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

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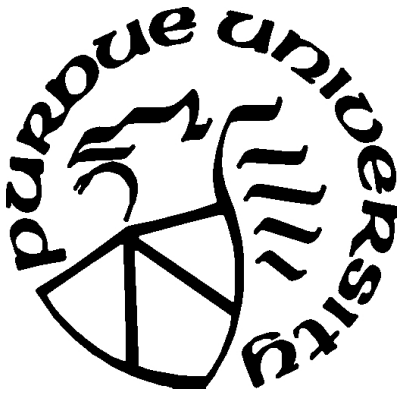
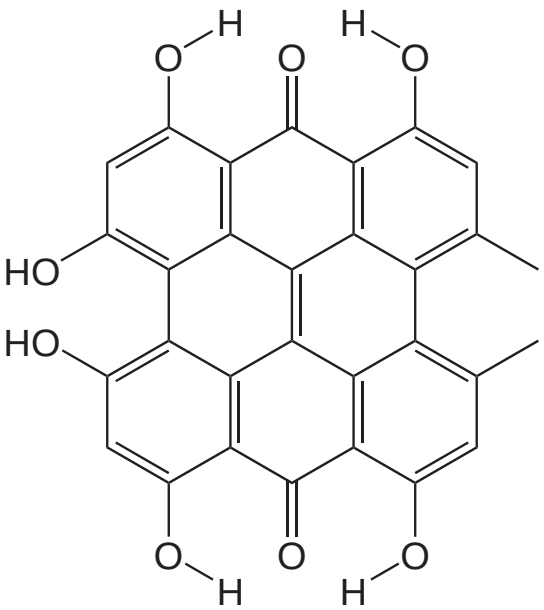
Georg-August-Universität Göttingen



International Symposium on Molecular Spectroscopy: 62nd Meeting – June 18–22, 2007

Motivation



Hypericin

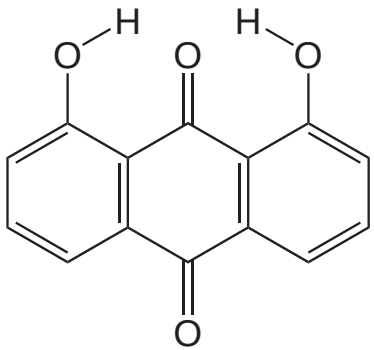
Hypericin: St. John's wort (*Hypericum perforatum*)

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

H. Falk, *Angew. Chem.*, **1999**, *111*, 3306.

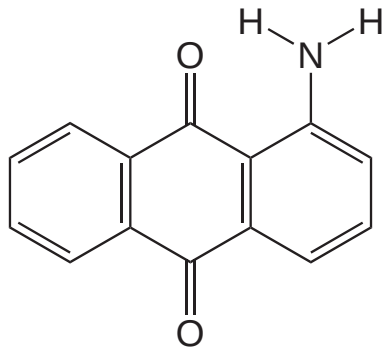
Dihydroxyanthraquinones

- Anthracycline antitumor antibiotics, e. g. adriamycin, aclacinomycin and daunomycin



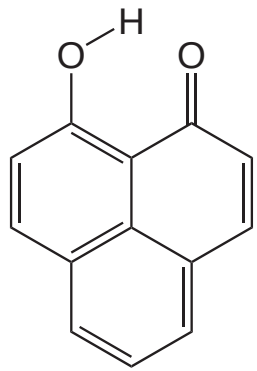
1,8-dihydroxyanthraquinone

1,8-DHAQ



1-aminoanthraquinone

1-AAQ

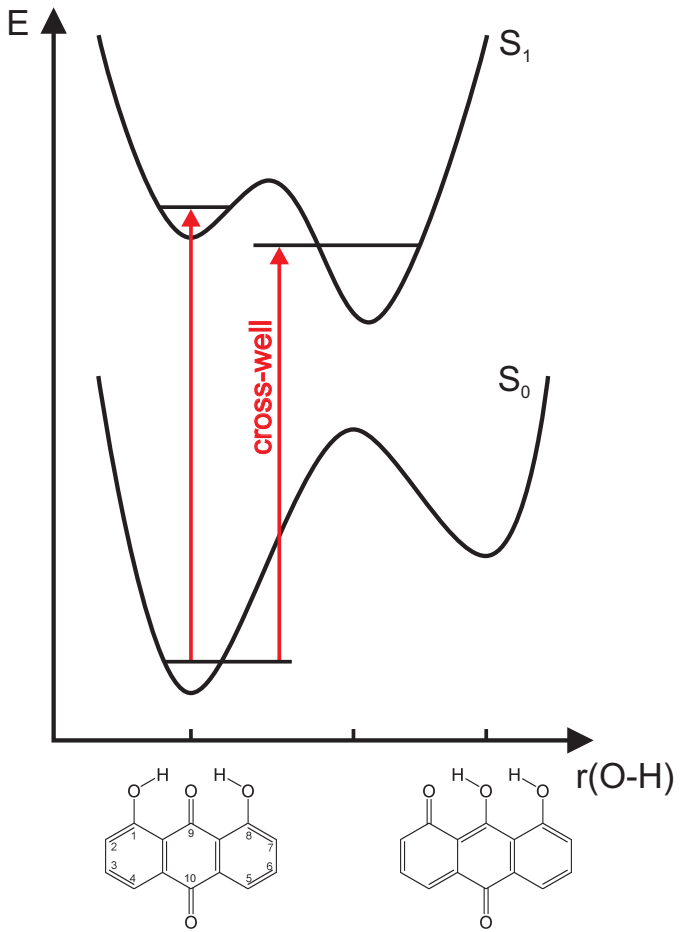


9-hydroxyphenalenone

9-HPA

Motivation

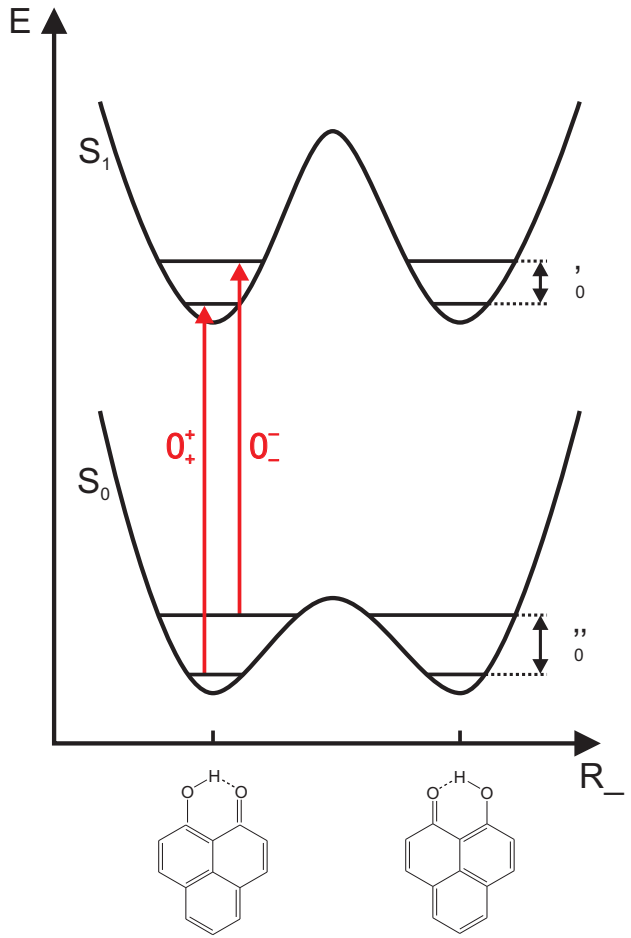
Asymmetric Lippincott-Schroeder Potentials



9,10-quinone 1,10-quinone

1,8-dihydroxyanthraquinone

Symmetric Double-Minimum Potentials



9-hydroxyphenalenone

E. R. Lippincott, R. Schroeder, *J. Chem. Phys.*, **1955**, *23*, 1099.

Outline

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?

