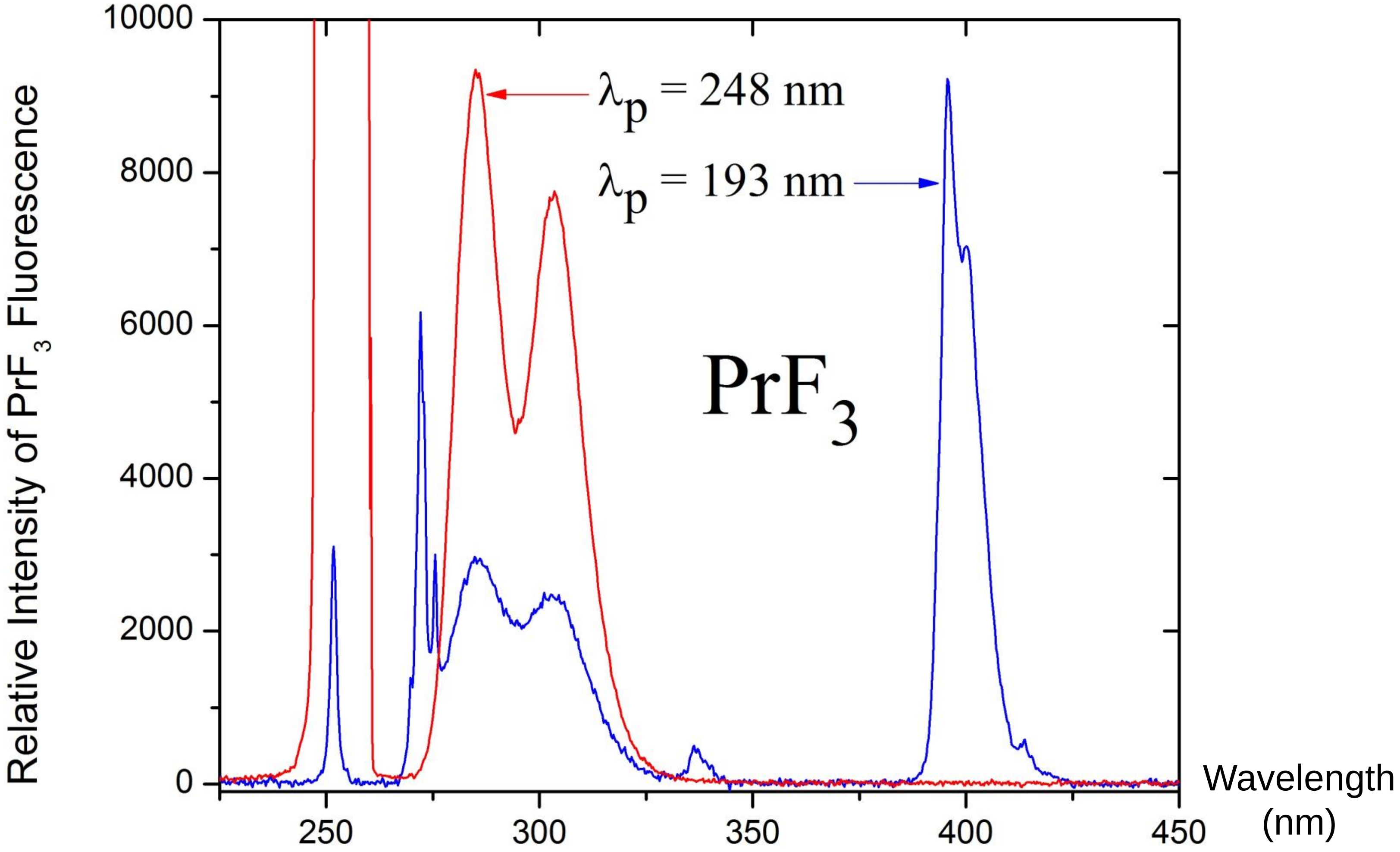
(excitation to a manifold)

