Intramolecular Hydrogen Bonding in Two Model Systems Studied by Picosecond Time-Resolved Fluorescence Spectroscopy in a Supersonic Jet

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Hypericin: St. John’s wort (*Hypericum perforatum*)

- Photoinduced virucidal and antitumor activities
- Photosensitizer in photodynamical therapy of cancer


**Dihydroxyanthraquinones**

- Anthracycline antitumor antibiotics, e.g. adriamycin, aclacinomycin and daunomycin
Asymmetric Lippincott-Schroeder Potentials

Symmetric Double-Minimum Potentials

\[ \text{9,10-quinone} \]

\[ \text{1,10-quinone} \]

\[ \text{1,8-dihydroxyanthraquinone} \]

\[ \text{9-hydroxyphenalenone} \]

1. Experimental Methods & Setups
   - Fluorescence Excitation Spectroscopy
   - Time-correlated Single Photon Counting

2. Frequency- & Time-domain Measurements
   - 1,8-Dihydroxyanthraquinone
   - 1-Aminoanthraquinone

3. Summary
   - What is the spectroscopic & kinetic evidence for the strength of a particular intramolecular hydrogen bond?
   - What is the evidence for the occurrence of excited-state intramolecular H-atom transfer?
Outline

1. **Experimental Methods & Setups**
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2. **Frequency- & Time-domain Measurements**
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Time-domain Experimental Method

Time-correlated Single Photon Counting

many excitation-detection-cycles without any detected photon

1st detected photon

many excitation-detection-cycles without any detected photon

2nd detected photon

…after many excitation-detection-cycles
**Time-correlated Single Photon Counting: Laser Setup**

**Nd:YVO₄**

**Dye Laser**

- 355 nm
- 10 ps, 80 MHz
- 1.2 W

**Auto-correlator**

- 396-473 nm
- 7-8 ps
- 1.6-2.5 cm⁻¹

**LF**

**PM**

**FM**

**P**

**M**

**BS**

**PD**

**OM**

**TCSPC Stop**
Time-correlated Single Photon Counting: Optical Setup

Experimental setup

Time Resolution: 50-70 ps
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Low-resolution FE Spectrum of 1,8-Dihydroxyanthraquinone

Energy Dependence of the Fluorescence Lifetimes $\tau_{fl}$
Two Energy Regimes: $< 600 \text{ cm}^{-1}$ and $> 600 \text{ cm}^{-1}$
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H-Atom Transfer Reaction Coordinate $R_-$

$$ R_- = \frac{R_{01H} - R_{02H}}{2} $$

Ab initio H-Atom Transfer Potentials

Relaxed Potential Energy Scans for 1,8-Dihydroxyanthraquinone
Ab initio H-Atom Transfer Potentials

Three Scenarios for the Static & Dynamic Fluorescence Properties
Ab initio H-Atom Transfer Potentials

First Scenario: Herzberg-Teller Coupling

< 600 cm$^{-1}$: \( A_2 \times B_2 = b_1 \) vibronic bands with \( c \)-type rotational structure

> 600 cm$^{-1}$: Symmetry-allowed vibronic transitions with \( a \)-type rotational structure
Second Scenario: Fast Intramolecular H-Atom Transfer

< 600 cm$^{-1}$: Symmetry-allowed vibronic transitions with $a$-type rotational structure

> 600 cm$^{-1}$: Fast intramolecular H-atom transfer & 1,10-quinone well fluorescence
< 600 cm$^{-1}$: Non-vertical cross-well excitation into the 1,10-quinone well

> 600 cm$^{-1}$: Vertical excitation into the 9,10-quinone well
Frequency-domain Measurements

Rotational Band Contour of the $0^0_0$ Transition

long-axis, parallel polarized transition dipole moment

$S_1$ state is of $B_2$ symmetry!

