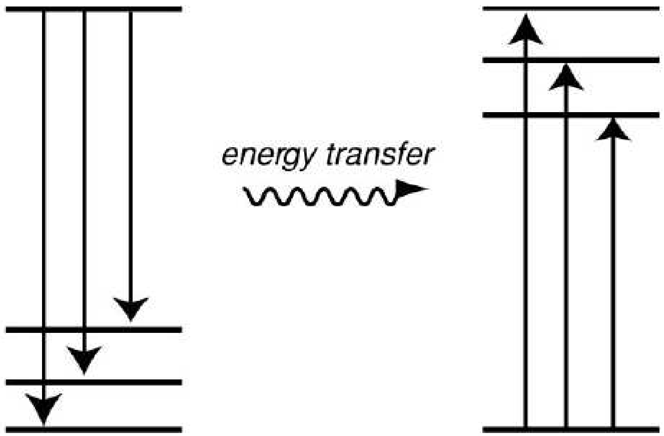
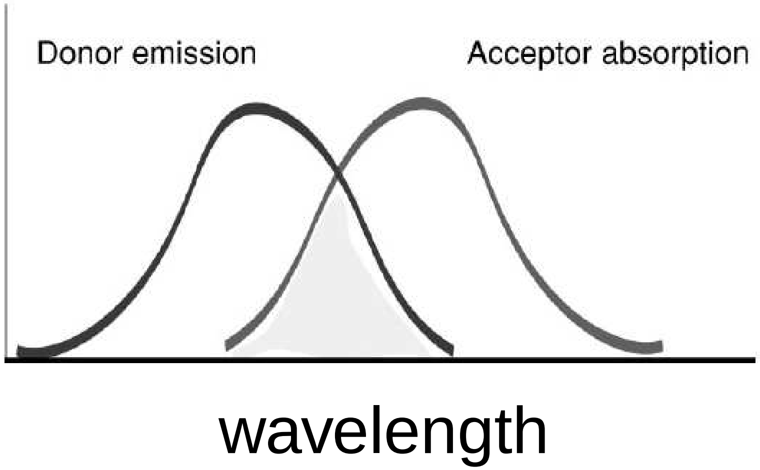
Excitation energy transfer

Gerrit C. Groenenboom

Theoretical Chemistry
Institute for Molecules and Materials
Radboud University Nijmegen
The Netherlands

Förster Resonant Energy Transfer





Scholes, Annu. Rev. Phys. Chem. **54**, 57 (2003)

$$DA \xrightarrow{h\nu} D^*A \rightarrow \begin{cases} DA + h\nu' \\ DA^* \end{cases}$$

FRET assumptions:

Condensed phase

Vibr. relaxation fast

Incoherent

Dipole-dipole interaction

T. Förster, Ann. Phys. 2, 55 (1948)

Fermi Golden rule:

$$\Gamma = \sum_f \frac{2\pi}{\hbar} |V_{fi}|^2 \delta(E_f - E_i)$$

Coupling matrix element

$$V_{fi} = \langle D_k {A^*}_l | \hat{V} | D^* A \rangle, \quad E_f = E_i + \epsilon_l^{(A)} - \epsilon_k^{(D)}$$

Dipole-dipole contribution:

$$V_{fi} = \frac{1}{R^3}[\boldsymbol{\mu}_k^{(D)} \cdot \boldsymbol{\mu}_l^{(A)} - 3(\hat{\boldsymbol{R}} \cdot \boldsymbol{\mu}_k^{(D)})(\hat{\boldsymbol{R}} \cdot \boldsymbol{\mu}_l^{(A)})] = \frac{\mu_k^{(D)} \mu_l^{(A)}}{R^3} \kappa$$

FRET (continued)

Combined:

$$\Gamma = \frac{2\pi}{\hbar}\frac{\kappa^2}{R^6}\sum_{kl}|\mu_k^{(D)}|^2|\mu_l^{(A)}|^2\delta(\epsilon_l^{(A)}-\epsilon_k^{(D)})$$

The trick:

$$\delta(\epsilon_l^{(A)}-\epsilon_k^{(D)}) = \int \delta(\epsilon-\epsilon_l^{(A)})\delta(\epsilon-\epsilon_k^{(D)})d\epsilon$$

Result:

$$\Gamma = \frac{2\pi}{\hbar}\frac{\kappa^2}{R^6}\int \underbrace{\left[\sum_k|\mu_k^{(D)}|^2\delta(\epsilon-\epsilon_k^{(D)})\right]}_{\sim D_{\text{emission}}(\epsilon)/\epsilon^3}\underbrace{\left[\sum_l|\mu_l^{(A)}|^2\delta(\epsilon-\epsilon_l^{(A)})\right]}_{\sim A_{\text{absorption}}(\epsilon)/\epsilon}d\epsilon$$