Vibrational interaction with the lattice under 248 nm excitation

Energy Diagram of La^{3+}

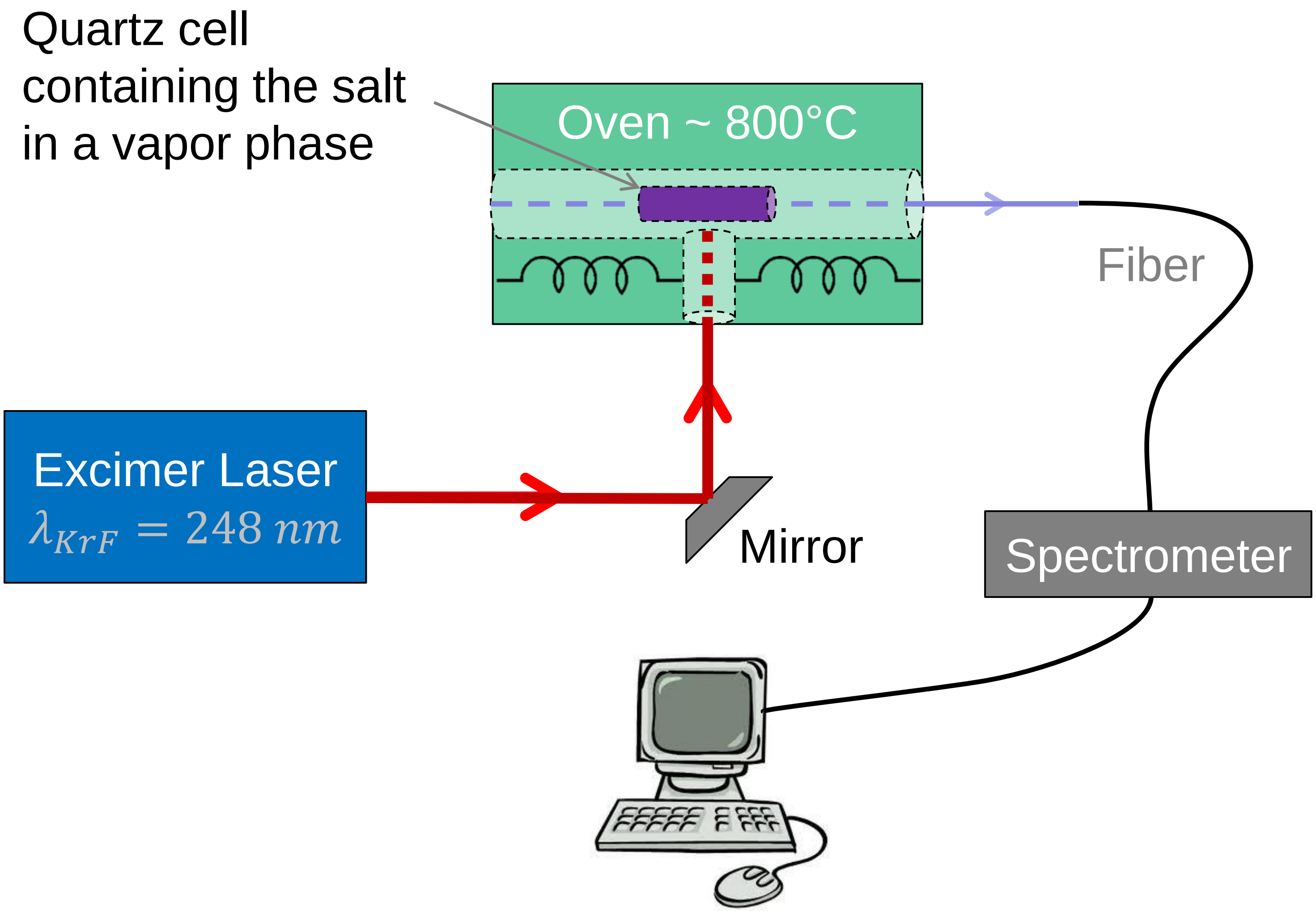


Praseodymium Tri-Fluoride Fluorescence