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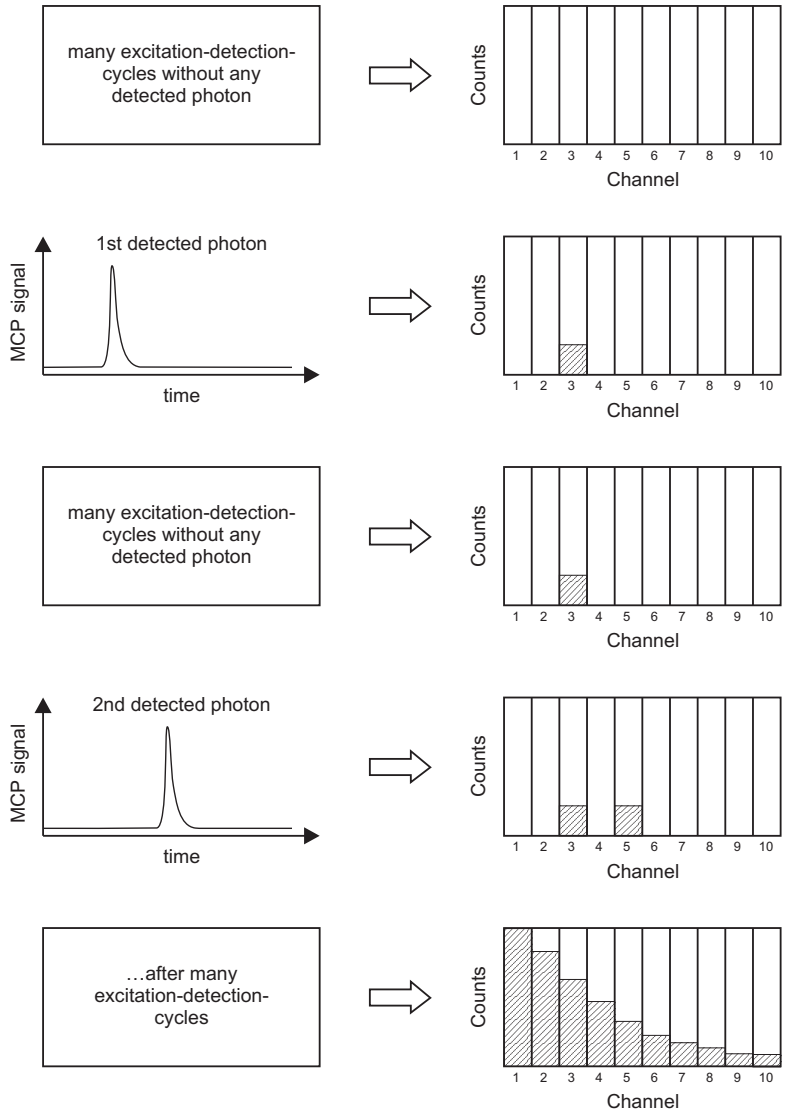
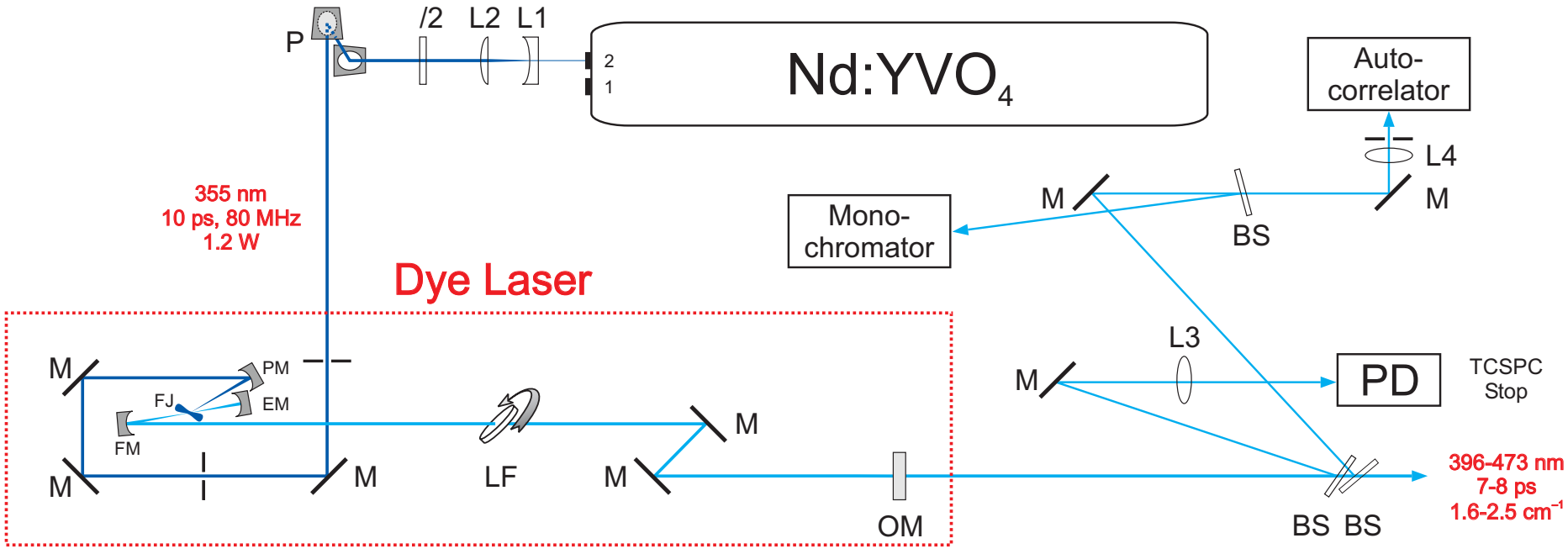
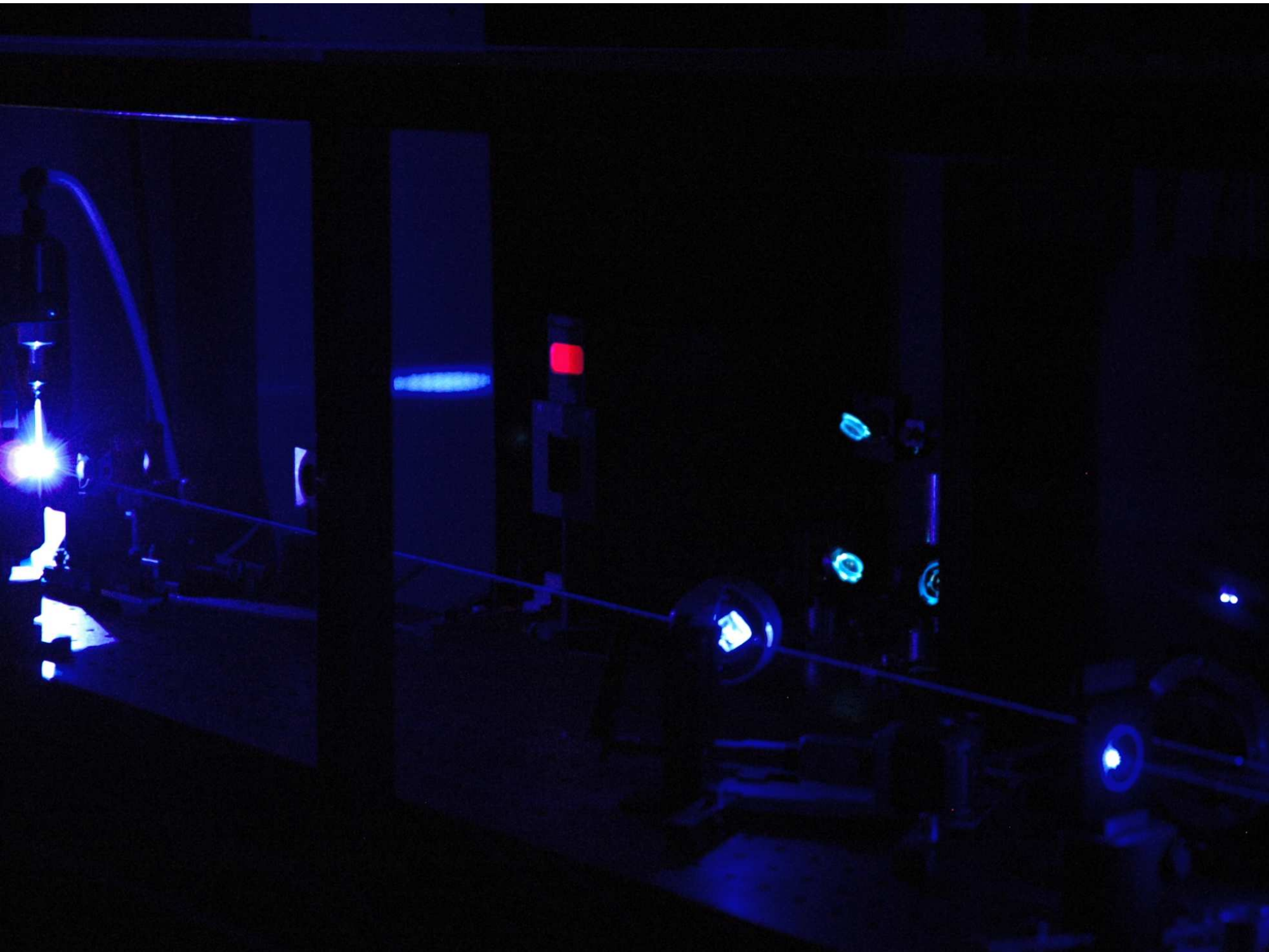
Time-domain Experimental Method

