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Intrinsic Fluorescence of Monomeric Chlorophyll-α at 674 nm: Stokes Shift–Linewidth Equivalence and the Vibronic Regime

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Abstract

Chlorophyll-α (Chl-α) fluoresces at 674 nm under monomeric conditions in ethanol, exhibiting a reproducible emission peak with a narrow homogeneous linewidth. This study analyzes the spectral parameters of this fluorescence using vibronic theory, interpreting the observed emission as resulting from an intrinsic balance between vibronic coupling and environmental dephasing. The near-equality of the Stokes shift and homogeneous linewidth, both $\approx 0.04\,eV$ are treated as an empirical relation, suggesting that the same low-frequency environmental modes influence both nuclear relaxation and dephasing. The Huang–Rhys factor $S \approx 0.225$ supports weak-to-intermediate vibronic coupling of the Qy excited state, placing Chl-α in a regime compatible with efficient energy transfer in photosynthetic systems. This work not only elucidates the spectroscopic properties of monomeric Chl-α but also provides a molecular baseline for determining how protein environments modulate spectral behavior and energy transfer.

Keywords: Monomeric Chl-α, Intrinsic Fluorescence, Stokes shift, Homogeneous linewidth, Qy transition.

1. Introduction

Chlorophyll-α (Chl-α) is the primary pigment in oxygenic photosynthesis, with its Qy transition dominating both absorption and fluorescence spectra. While fluorescence peaks typically range from 668 to 680 nm depending on solvent and concentration (Rätsep et al., 2009; Taniguchi & Lindsey, 2021), monomeric Chl-α in ethanol exhibits a reproducible emission maximum at 674 nm, with a homogeneous linewidth of $\Gamma_E \approx 14 \pm 1\,nm$. The absorption maximum near 660 nm, and the emission value were measured under controlled conditions (room temperature and low concentration to avoid aggregation) in a previous work (Peled & Popescu, 2024).

Here, we analyze these spectral parameters within the framework of vibronic theory. We propose that the near-equality of the Stokes shift ΔE_{Stokes} and homogeneous linewidth Γ_E reflects a spectroscopic balance, where the same low-frequency environmental modes influence both nuclear relaxation and dephasing. This balance places Chl-α in an intermediate vibronic regime, compatible with efficient energy transfer once embedded in antenna complexes. While prior studies have explored Chl-α fluorescence in various solvents, the 674 nm peak in ethanol stands out for its reproducibility and narrow linewidth, suggesting minimal environmental perturbation.

2. Spectroscopic Energy Scales in Chlorophyll-α

The Qy absorption maximum of Chl-α is near 660 nm, and the monomeric fluorescence peaks at 674 nm (Peled & Popescu, 2024). Using $E = hc/\lambda$ and the constant $hc = 1240\, eV \cdot nm$, the corresponding photon energies are $1.879\, eV$ and $1.840\, eV$, respectively, yielding a Stokes shift of $\Delta E_{Stokes} = 1.879 - 1.840 = 0.039\, eV$.

Using the differential relation $\Delta E \approx (hc/\lambda^2)\Delta\lambda$ and $\Delta\lambda = 14\, nm$ at $\lambda = 674\, nm$, the homogeneous linewidth is $\Gamma_E \approx 0.038\, eV$. The near-equality $\Delta E_{Stokes} \approx \Gamma_E \approx 0.039\, eV$ observed here is a noteworthy empirical relation, although not proof of a single microscopic mechanism. The error margin of $\pm 1\, nm$ in Γ_E does not significantly affect this interpretation, as the overlap with ΔE_{Stokes} remains within experimental uncertainty. This near-equality is however consistent with an intermediate vibronic regime, where coherent delocalization and incoherent relaxation are balanced.

3. Vibronic Regime and Transport

3.1 Vibronic Structure of the Qy Transition

The Qy excited state of Chl-α is best described as a vibronic manifold rather than a pure electronic level. Optical excitation drives geometric reorganization and redistributes Franck–Condon intensity across vibronic levels, particularly for modes in the $700 - 750\, cm^{-1}$ range associated with skeletal deformations of the porphyrin macrocycle (Reimers et al., 2022; Rätsep et al., 2009).