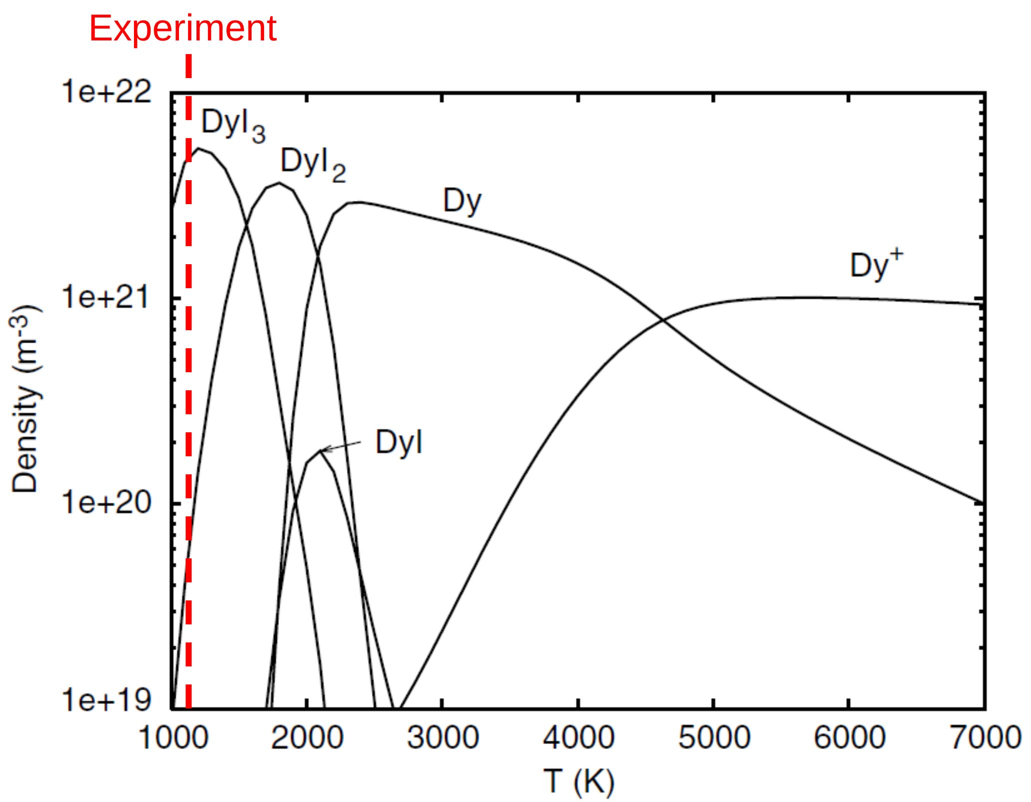
Spectral features observed only under ArF photopump : 272, 275, 336, 395, 400 nm
→ some molecular levels are only reached with the more energetic ArF beam (6.4 eV)