Time-correlated Single Photon Counting

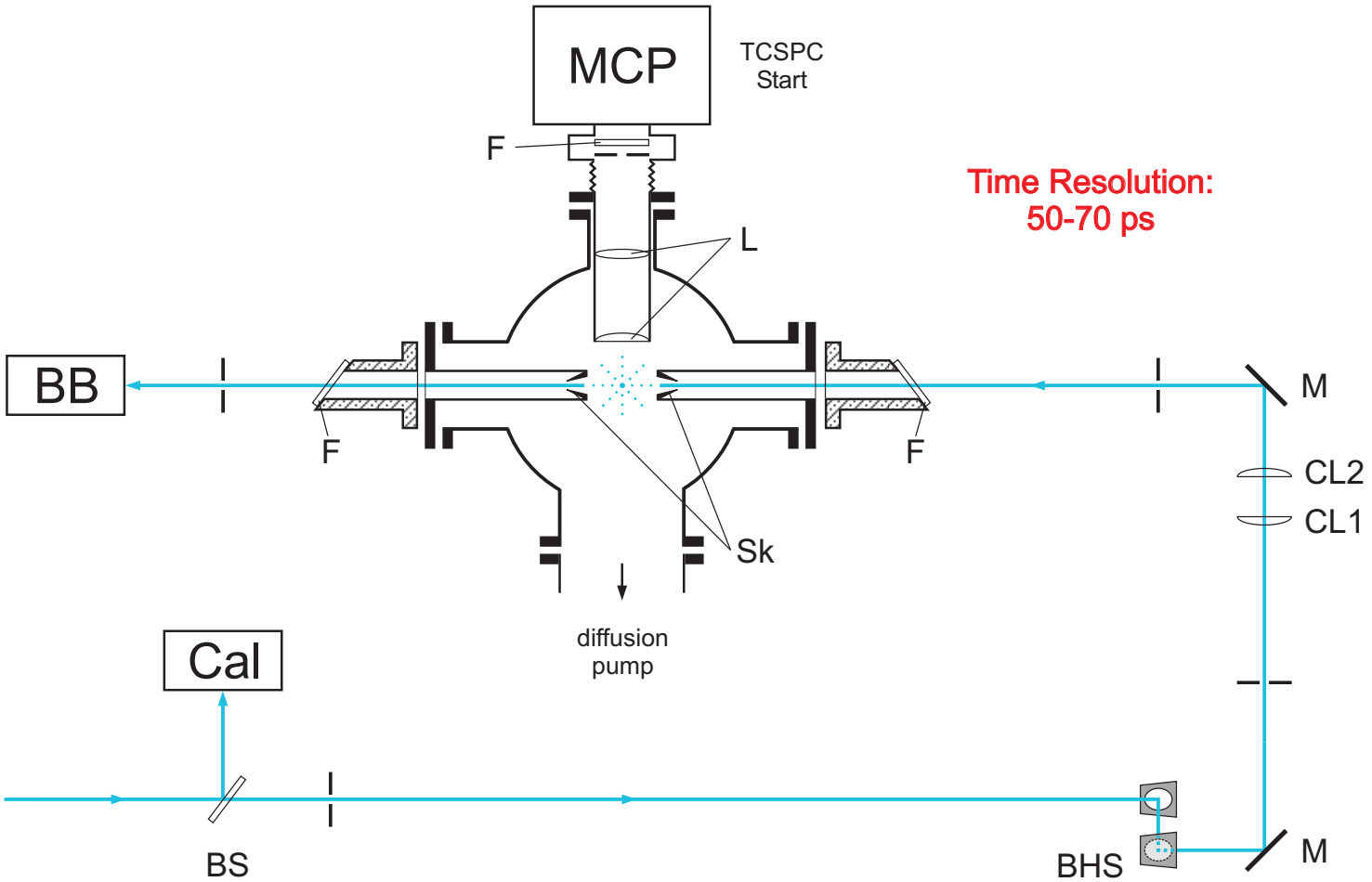


Time-correlated Single Photon Counting: Laser Setup





Time-correlated Single Photon Counting: Optical Setup



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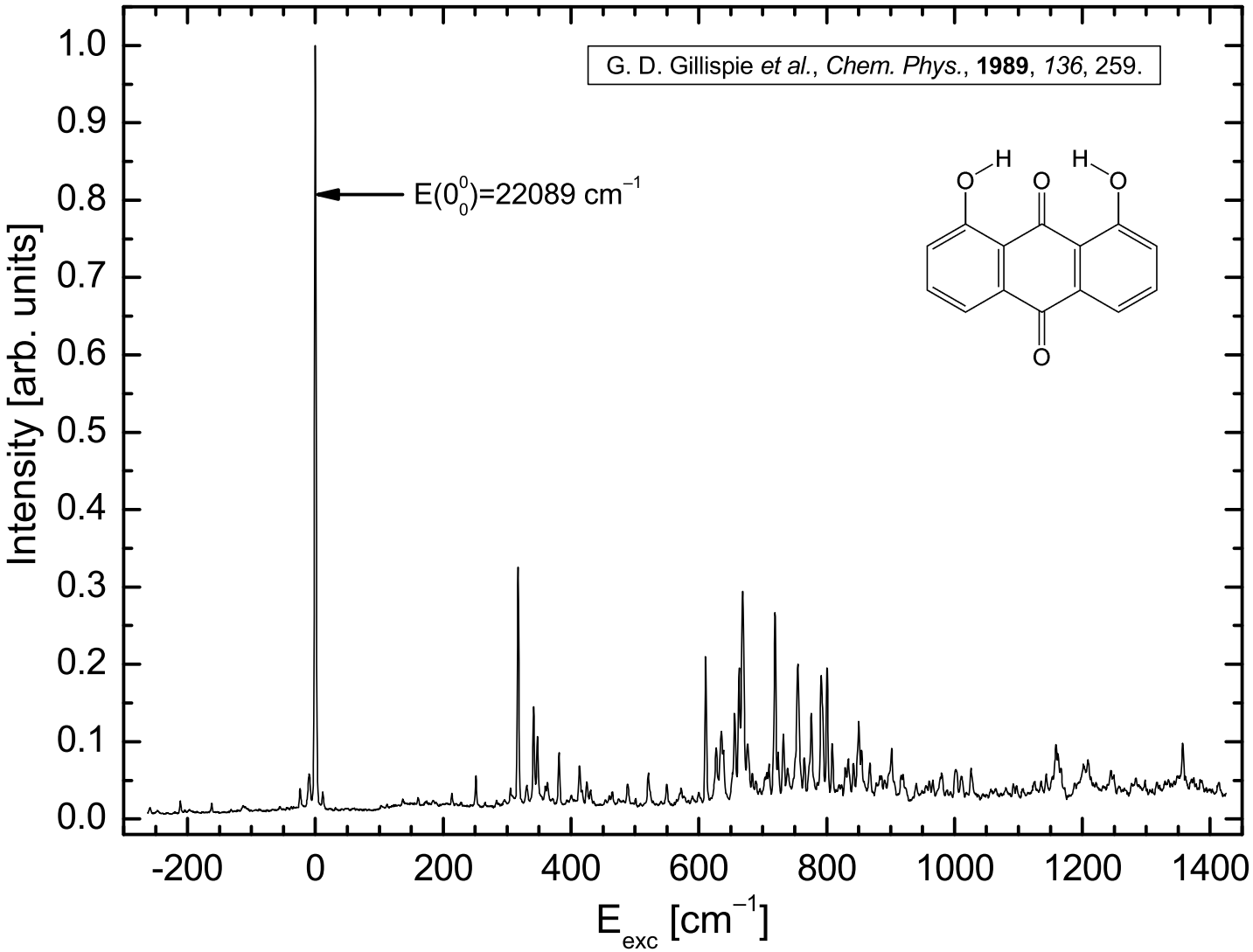
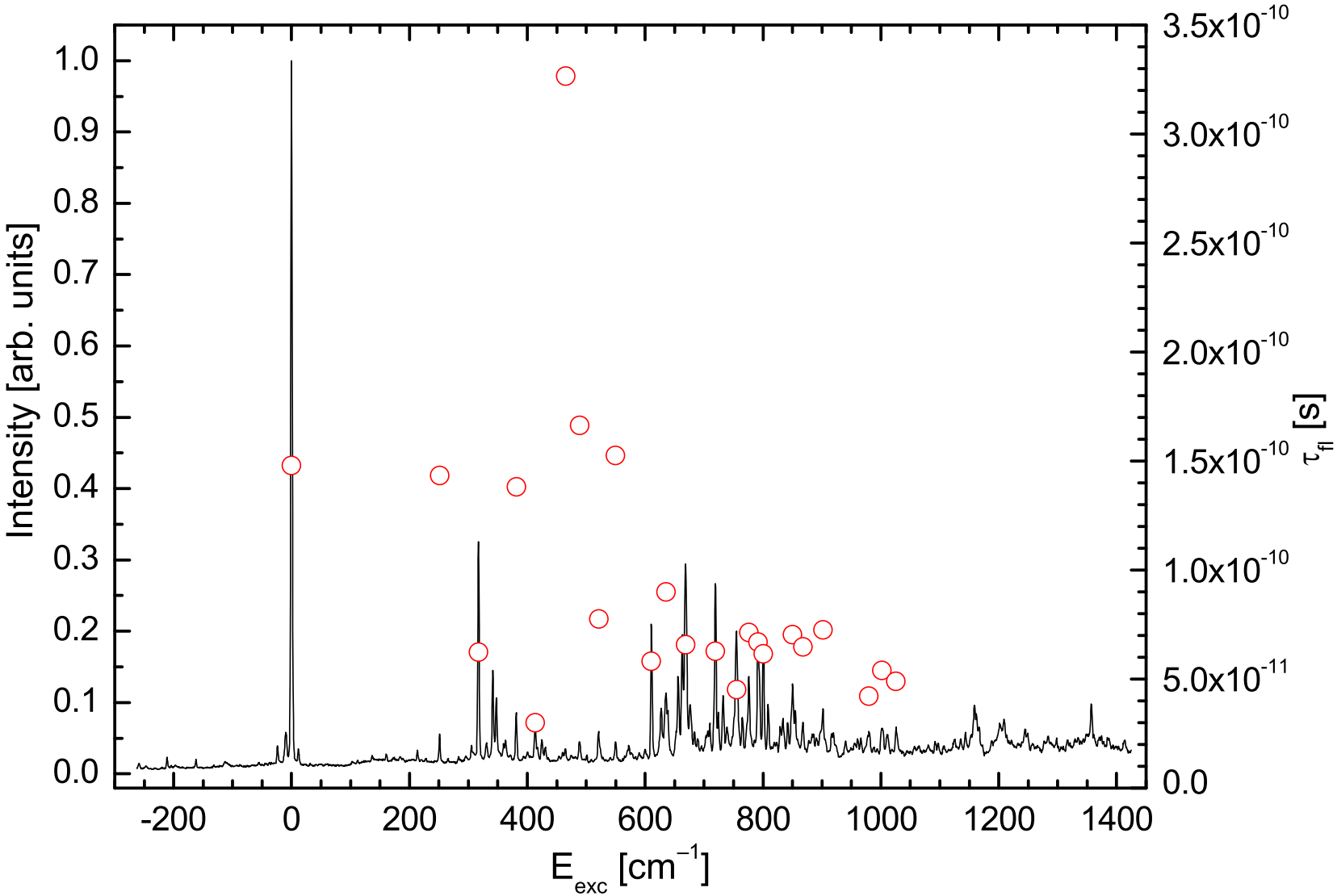
Frequency-domain Measurements

Low-resolution FE Spectrum of 1,8-Dihydroxyanthraquinone