Measuring distance

Competition between energy transfer

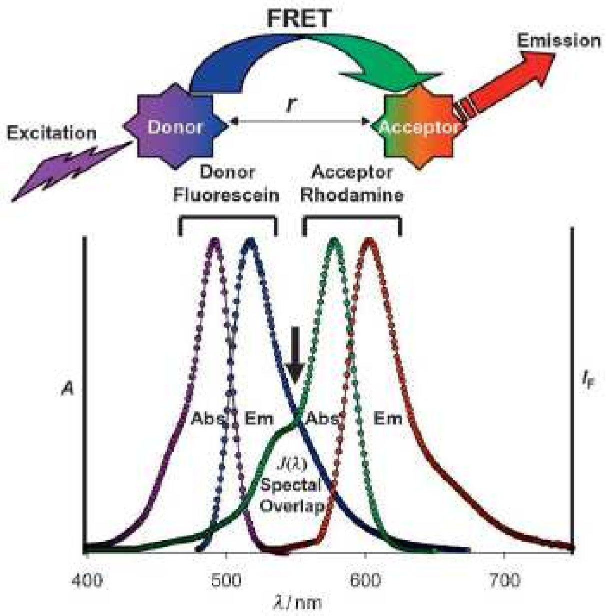
$$\Gamma^{(ET)} \sim R^{-6}$$

and donor fluorescense gives FRET efficiency:

$$E = \frac{1}{1 + (R/R_0)^6}$$

- Typical range: $R_0 = 10 \ldots 100$ Å
- Correction for medium refractive index: n^{-4}
- Shorter distances: wave function overlap (Dexter) $\sim e^{-\alpha R}$
- Longer distances: real photons (QED) $\sim R^{-2}$

Bio applications



Sapsford *et al.*, Angew. Chemie **45**, 4562 (2006)

quote:

P. R. Selvin, Nature struct. biol. (2000):

"Tsien *et al.*^{5} and other workers have developed several GFP FRET constructs that are used to monitor the biochemical environment inside living cells."

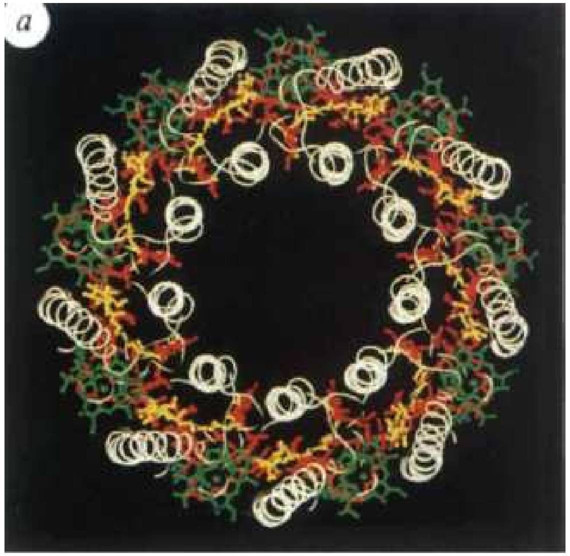
- Single molecule FRET
- time-resolved FRET
- Multi-chromophoric FRET
- Quantum dot FRET
- Two-photon FRET
- Polarized FRET
- . . .

Company: Black Hole Quencher $^{\mathrm{TM}}$

Light Harvesting systems

Coherence in the B800 Ring of Purple Bacteria LH2

Cheng and Silbey, Phys. Rev. Lett. (2006)



McDemott *et al.*, Nature (1995)

$$\hat{H} = \sum_{n=1}^{9} E_n |n\rangle\langle n| + \sum_{n=m\pm1} J_{nm} |n\rangle\langle m|$$

$$|\psi_\alpha\rangle = \sum_n |n\rangle c_n^{(\alpha)}$$

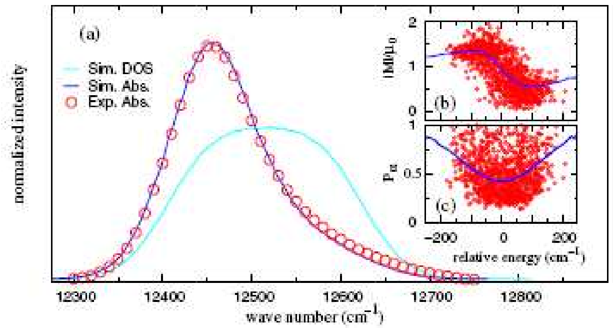
$$\vec{M}_\alpha = \sum_n c_n^{(\alpha)} \vec{\mu}_n$$

$$I(\omega) = \left\langle \sum_\alpha |\vec{M}_\alpha|^2 \delta(\omega - \epsilon_\alpha) \right\rangle_s$$

Coherence in B800

Fit with 100 000 Monte Carlo simulations:

- $J = -27$ cm^{-1}
- Intercomplex disorder: $\sigma_I = 10$ cm^{-1}
- Intracomplex disorder: $\sigma_D = 60$ cm^{-1}
- Nearest neighbor coupling disorder: $\sigma_D = 60$ cm^{-1}