For a dominant vibrational mode ω, the Stokes shift and the Huang–Rhys factor S are related by $\Delta E_{Stokes} = 2S\hbar\omega$ (de Jong et al., 2015; Reimers et al., 2022). With $\Delta E_{Stokes} = 0.039\, eV$ and $\hbar\omega \approx 0.087\, eV$ for a $700\, cm^{-1}$ mode, $S \approx 0.225$. This places Chl-α in the weak-to-intermediate coupling regime, where the 0–0 transition remains prominent but the vibronic structure is clearly visible. This value is consistent with prior reports for Chl-α in non-polar solvents but contrasts with stronger coupling observed in protein-bound pigments (Rätsep et al., 2009).

3.2 Coherence and Dephasing

A simple estimate for the coherence time is $\tau_{coh} \approx \frac{\hbar}{\Gamma_E}$. For $\Gamma_E \approx 0.04\, eV$, this gives $\tau_{coh} \approx 1.6 \times 10^{-14}\, s$, or approximately $16\, fs$. This estimate reflects rapid dephasing at physiological temperature and should not be confused with the excited-state lifetime. Environmental fluctuations on this timescale not only destroy coherence but also assist energy redistribution by preventing localization and improving spectral overlap. Direct experimental confirmation via time-resolved spectroscopy would be of significant value.

3.3 Intermediate Regime

The balance between vibronic coupling and dephasing is consistent with an intermediate regime between coherent delocalization and incoherent hopping. It is important to clarify that monomeric fluorescence does not by itself demonstrate optimal energy transport. Rather, the observed spectral parameters place Chl-α in a regime that is compatible with efficient transport once the molecule is embedded in an antenna complex (Rebentrost et al., 2009). This hypothesis predicts that perturbations, such as changes in temperature or solvent polarity, should shift the system away from this balance, offering a testable experimental avenue.

4. Interpretation of the 674 nm Peak

The 674 nm fluorescence maximum can be interpreted as the 0–0 transition-dominated emission of monomeric Chl-α, shaped by vibronic coupling and modest environmental broadening. Unlike fluorescence in polar solvents, which typically exhibits broader, red-shifted peaks, the 674 nm emission in ethanol is remarkably narrow, supporting its assignment as an intrinsic chromophore property (Peled & Popescu, 2024).

The broader implication is that Chl-α's monomeric emission profile provides a useful baseline for understanding how protein environments alter spectral position, linewidth, and energy-transfer behavior *in vivo*. This is a physically reasonable hypothesis supported by the present spectral evidence, though it is not yet a settled conclusion.

5. Implications for Photosynthetic Systems

In antenna complexes, coherence can help a wave packet explore local configurations quickly, while dephasing can prevent trapping in suboptimal states. A body of literature supports the idea that environmental noise can improve transport efficiency under certain conditions (Rebentrost et al., 2009; Panitchayangkoon et al., 2010). While the wavelike energy-transfer interpretation advanced in some early studies (Engel et al., 2007) has been substantially debated, the mechanistic picture of environment-assisted transport remains an active research area.

Chl-α monomers do not inherently demonstrate optimal energy transport, but their spectroscopic parameters may position them near a useful crossover regime between coherent and incoherent transport. Protein scaffolds further tune coupling, linewidth, and reorganization energy to optimize function in the full complex. The 674 nm peak could therefore serve as a reference for engineering artificial photosynthetic systems or probing protein-induced spectral shifts.

6. Conclusions

Monomeric Chl-α in ethanol fluoresces at 674 nm, with a Stokes shift and homogeneous linewidth both near $0.04\ eV$ (Peled & Popescu, 2024). The Huang–Rhys factor ($S \approx 0.225$) supports weak-to-intermediate vibronic coupling. We interpret the near-equality $\Delta E_{Stokes} \approx \Gamma_E$ as a noteworthy empirical observation that warrants further theoretical and experimental investigation, though not as proof of a single mechanism. If confirmed across solvents and temperatures, this balance could serve as a molecular baseline for understanding how protein environments modulate spectral behavior and energy transfer in photosynthetic systems, with potential implications for bio-inspired light-harvesting materials. Future work should explore the generality of this balance and connect it to full spectral-density models.

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