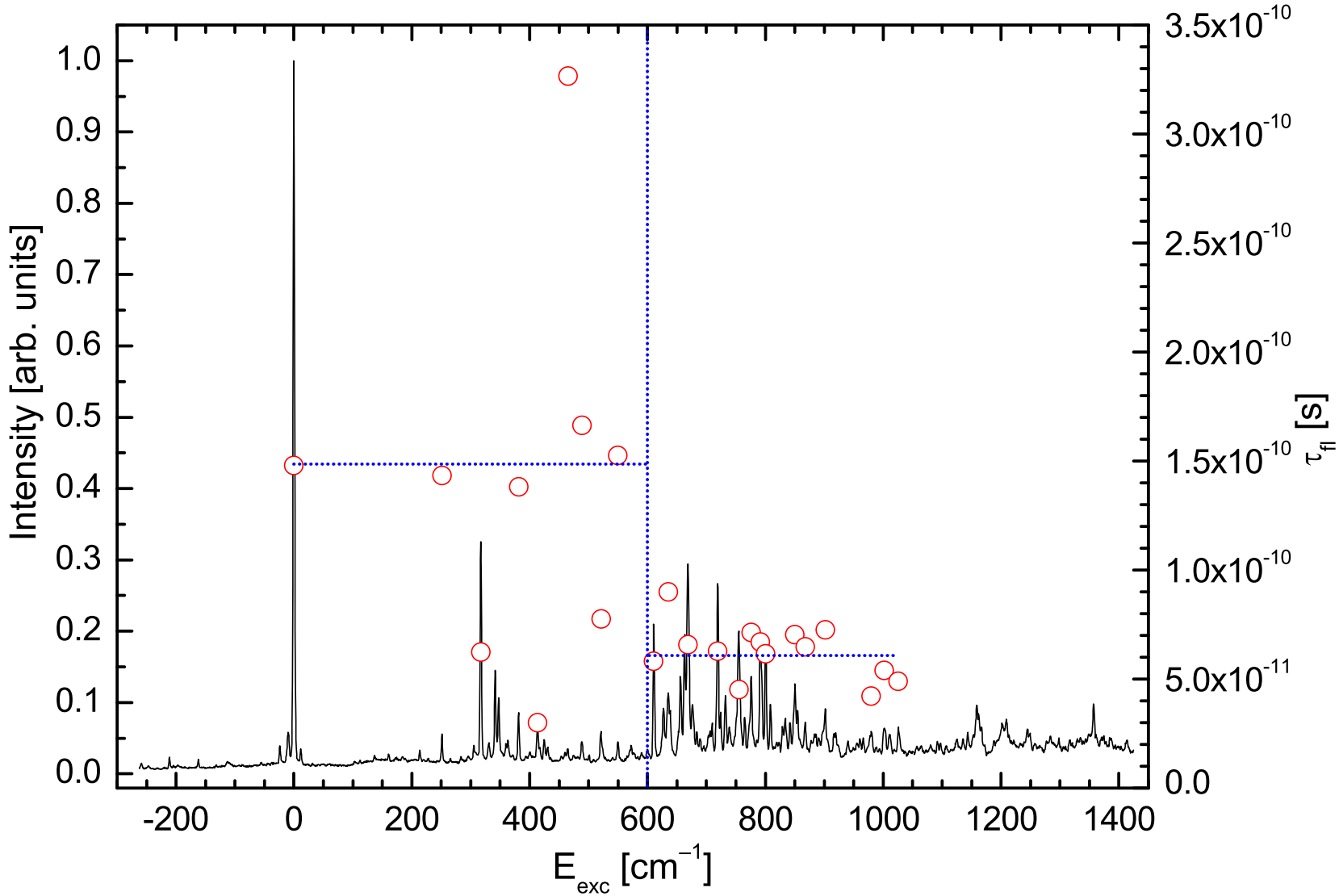


Energy Dependence of the Fluorescence Lifetimes τ_{fl}



Time-domain Measurements

Two Energy Regimes: $< 600\,\mathrm{cm}^{-1}$ and $> 600\,\mathrm{cm}^{-1}$



Frequency-domain Measurements

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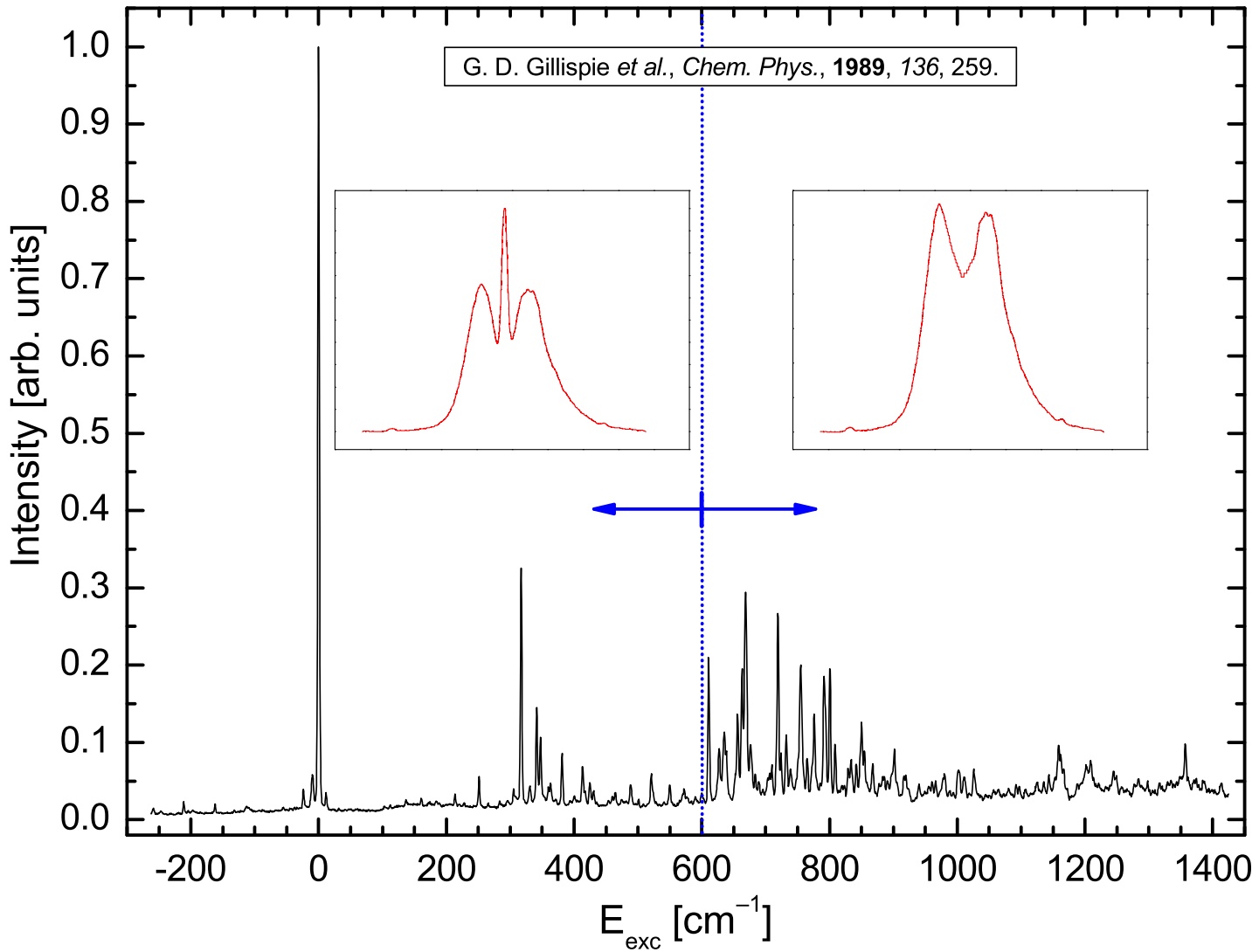
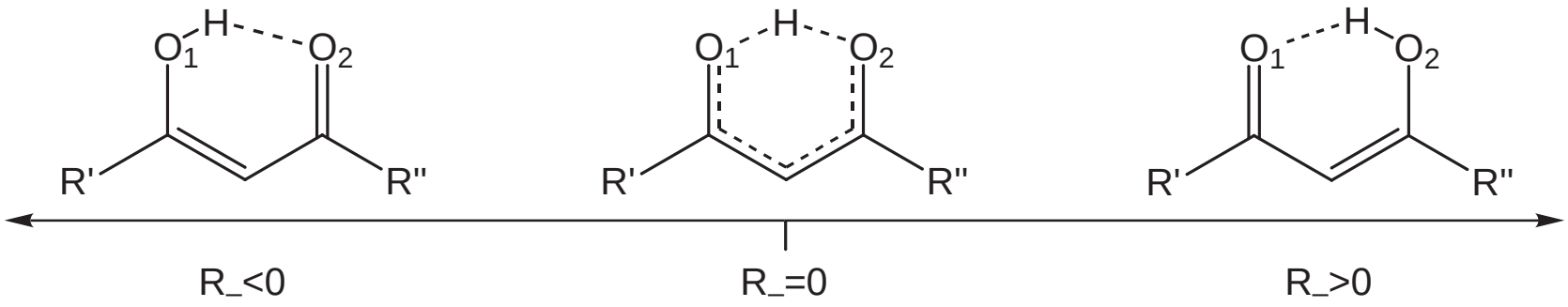