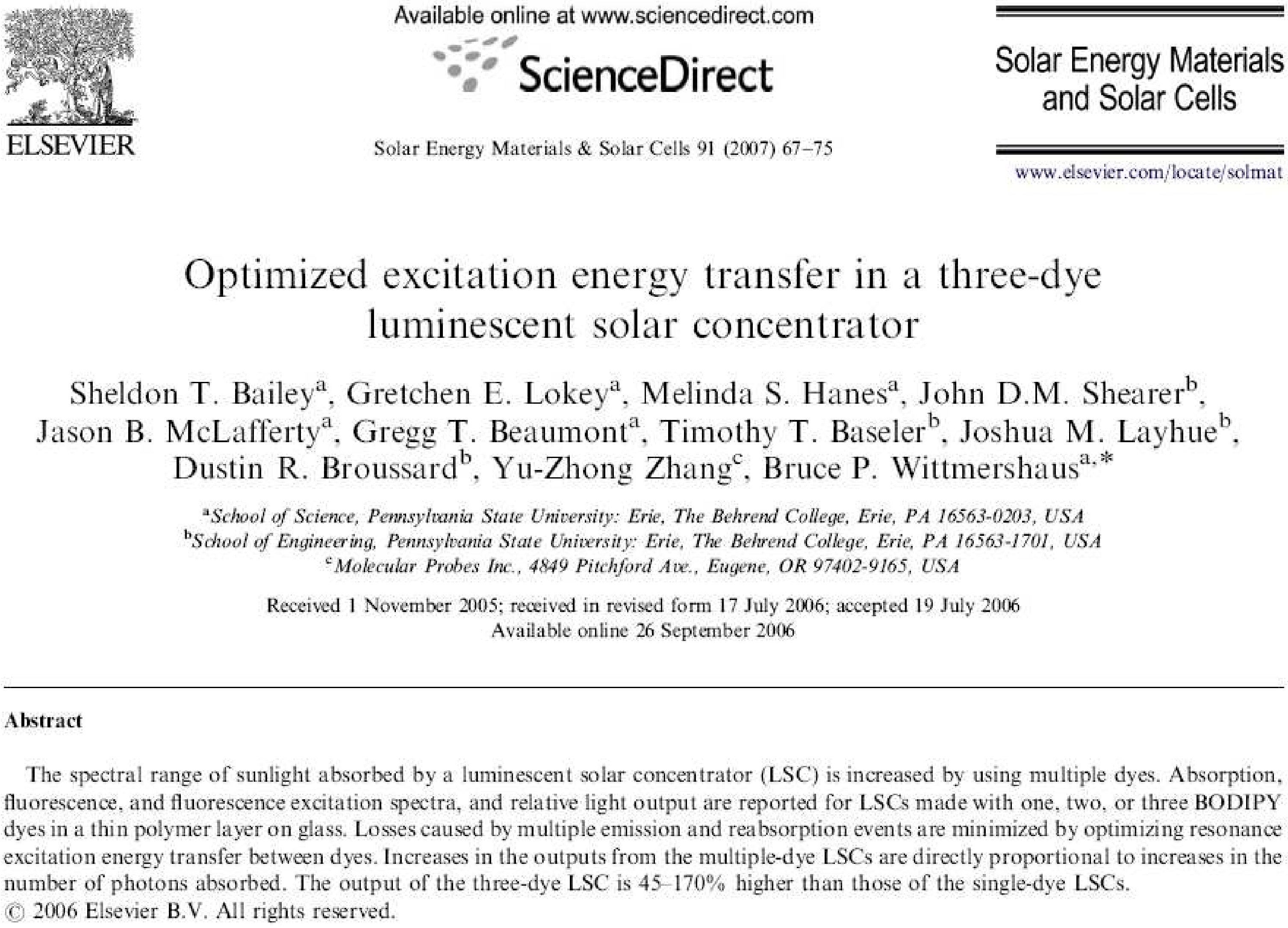


$$P_\alpha = \sum_{n=1}^{9} |c_n^{(\alpha)}|^4$$

Localized: $P_\alpha = 1$

Delocalized: $P_\alpha = 1/9$

Application organic solar cells



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Solar Energy Materials & Solar Cells 91 (2007) 67–75

Solar Energy Materials and Solar Cells

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Optimized excitation energy transfer in a three-dye luminescent solar concentrator

Sheldon T. Bailey[a], Gretchen E. Lokey[a], Melinda S. Hanes[a], John D.M. Shearer[b], Jason B. McLafferty[a], Gregg T. Beaumont[a], Timothy T. Baseler[b], Joshua M. Layhue[b], Dustin R. Broussard[b], Yu-Zhong Zhang[c], Bruce P. Wittmershaus[a,*]

[a] *School of Science, Pennsylvania State University: Erie, The Behrend College, Erie, PA 16563-0203, USA*
[b] *School of Engineering, Pennsylvania State University: Erie, The Behrend College, Erie, PA 16563-1701, USA*
[c] *Molecular Probes Inc., 4849 Pitchford Ave., Eugene, OR 97402-9165, USA*

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Abstract

The spectral range of sunlight absorbed by a luminescent solar concentrator (LSC) is increased by using multiple dyes. Absorption, fluorescence, and fluorescence excitation spectra, and relative light output are reported for LSCs made with one, two, or three BODIPY dyes in a thin polymer layer on glass. Losses caused by multiple emission and reabsorption events are minimized by optimizing resonance excitation energy transfer between dyes. Increases in the outputs from the multiple-dye LSCs are directly proportional to increases in the number of photons absorbed. The output of the three-dye LSC is 45–170% higher than those of the single-dye LSCs.