Laser Photoexcitation of Sc (Dy)– Tri-Halides



Dy Compounds Vs Temperature

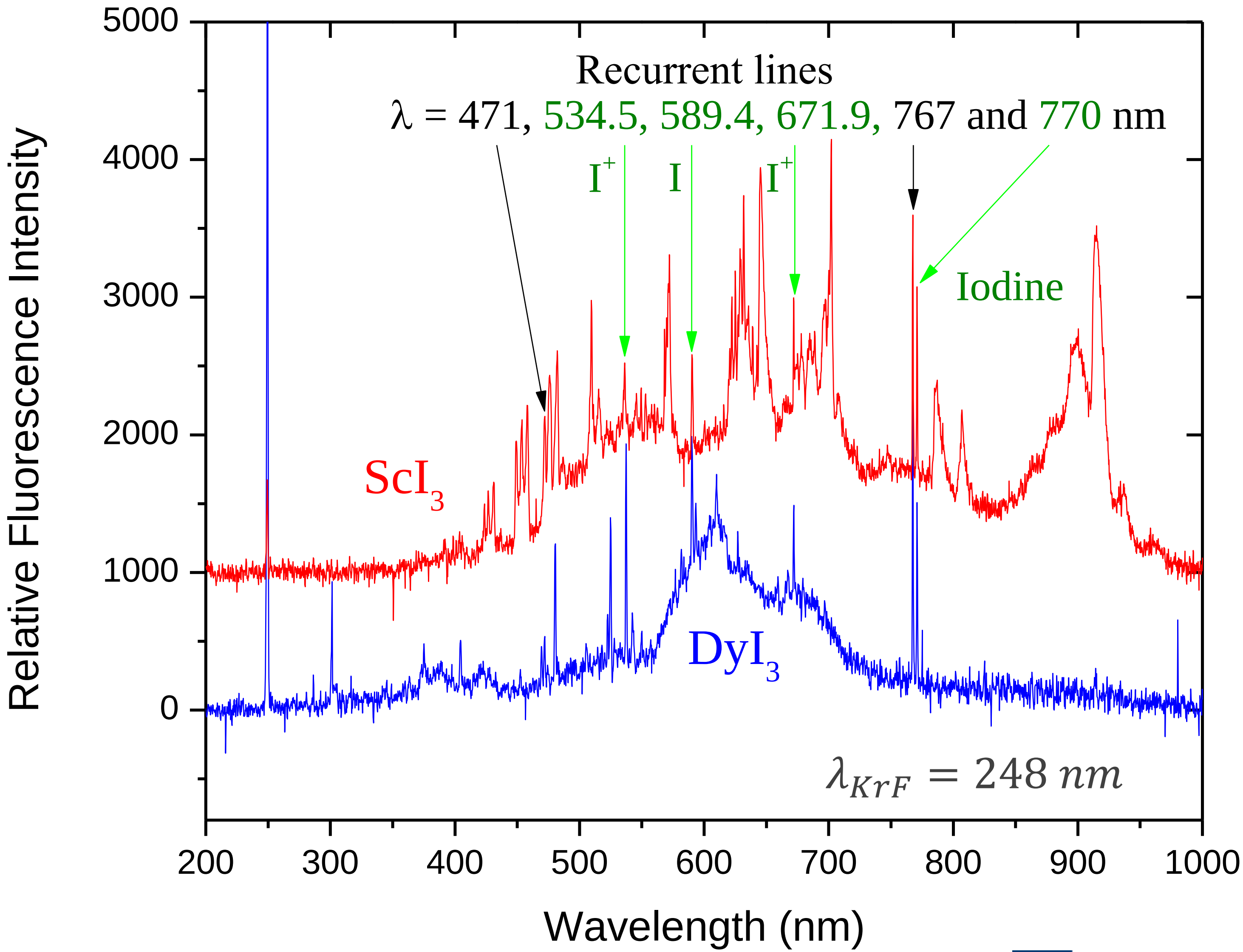
DyI_3 prevailing below 1000 K where noticeable amounts of DyI_2 appear and dominate above 1500 K