H-Atom Transfer Potentials

H-Atom Transfer Reaction Coordinate R_{-}

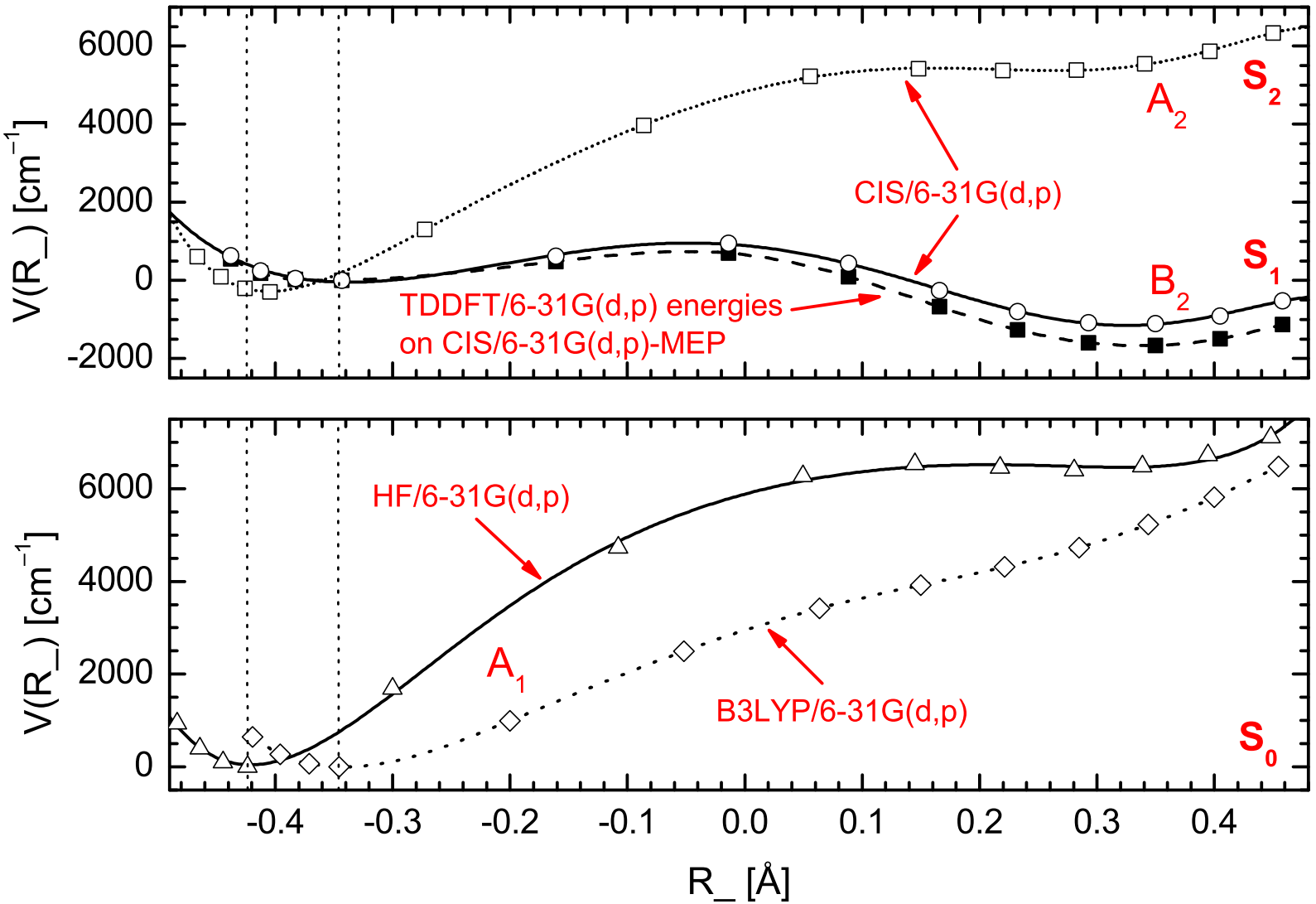


$$R_{-} = \frac{R_{0_1\mathrm{H}} - R_{0_2\mathrm{H}}}{2}$$

A. L. Sobolewski, W. Domcke, *Chem. Phys.*, 1998, *232*, 257.

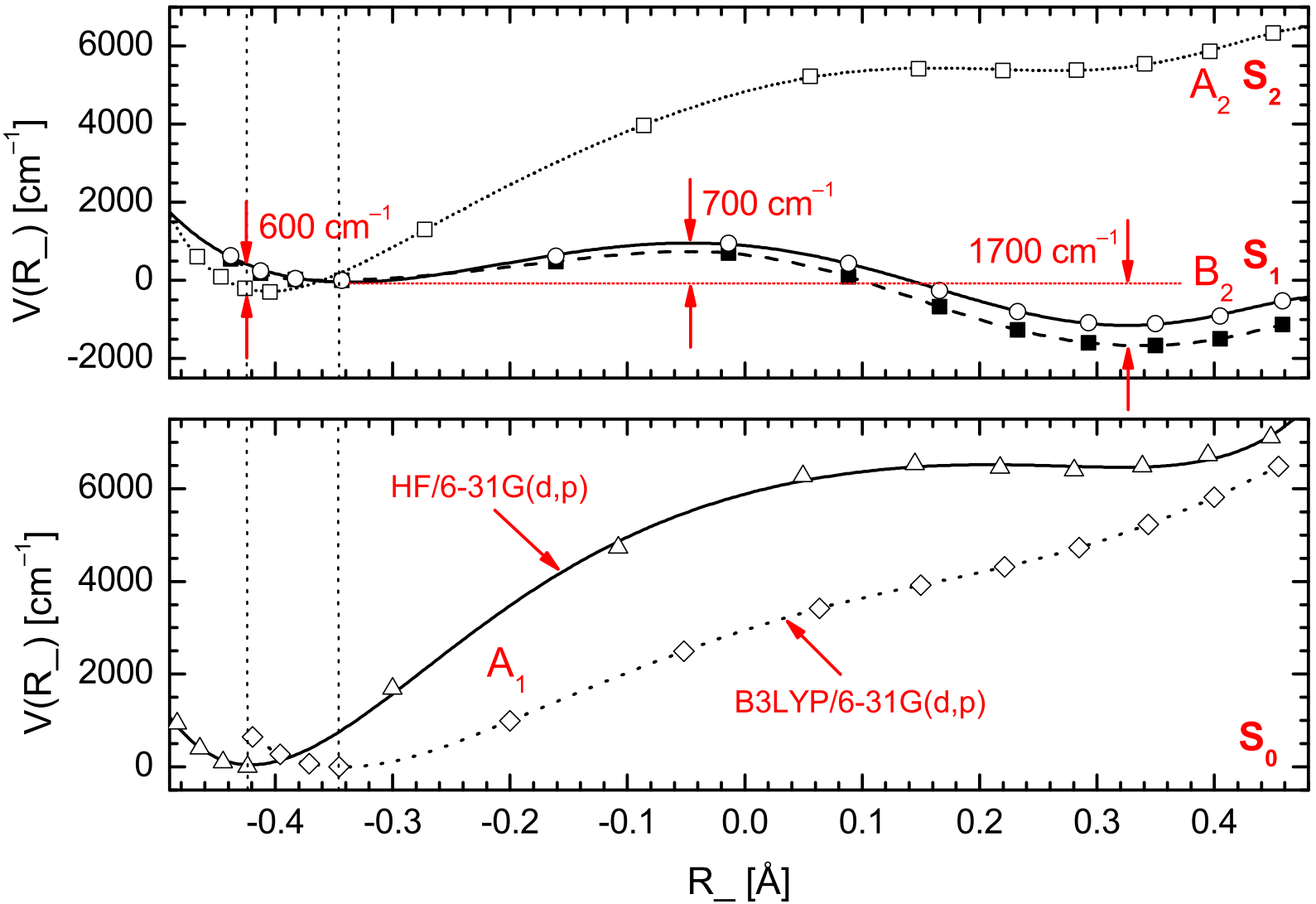
Ab initio H-Atom Transfer Potentials

Relaxed Potential Energy Scans for 1,8-Dihydroxyanthraquinone



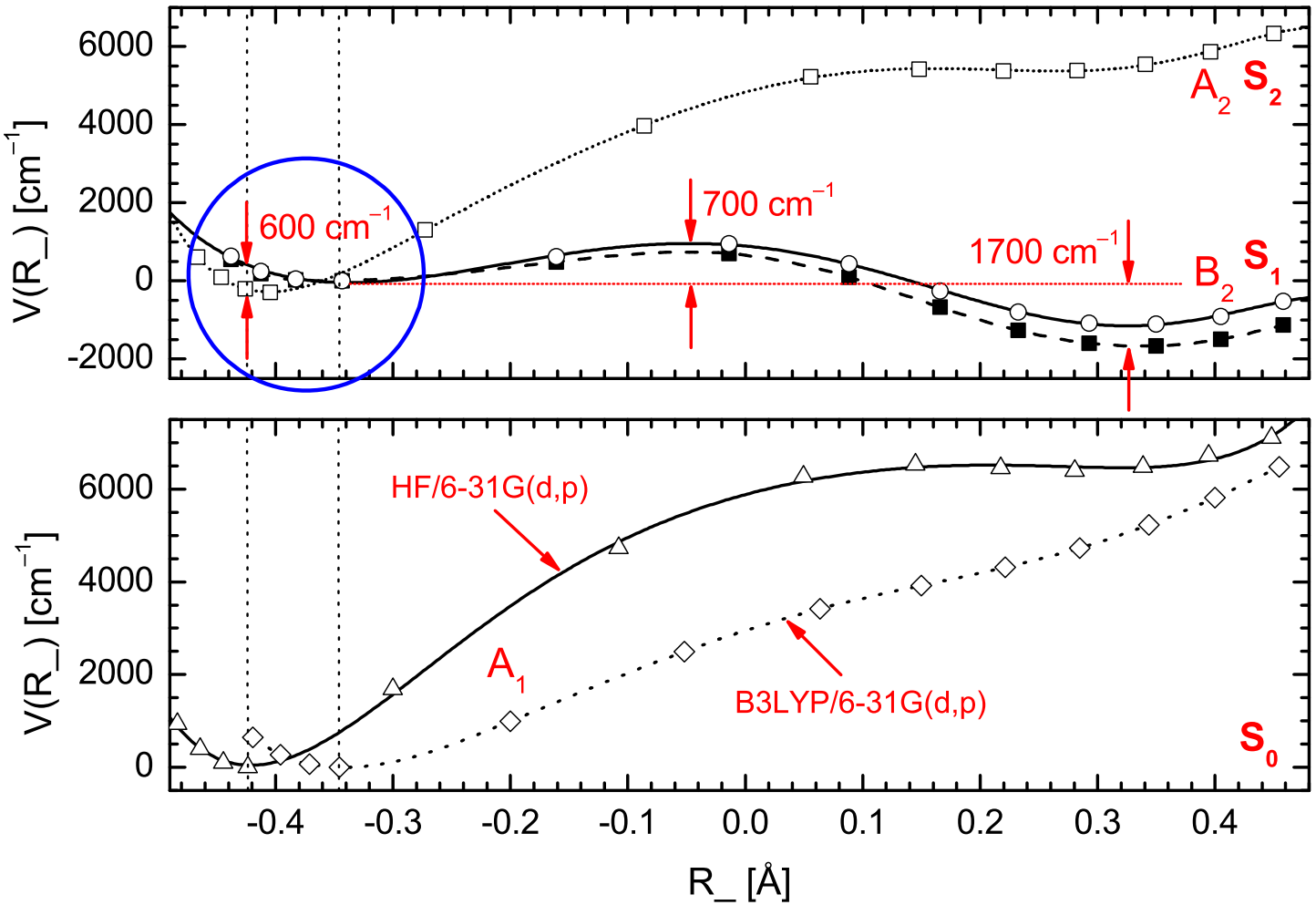
Ab initio H-Atom Transfer Potentials

Three Scenarios for the Static & Dynamic Fluorescence Properties



Ab initio H-Atom Transfer Potentials

First Scenario: Herzberg-Teller Coupling

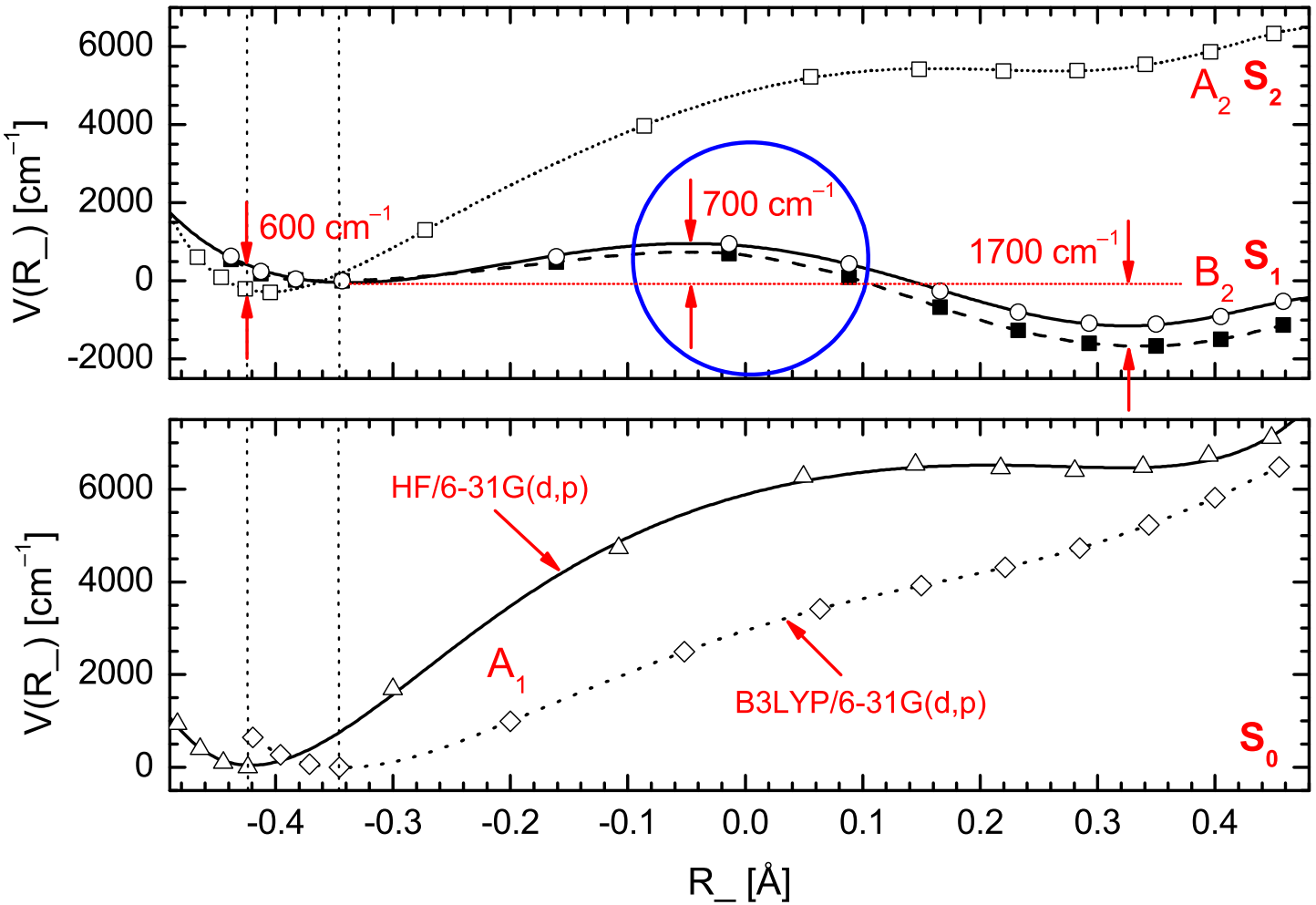


$< 600\,\mathrm{cm}^{-1}$: $A_2 \times B_2 = b_1$ vibronic bands with c-type rotational structure

$> 600\,\mathrm{cm}^{-1}$: Symmetry-allowed vibronic transitions with a-type rotational structure

Ab initio H-Atom Transfer Potentials

Second Scenario: Fast Intramolecular H-Atom Transfer

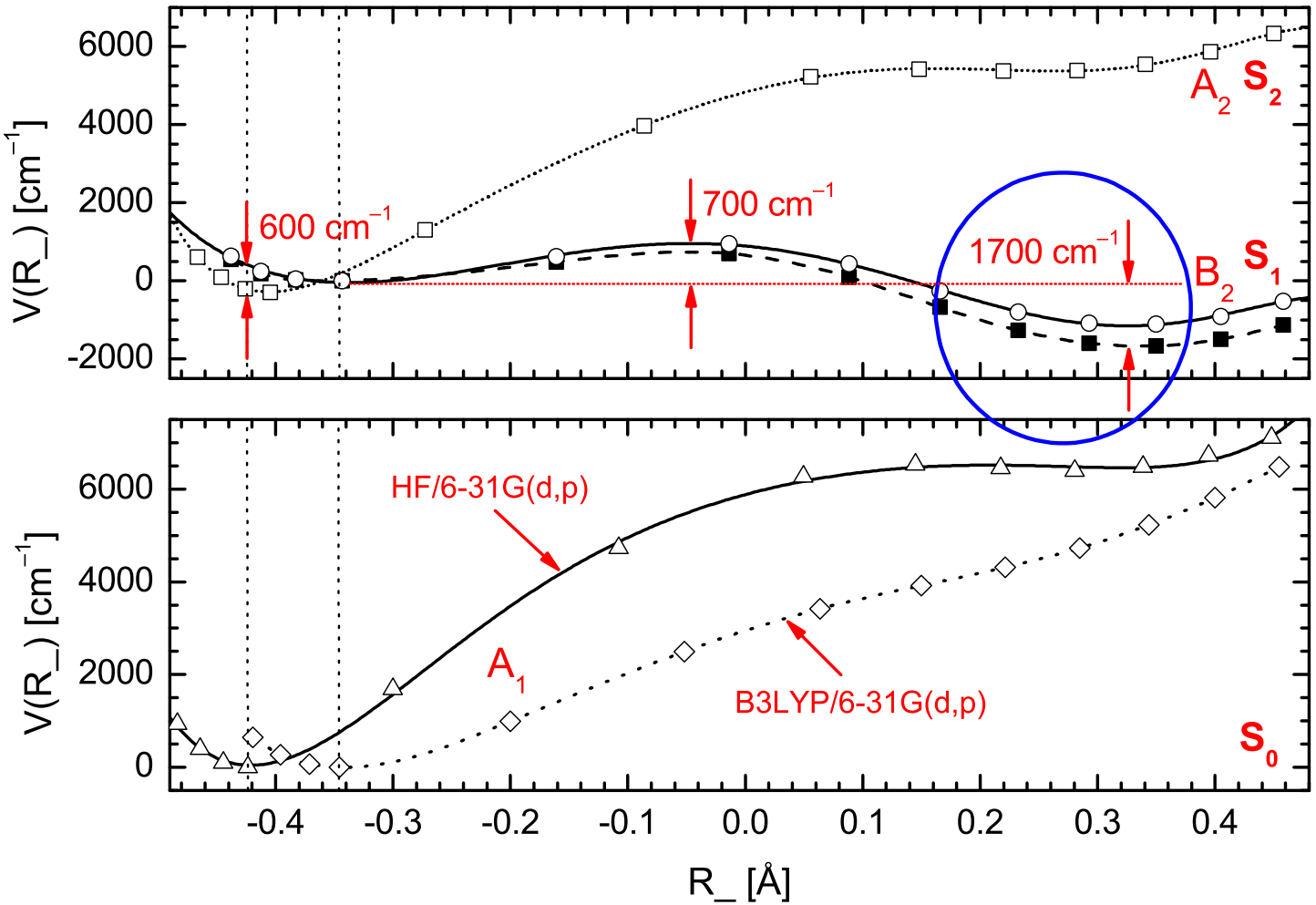


$< 600\,\mathrm{cm}^{-1}$: Symmetry-allowed vibronic transitions with a-type rotational structure

$> 600\,\mathrm{cm}^{-1}$: Fast intramolecular H-atom transfer & 1,10-quinone well fluorescence