FRET in transition metal complexes

Hauser *et al.*, Top. Curr. Chem. **241**, 65 (2004)

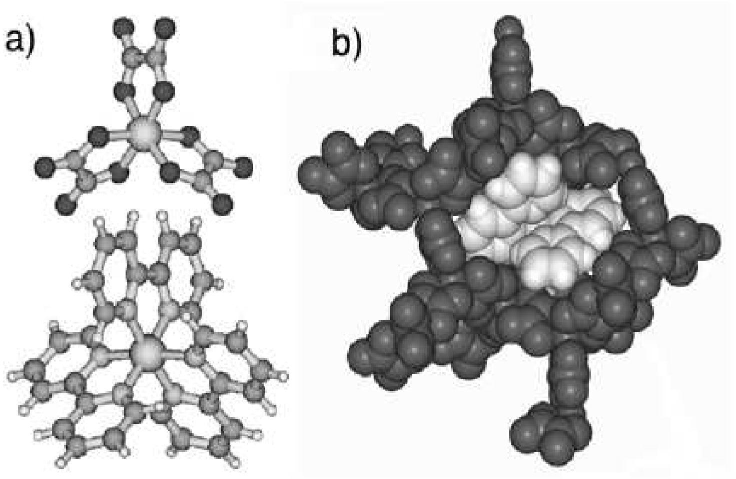
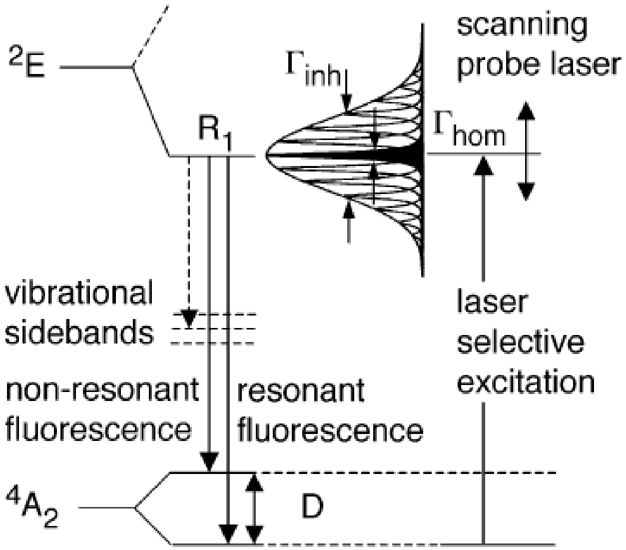


Fig. 3 **a** The building blocks $[Cr(ox)_3]^{3-}$ and $[Cr(bpy)_3]^{3+}$. **b** Space-filling model of the three-dimensional oxalate network (*dark*) encapsulating the tris-bipyridine cation (*light*) as in $[NaCr(ox)_3][Cr(bpy)_3]ClO_4$

Doped in photophysically inert $[Rh(bpy)_3][NaAl(ox)_3]ClO_4$.

Hauser *et al.* Top. Curr. Chem. 241, 65 (2004)



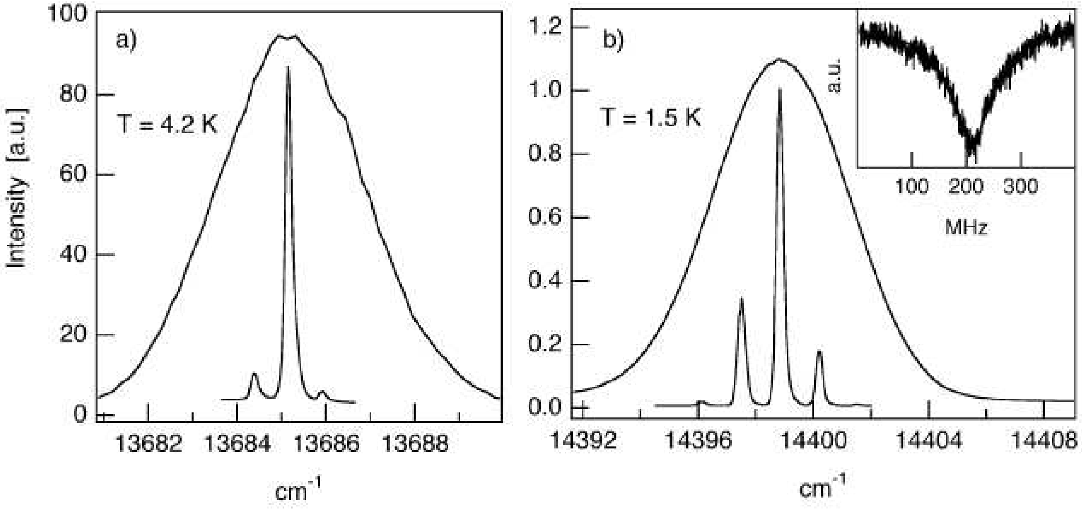


Fig. 8 a FLN spectrum of $[Rh_{1-y}Cr_y(bpy)_3][NaAl(ox)_3]ClO_4$, y=0.5%, at 4.2 K. b FLN spectrum of $[Rh(bpy)_3][NaAl_{1-x}Cr_x(ox)_3]ClO_4$, x=0.5%, at 1.8 K. *Insert*: transient hole burning spectrum at 1.5 K

Hauser *et al.* Top. Curr. Chem. 241, 65 (2004)