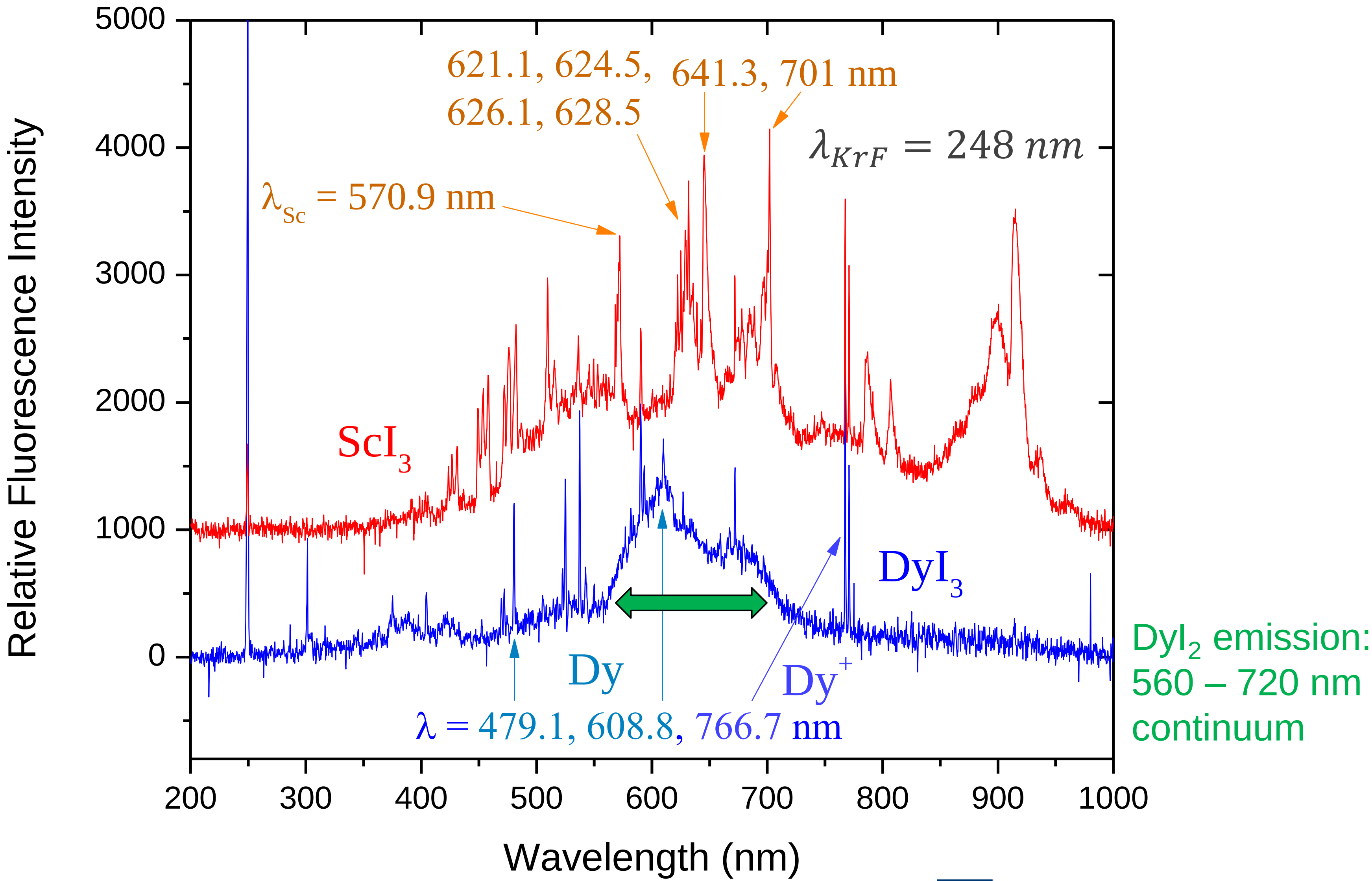
Density of species containing dysprosium calculated for a mixture containing dysprosium and iodine.

M. L. Beks, M. Haverlag, and J. J. A. M. van der Mullen, "A model for additive transport in metal halide lamps containing mercury and dysprosium tri-iodide," *Journal of Physics D: Applied Physics*, vol.41, no.12, May 2008.