Ab initio H-Atom Transfer Potentials

Third Scenario: Dual Absorption

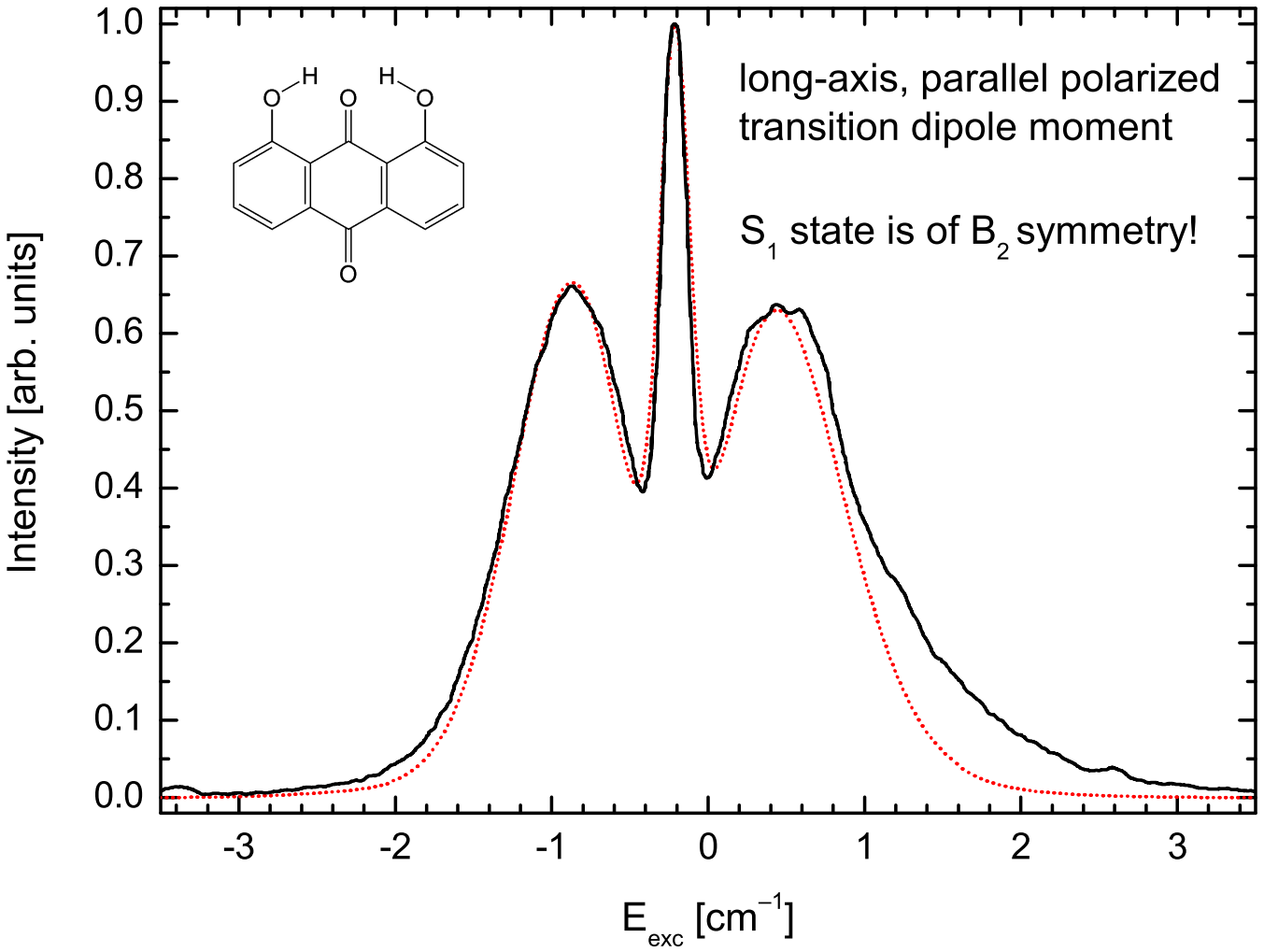


$< 600\,\mathrm{cm}^{-1}$: Non-vertical cross-well excitation into the 1,10-quinone well

$> 600\,\mathrm{cm}^{-1}$: Vertical excitation into the 9,10-quinone well

Frequency-domain Measurements

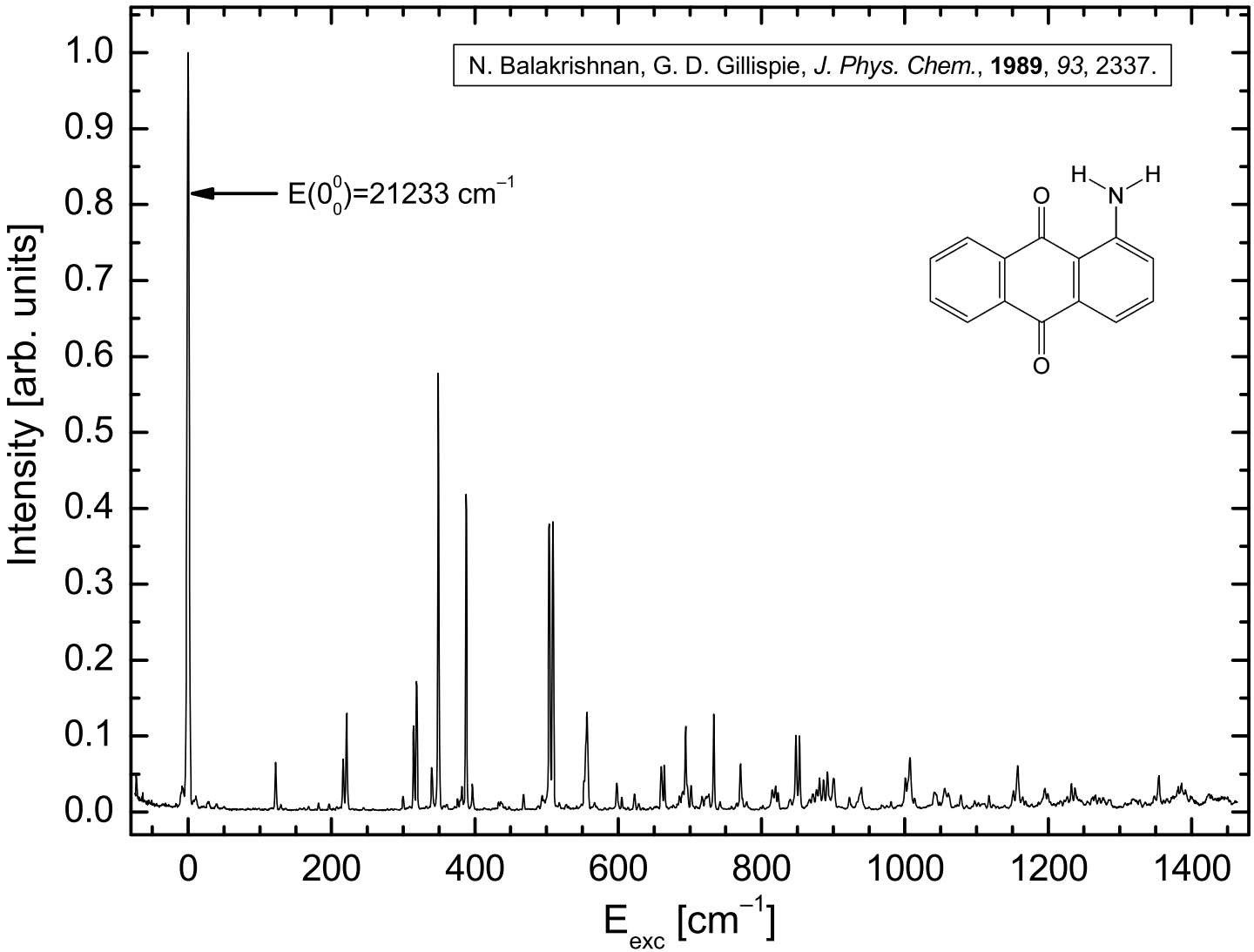
Rotational Band Contour of the 0_0^0 Transition



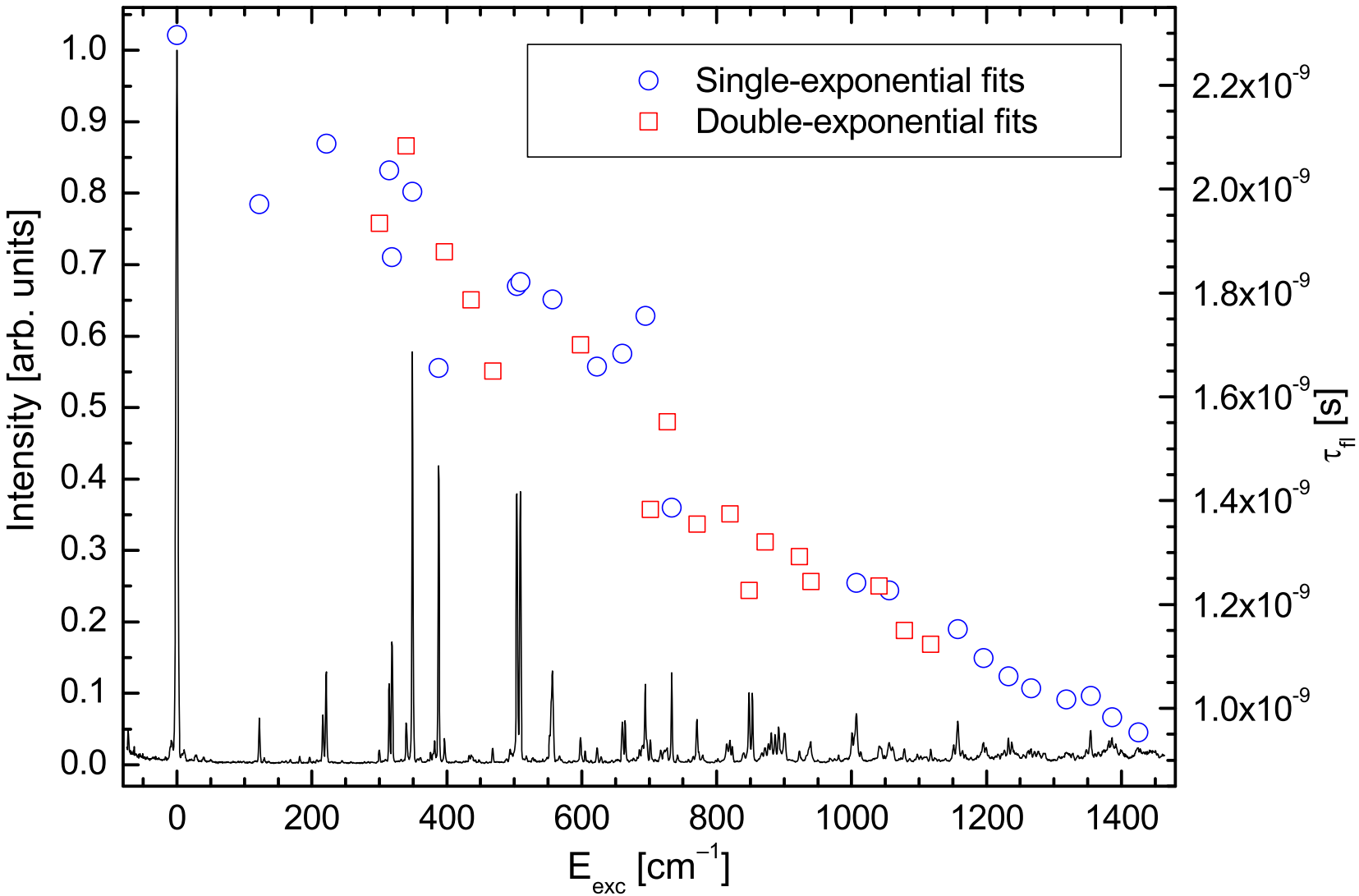
G. D. Gillispie *et al.*, *Chem. Phys.*, 1989, *136*, 259.