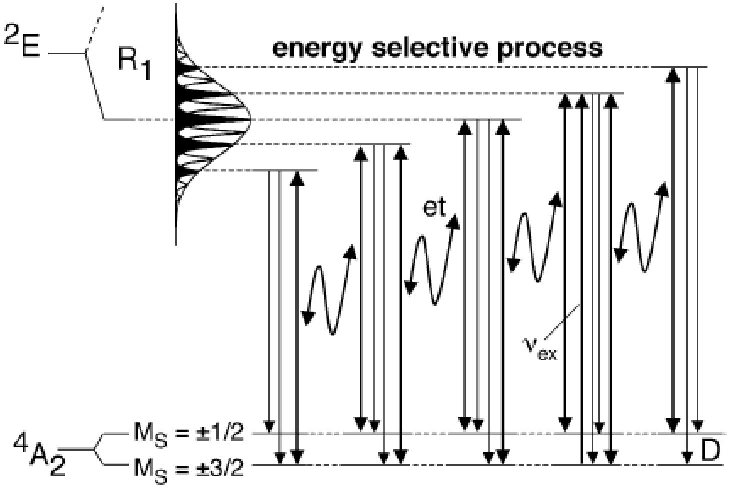
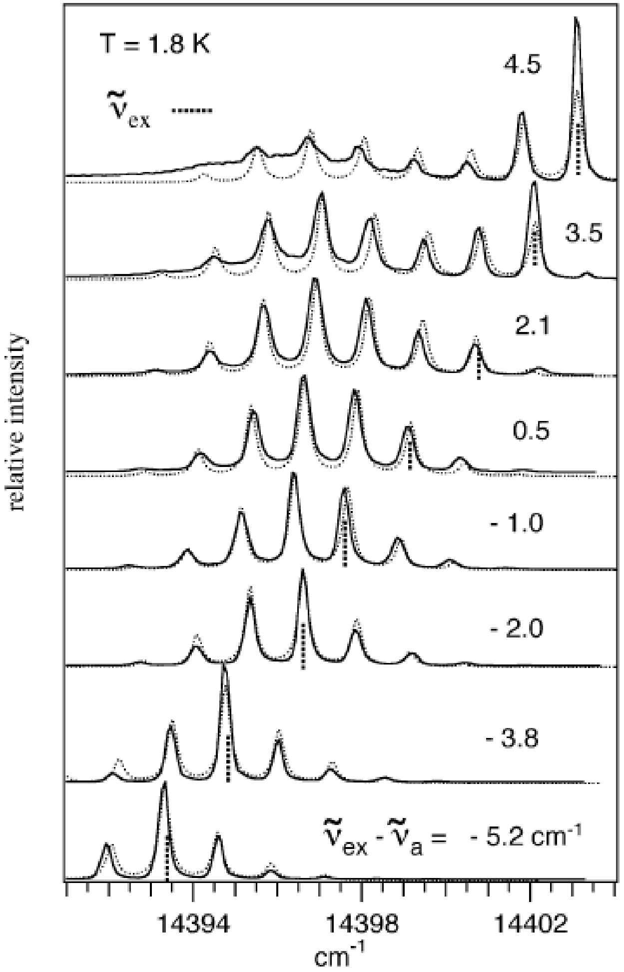
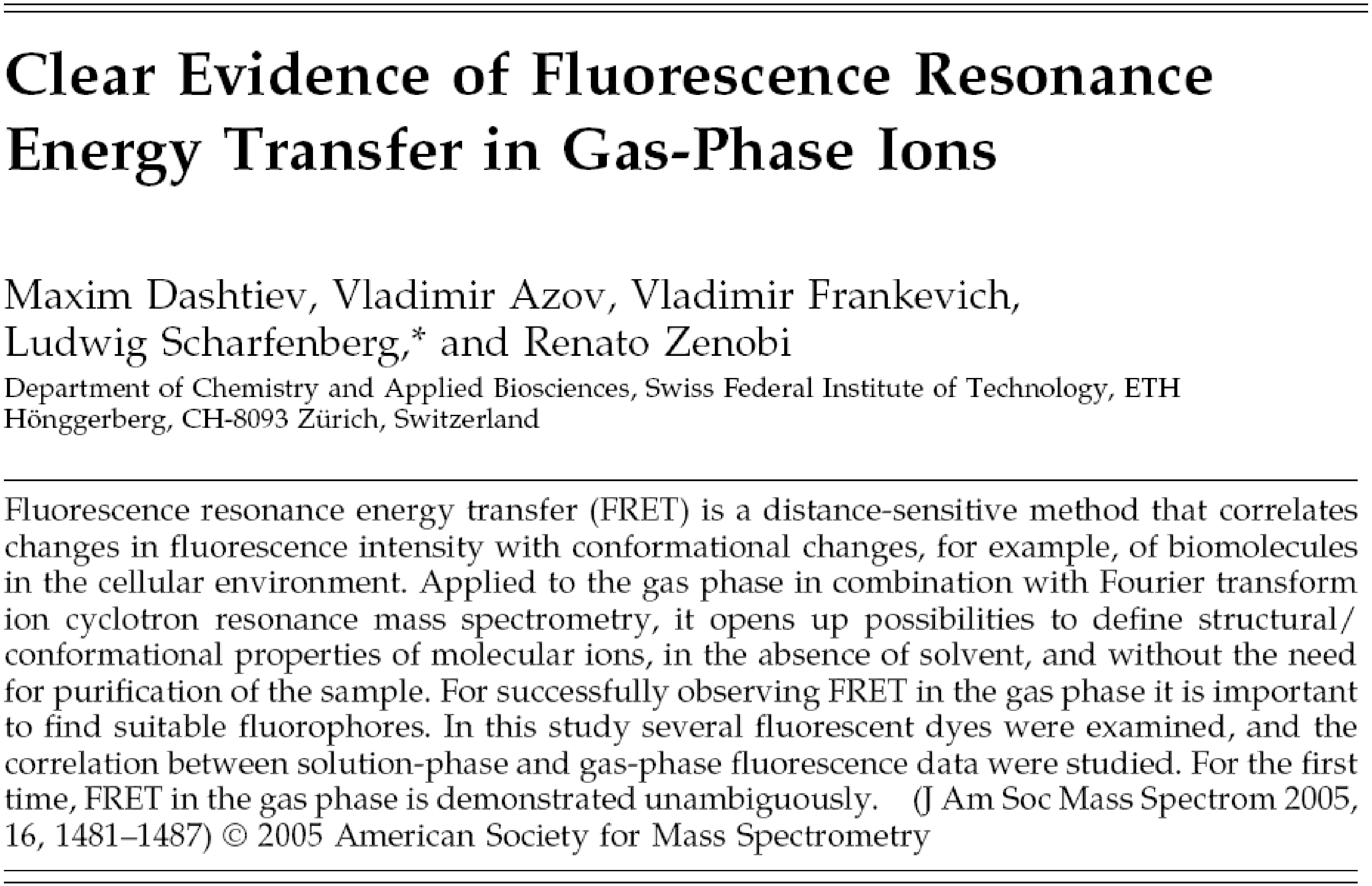