Spectral Overview



Fluorescence Measurements



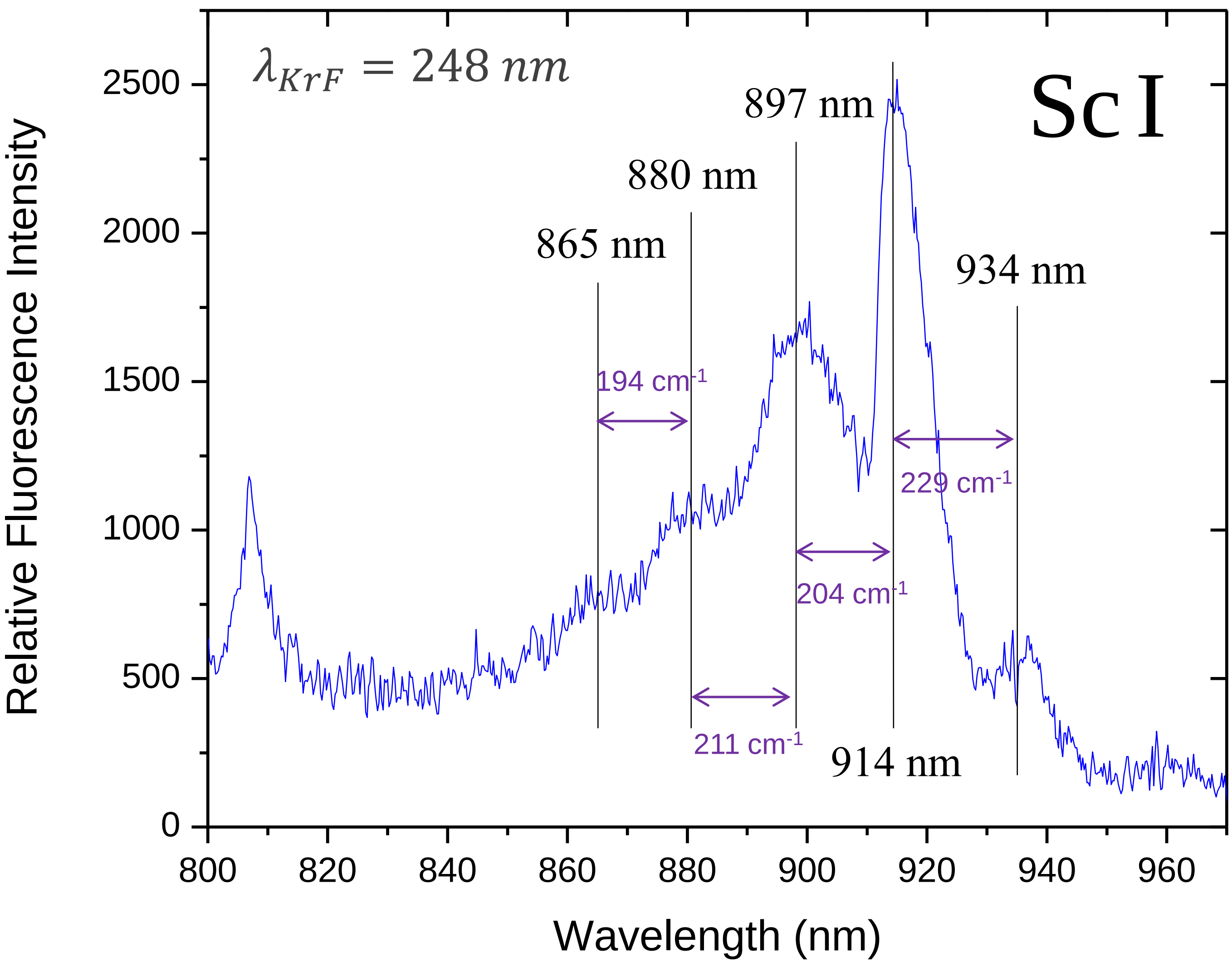
Fluorescence Lines Measured

Observed wavelengths (nm) matching with atomic lines

Iodine		Dysprosium	Scandium	
534.51	$^3F_4 \rightarrow {}^3D°_3$	479.13	570.86	$^4G°_{9/2} \rightarrow {}^4F_{9/2}$
589.40	$^2[1]°_{3/2} \rightarrow {}^2[2]_{3/2}$	608.83	621.07	$^2D°_{3/2} \rightarrow {}^2D_{3/2}$
671.88	$^3P_2 \rightarrow {}^5D°_1$	766.68	624.46	$^4D°_{1/2} \rightarrow {}^2D_{3/2}$