Frequency-domain Measurements

Low-resolution Fluorescence Spectrum of 1-Aminoanthraquinone

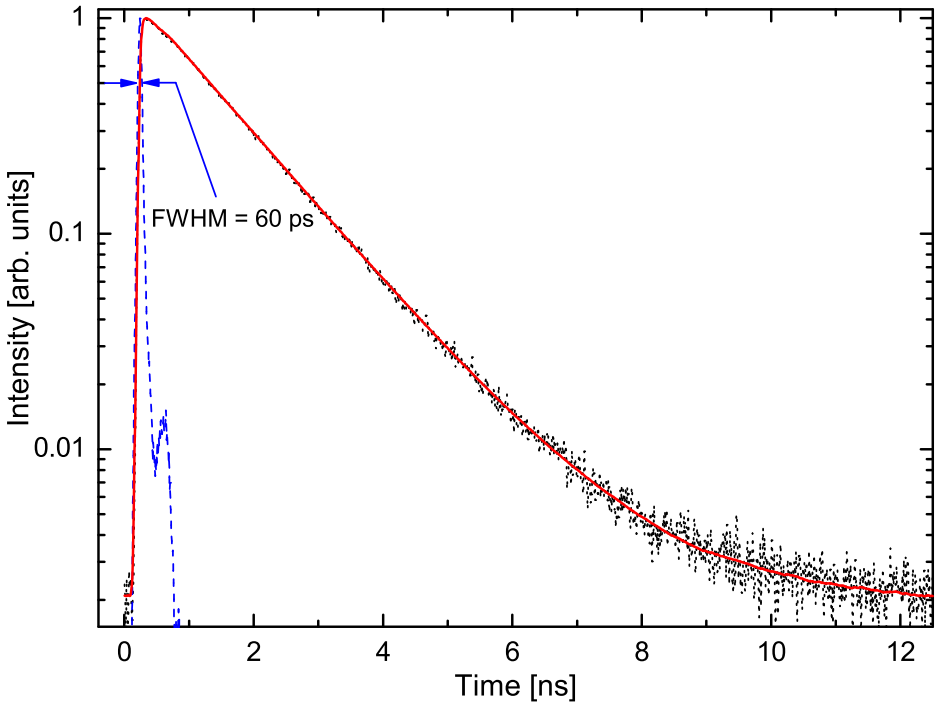


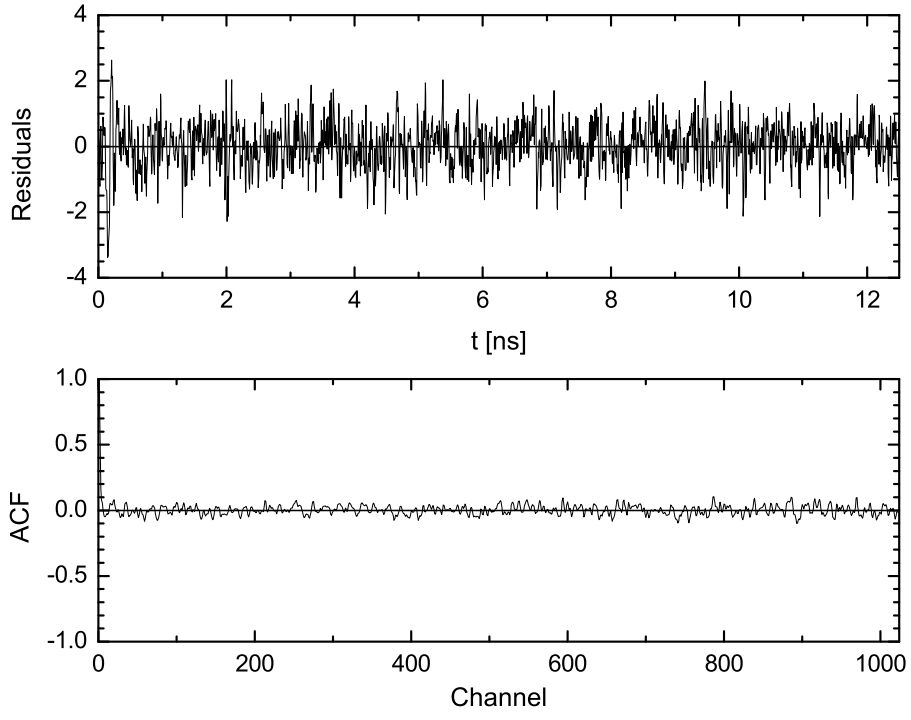
Energy Dependence of the Fluorescence Lifetimes $\bar{\tau}_{\mathrm{fl}}$



Time-domain Measurements

Fluorescence Decay Curves

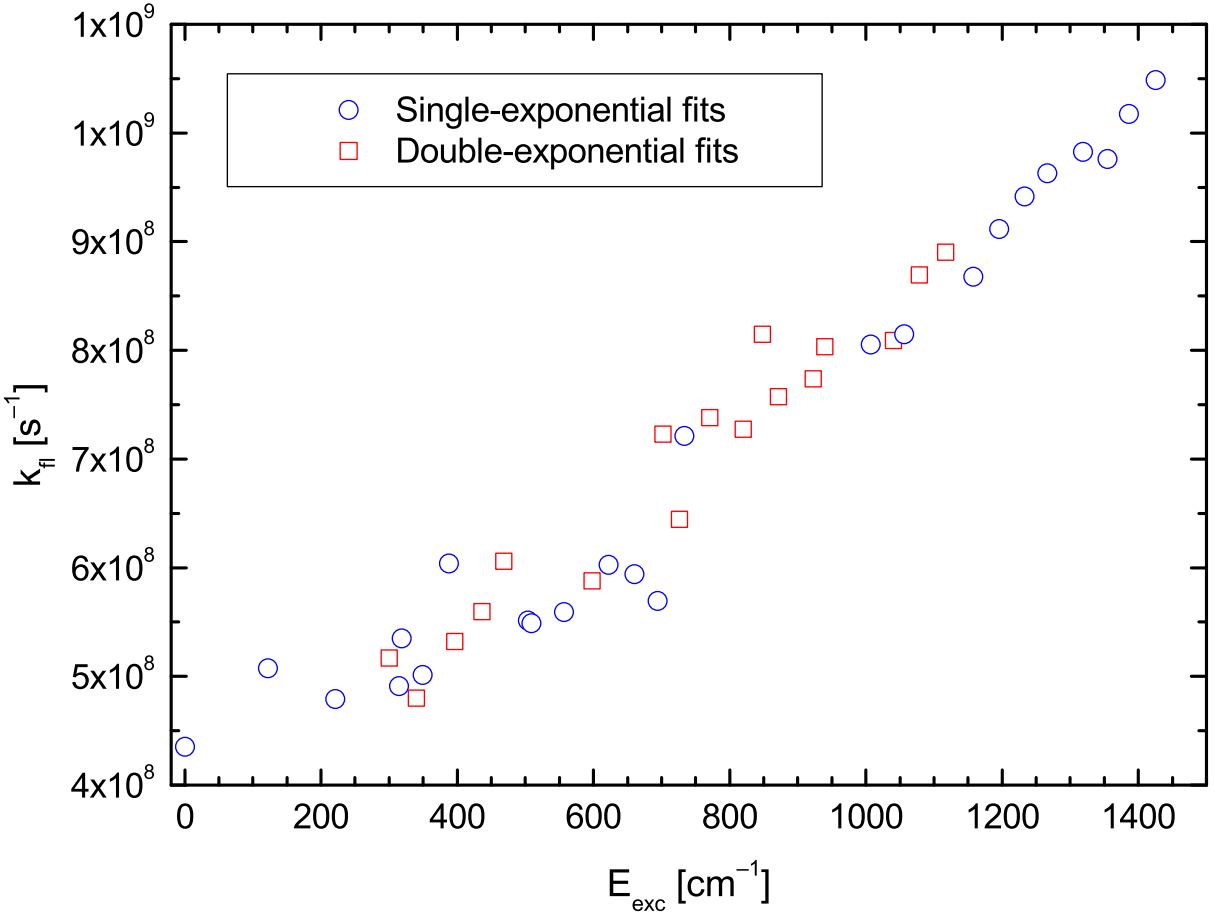




Double-exponential fit: $\bar{\tau}_{\mathrm{fl}} = 1.243\,\mathrm{ns}$ at $E_{\mathrm{exc}} = 940\,\mathrm{cm}^{-1}$