Fig. 17 Scheme for the resonant energy migration within the R_1 line of $[Cr(ox)_3]^{3-}$ in $[Rh(bpy)_3][NaCr(ox)_3]ClO_4$



Solid line: experiment, dashed line: rate model

Gas phase FRET

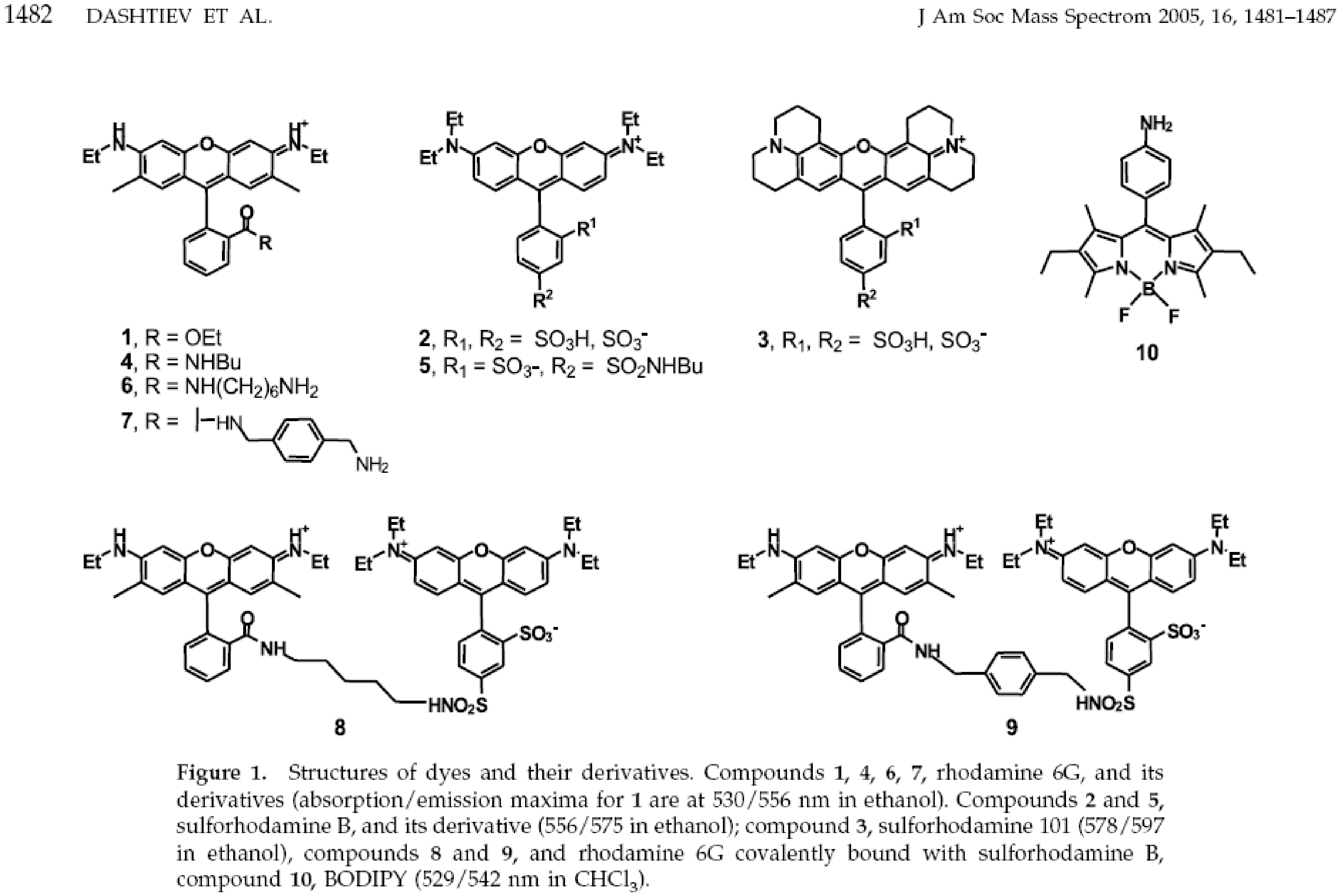


Clear Evidence of Fluorescence Resonance Energy Transfer in Gas-Phase Ions

Maxim Dashtiev, Vladimir Azov, Vladimir Frankevich,
Ludwig Scharfenberg,* and Renato Zenobi
Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH
Hönggerberg, CH-8093 Zürich, Switzerland

Fluorescence resonance energy transfer (FRET) is a distance-sensitive method that correlates changes in fluorescence intensity with conformational changes, for example, of biomolecules in the cellular environment. Applied to the gas phase in combination with Fourier transform ion cyclotron resonance mass spectrometry, it opens up possibilities to define structural/conformational properties of molecular ions, in the absence of solvent, and without the need for purification of the sample. For successfully observing FRET in the gas phase it is important to find suitable fluorophores. In this study several fluorescent dyes were examined, and the correlation between solution-phase and gas-phase fluorescence data were studied. For the first time, FRET in the gas phase is demonstrated unambiguously. (J Am Soc Mass Spectrom 2005, 16, 1481–1487) © 2005 American Society for Mass Spectrometry

Gas phase FRET