770.02	$^2[3]°_{7/2} \rightarrow {}^2[3]_{5/2}$		626.22	$^4D_{5/2} \rightarrow {}^4P°_{3/2}$
			628.47	$^4D_{3/2} \rightarrow {}^4P°_{3/2}$
			641.33	$^4F°_{5/2} \rightarrow {}^2D_{5/2}$
			701.02	N/A
			769.78	$^2D°_{5/2} \rightarrow {}^2P_{3/2}$

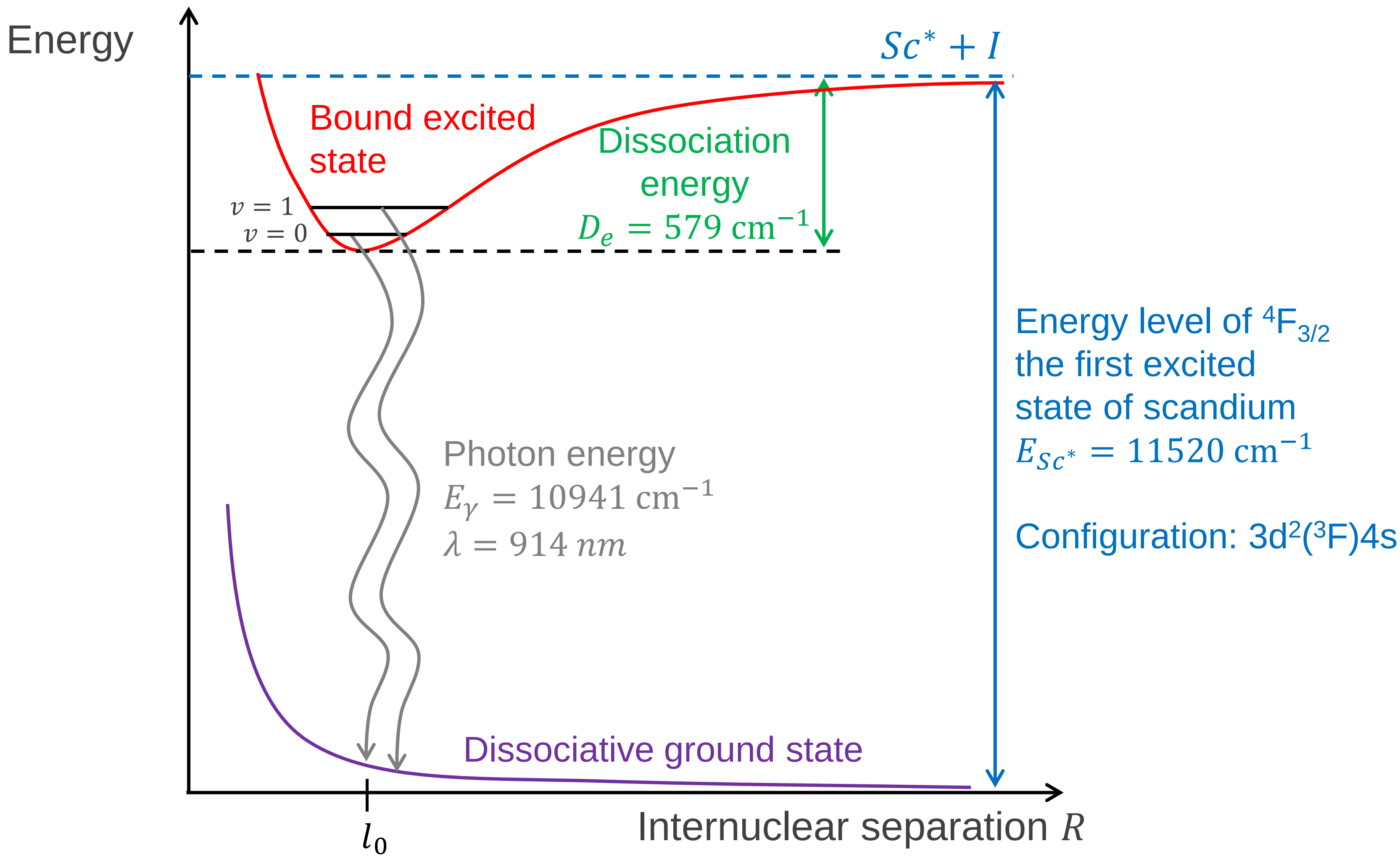
Kramida, A., Ralchenko, Yu., Reader, J. and NIST ASD Team (2012). *NIST Atomic Spectra Database*, National Institute of Standards and Technology, Gaithersburg, MD.