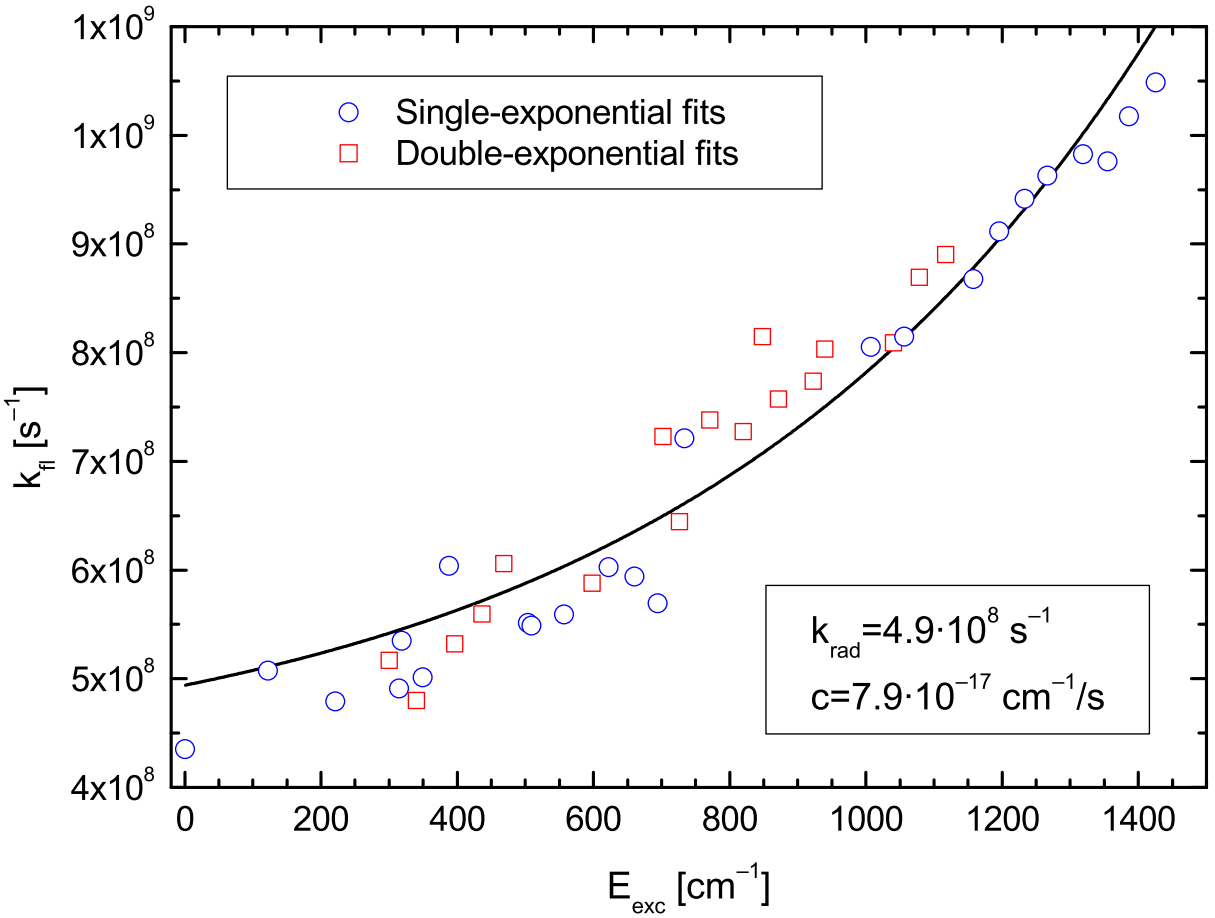
Time-domain Measurements

Energy Dependence of the Rate Constant k_{fl} of Fluorescence



Time-domain Measurements

Fit according to Fermi's Golden Rule

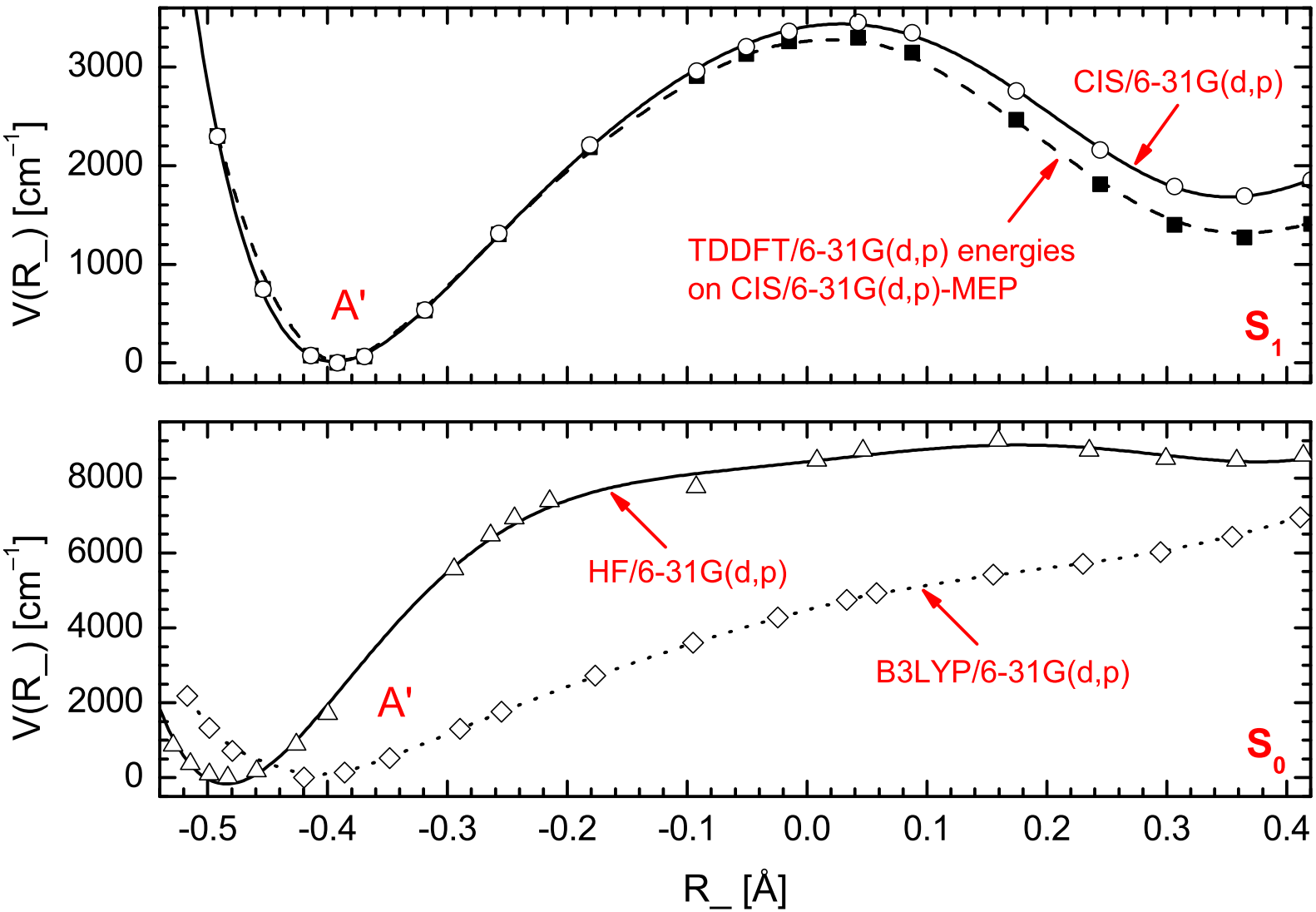


Fermi's Golden Rule:

$$\frac{1}{\bar{\tau}_{\mathrm{fl}}(E)} = k_{\mathrm{fl}}(E) = k_{\mathrm{rad}} + \underbrace{\frac{2\pi}{\hbar}\,|V_{if}|^2}_{c}\,\rho_{\mathrm{S}_0}(E)$$

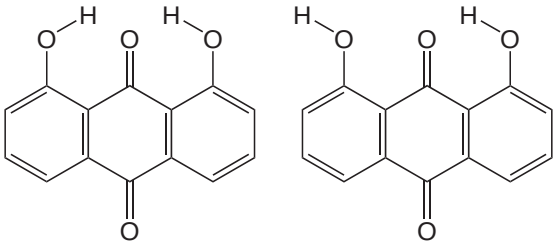
Ab initio H-Atom Transfer Potentials

Relaxed Potential Energy Scans for 1-Aminoanthraquinone

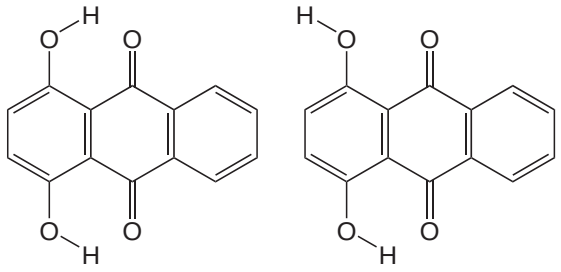


Strength of Intramolecular Hydrogen Bonds

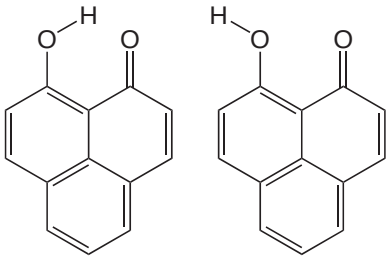
Molecules with Different Rotamers



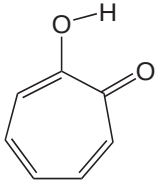
1,8-dihydroxyanthraquinone



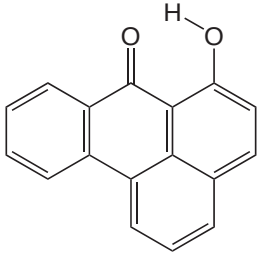
1,4-dihydroxyanthraquinone



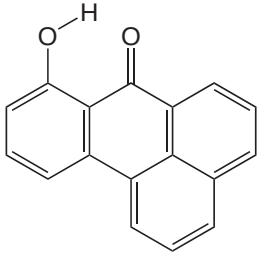
9-hydroxyphenalenone



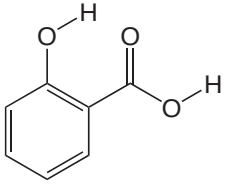
tropolone



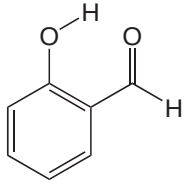
6-benzanthrone



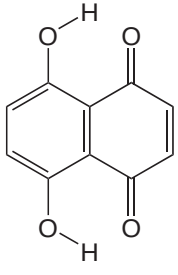
7-benzanthrone



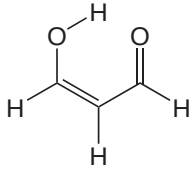
salicylic acid



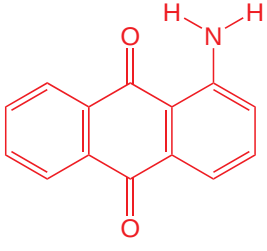
o-hydroxybenzaldehyde



naphthazarine



malonaldehyde



1-aminoanthraquinone

?

Quantum Theory of Atoms in Molecules (QTAIM)

Total Charge Density $\rho(\mathbf{r}_c)$ 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:

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

- 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 $(3, -1)$.

R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford, 1990.

Intermolecular Hydrogen Bonds

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

  R. J. Boyd, S. C. Choi, *Chem. Phys. Lett.*, **1985**, *120*, 80.

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

  R. J. Boyd, S. C. Choi, *Chem. Phys. Lett.*, **1986**, *129*, 62.

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

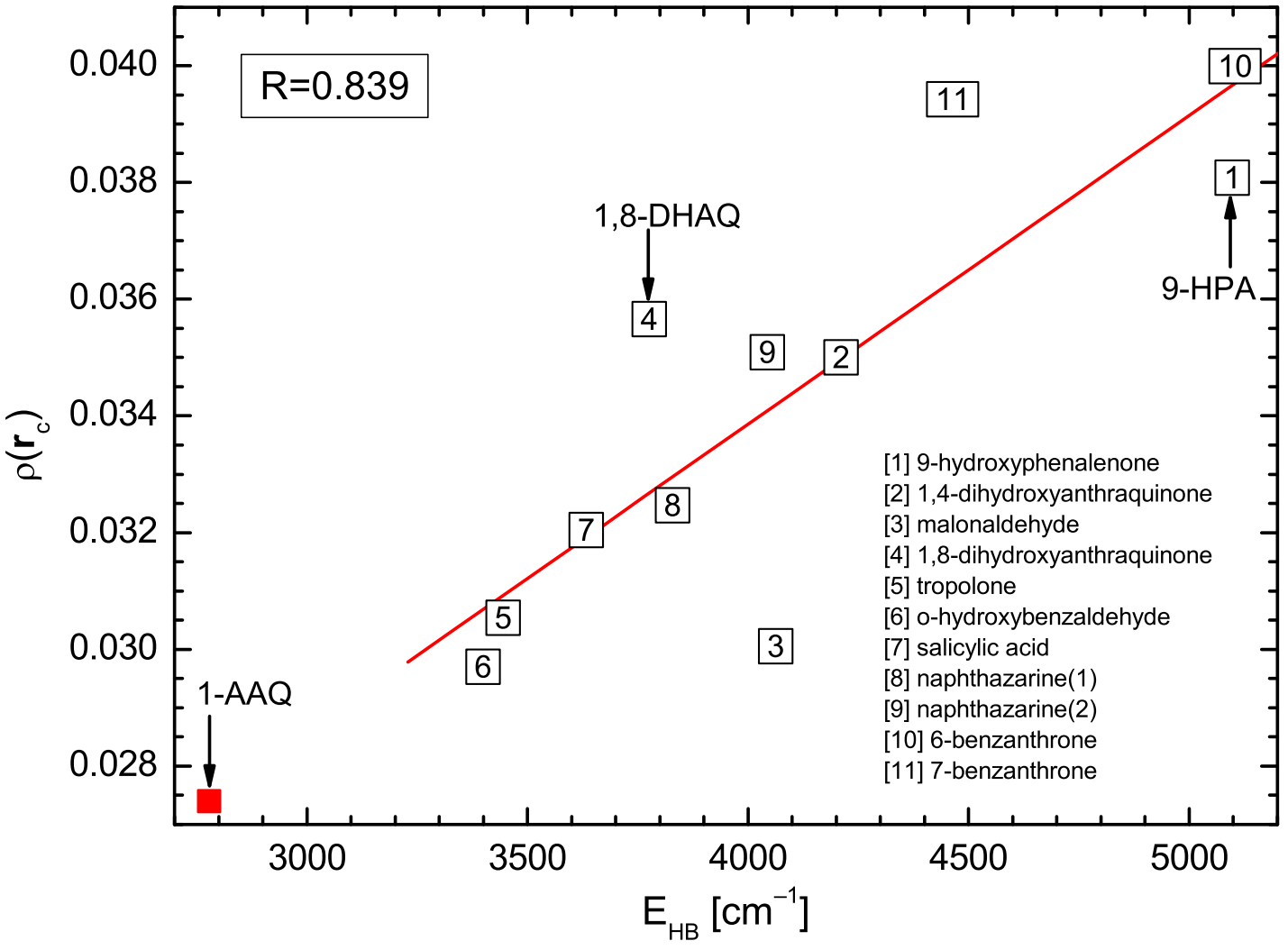
  M. T. Carroll, R. F. W. Bader, *Mol. Phys.*, **1988**, *65*, 695.

- Linear $\rho(\mathbf{r}_c)$–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), $R = 0.998$)

  U. Koch, P. L. A. Popelier, *J. Phys. Chem.*, **1995**, *99*, 9747.

Quantum Theory of Atoms in Molecules (QTAIM)

Linear $\rho(\mathbf{r}_c)$–E_{HB} Relationship for *Intra*molecular Hydrogen Bonds



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   - What is the evidence for the occurrence of excited-state intramolecular H-atom transfer?

Summary

Results on 1,8-dihydroxyanthraquinone

- FE Spectrum exhibits two distinct excess energy ranges.
- Fluorescence bands *below* $\sim 600\,\mathrm{cm}^{-1}$ originate in the 9,10-quinone well.
- Fluorescence bands *above* $\sim 600\,\mathrm{cm}^{-1}$ originate in the proton-transferred 1,10-quinone well.
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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 $\rho(\mathbf{r}_\mathrm{c})$ 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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