1482 DASHTIEV ET AL. J Am Soc Mass Spectrom 2005, 16, 1481–1487

Figure 1. Structures of dyes and their derivatives. Compounds **1**, **4**, **6**, **7**, rhodamine 6G, and its derivatives (absorption/emission maxima for **1** are at 530/556 nm in ethanol). Compounds **2** and **5**, sulforhodamine B, and its derivative (556/575 in ethanol); compound **3**, sulforhodamine 101 (578/597 in ethanol), compounds **8** and **9**, and rhodamine 6G covalently bound with sulforhodamine B, compound **10**, BODIPY (529/542 nm in $CHCl_3$).

S_1/S_2 exciton splitting in the (2-pyridone)$_2$ dimer

Müller, Talbot, and Leutwyler, J. Chem. Phys. **116**, 2836 (2002)

Frenkel exciton theory

$$
\begin{aligned}
|S_0\rangle &= |A\rangle|B\rangle \\
|S_2\rangle &= \frac{|A\rangle^*|B\rangle + |A\rangle|B\rangle^*}{\sqrt{2}} \\
|S_1\rangle &= \frac{|A\rangle^*|B\rangle - |A\rangle|B\rangle^*}{\sqrt{2}}
\end{aligned}
$$

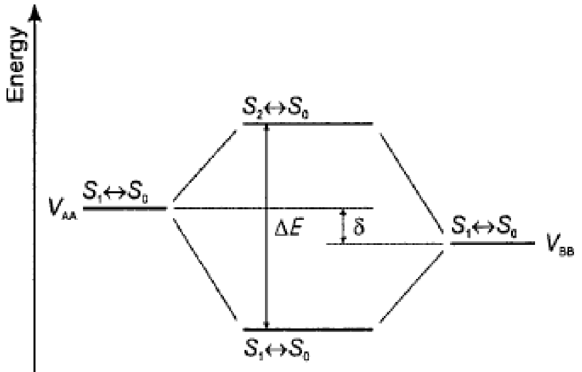


FIG. 2. Schematic energy level diagram for the Frenkel exciton splitting in a slightly unsymmetrical molecular dimer, such as $(2PY)_2-{}^{13}C$ or $(2PY)_2-d_1$. V_{AA}, V_{BB} are Coulomb integrals of the individual chromophores corresponding to the monomer $S_1 \leftrightarrow S_0$ transition energies, $\delta = |V_{AA} - V_{BB}|$ is the difference of monomer excitation energies, ΔE is the S_1/S_2 exciton splitting energy.

$$
E_\pm = \frac{V_{AA} + V_{BB} \pm \sqrt{(V_{AA} - V_{BB})^2 + 4V_{AB}^2}}{2}
$$