Low-resolution Fluorescence Spectrum of 1-Aminoanthraquinone


E(0^0) = 21233 cm\(^{-1}\)
Time-domain Measurements

Energy Dependence of the Fluorescence Lifetimes $\bar{\tau}_{fl}$
Time-domain Measurements

Fluorescence Decay Curves

Double-exponential fit: \( \bar{\tau}_{\text{fl}} = 1.243 \text{ ns} \) at \( E_{\text{exc}} = 940 \text{ cm}^{-1} \)
Energy Dependence of the Rate Constant $k_{fl}$ of Fluorescence
Fit according to Fermi’s Golden Rule

Fermi’s Golden Rule:

\[
\frac{1}{\tau_{\text{fl}}(E)} = k_{\text{fl}}(E) = k_{\text{rad}} + \frac{2\pi}{\hbar} |V_{zf}|^2 \rho_{S_0}(E)
\]
Ab initio H-Atom Transfer Potentials

Relaxed Potential Energy Scans for 1-Aminoanthraquinone

\[ V(R_{\perp}) \text{[cm}^{-1}] \]

- TDDFT/6-31G(d,p) energies on CIS/6-31G(d,p)-MEP
- CIS/6-31G(d,p)
- HF/6-31G(d,p)
- B3LYP/6-31G(d,p)

\[ R_{\perp} \text{[Å]} \]
Strength of Intramolecular Hydrogen Bonds

Molecules with Different Rotamers

1,8-dihydroxyanthraquinone

1,4-dihydroxyanthraquinone

9-hydroxyphenalenone

tropolone

6-benzanthrone

7-benzanthrone

salicylic acid

o-hydroxybenzaldehyde

naphthazarine

malonaldehyde

1-aminoanthraquinone
Total Charge Density $\rho(r_c)$ at the Bond Critical Point $(3, -1)$

- **Atom in a molecule:**
  Region of 3D-space bounded by a surface that satisfies the quantum boundary condition of zero flux in the gradient vector field of the charge density:

  $$\nabla \rho(r) \cdot n(r) = 0 \quad \text{for} \quad \forall r.$$

- **Necessary condition for a bond between two atoms**
  The existence of unique line along which the electronic charge density is a maximum with respect to any neighbouring line and which is defined by the two vectors of $\nabla \rho$ which originate at the bond critical point $(3, -1)$.

Intermolecular Hydrogen Bonds

- **Linear \( \rho(r_c) - E_{HB} \)** for intermolecular hydrogen bonds between different nitriles and hydrogen fluoride (HF/6-31G(d,p), \( R = 0.999 \))
  

- **Linear \( \rho(r_c) - E_{HB} \)** for for intermolecular hydrogen bonds between different nitriles and hydrogen chloride (HF/6-31G(d,p), \( R = 0.998 \))
  

- **Linear \( \rho(r_c) - E_{HB} \)** relationship for intermolecular hydrogen bonds between different bases and hydrogen fluoride (HF/6-311++G(d,p)//6-31G(d,p), \( R = 0.869 \))
  

- **Linear \( \rho(r_c) - E_{HB} \)** relationship for the van der Waals complexes formaldehyde–chloroform, acetone–chloroform, benzene–formaldehyde and 1,1-dichloroethane–acetone (HF/6-31G(d,p), \( R = 0.998 \))
  
Linear $\rho(r_c)-E_{\text{HB}}$ Relationship for Intramolecular Hydrogen Bonds
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## Results on 1,8-dihydroxyanthraquinone

- FE Spectrum exhibits two distinct excess energy ranges.
- Fluorescence bands *below* \( \sim 600 \text{ cm}^{-1} \) originate in the 9,10-quinone well.
- Fluorescence bands *above* \( \sim 600 \text{ cm}^{-1} \) originate in the proton-transferred 1,10-quinone well.
- The \( S_1 \) potential is double-minimum-type. But the Lippincott-Schroeder picture has to be modified partially.
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Results on 1-aminoanthraquinone

- The \( S_1 \) potential is single-minimum-type.
- Uniform energy dependence of the fluorescence lifetimes can be accounted for by Fermi’s Golden Rule and is attributed to internal conversion to \( S_0 \).
- Low charge density at the bond critical point \( \rho(r_c) \) in \( S_0 \) and the high H-atom transfer barrier in \( S_1 \) indicate the weakness of the intramolecular hydrogen bond.
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