Focus on the ScI_3 Fluorescence Spectrum



Infrared feature associated to a ScI molecular bound → free transition

Quantitative Energy Diagram



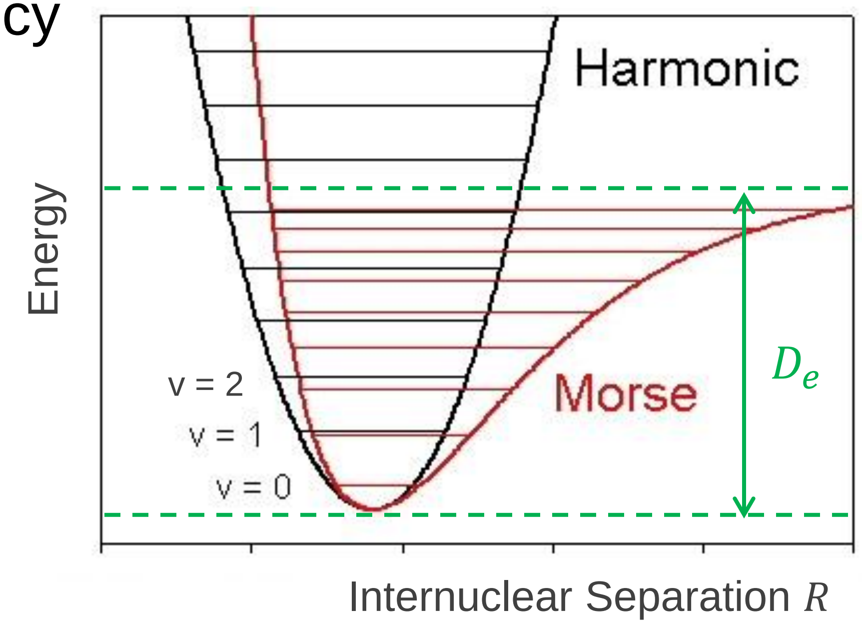
Vibrational Motion – Morse Potential

- $V_{Morse} = D_e\left(1 - e^{-a_e(l-l_0)}\right)^2$

- $E_v = \hbar\omega_e(v + 1/2) - \hbar\omega_e\chi_e(v + 1/2)^2$
- $\Delta E_v = \hbar\omega_e - 2\hbar\omega_e\chi_e(v + 1)$

- Harmonic vibrational frequency
  $\omega_e = a_e\sqrt{\frac{2D_e}{m}} \simeq \Delta E_v/\hbar$
  $\sim 200\ cm^{-1} = 6\ THz$
  $= 17\ nm$ around 914 nm

- Anharmonicity constant
  $\chi_e = \frac{\hbar\omega_e}{4D_e} \simeq 8.6\ \%$
  $\Rightarrow \omega_e\chi_e = 17\ cm^{-1}$



Conclusion

- Observation of coupling between lattice vibrations and the La^{3+} ion
- Observation of ScI bound → free transition after photoexcitation in the ultraviolet by 248 nm radiation from an KrF excimer laser
- Applications
  - Random lasers
  - Lighting : arc discharge lamps

Acknowledgments

- Thanks to
  - II-VI Foundation for $
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  - Labmates
  - You for you attention