Exciton splitting

$$
\Delta E = |E_+ - E_-| = \sqrt{(V_{AA} - V_{BB})^2 + 4V_{AB}^2}
$$

Leutwyler *et al.*

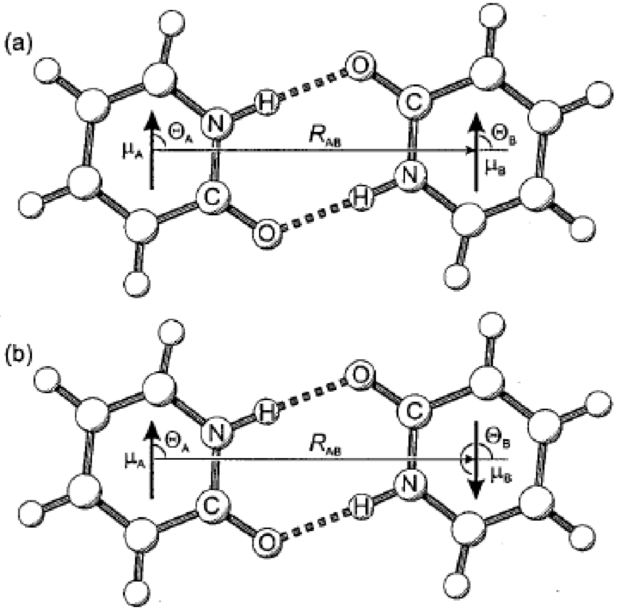


FIG. 1. Geometric structure of (2PY)$_2$ [B3LYP/6-311++G(d,p)] and interaction between the electronic transition dipole moments $\vec{\mu}_A$, $\vec{\mu}_B$ of the 2-pyridone moieties: (a) in-phase combination or parallel alignment, corresponding to the allowed $S_2 \leftrightarrow S_0$ $({}^1B_u \leftrightarrow {}^1A_g)$ electronic transition, (b) out-of-phase combination or antiparallel alignment, corresponding to the forbidden $S_1 \leftrightarrow S_0$ $({}^1A_g \leftrightarrow {}^1A_g)$ transition. $R_{AB} = 5.36$ Å is the center-of-mass distance between the dimers.

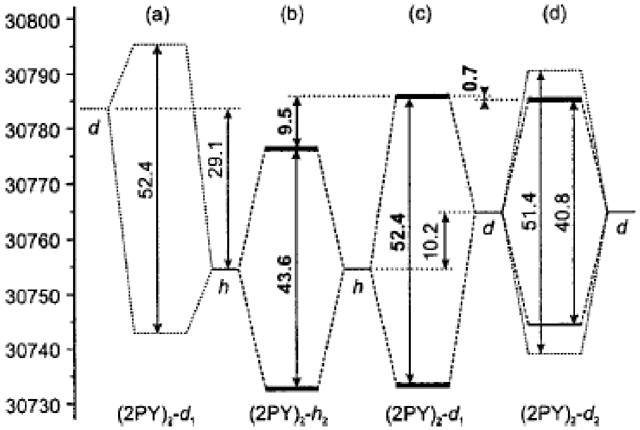


FIG. 7. Schematic representation of the observed exciton splittings and the $S_1 \leftrightarrow S_0$ and $S_2 \leftrightarrow S_0$ transition energies of (b) (2PY)$_2 - h_2$, (c) (2PY)$_2 - d_1$, and (d) (2PY)$_2 - d_2$, represented by thick horizontal lines. UV transition wave numbers are marked on the left. The observed exciton splittings and $S_2 \leftrightarrow S_0$ deuteration shifts are labeled with boldface numbers. On the left and right are calculated exciton splittings of (a) (2PY)$_2 - d_1$ and (d) (2PY)$_2 - d_2$, which are marked with dotted lines, the splittings are labeled in standard font. For details of the model calculations, see the text.

Ab initio

Assessment of quantum chemical methods and basis sets for excitation energy transfer

R. F. Fink *et al.*, Chem. Phys. **346**, 275 (2008)

Test: Benzene dimer

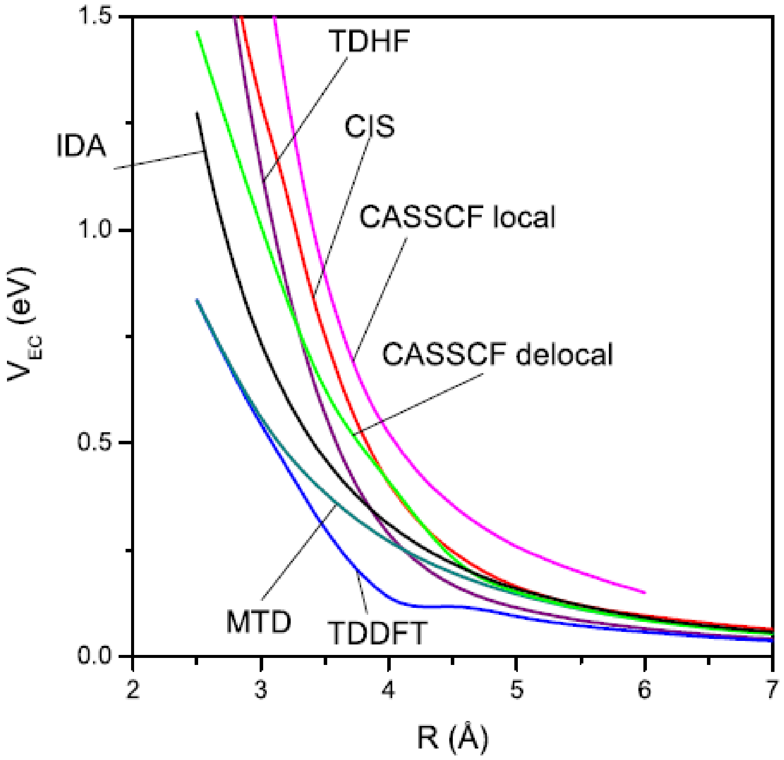


Fig. 6. Electronic coupling parameter of the states with $1\,^1\mathcal{E}_{1u}$-character as function of the distance, *R*, obtained with the cc-pVDZ basis and different approaches.

Conclusion

- FRET is fun