

Test required to obtain credit and grade in the course

C9911 Molecular and Supramolecular Photochemistry (Autumn 2024)

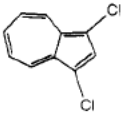

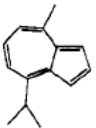
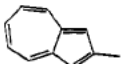
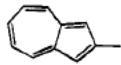
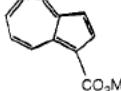
Answer all questions and submit the answer sheets to Prof. Petr Klan by
January 15, 2025.

Note: All answers are available in the lecture notes (pdf) posted on MUNI course website. If you need more information, please read N. J. Turro, J. C. Scaiano, and V. Ramamurthy, *Modern Molecular Photochemistry of Organic Molecules*. University Science Books, 2010; (Ch 1-7) or P. Klán and J. Wirz, *Photochemistry of Organic Compounds: From Concepts to Practice*, Wiley-Blackwell, 2009

NAME:

(1) In the table below fluorescence quantum yields of several azulenes are listed.

TABLE I. Fluorescence Quantum Yields and the Energies of the First Two Excited Singlet States of Substituted Azulenes^a

	Φ_{fl}	E_{S_1} , kcal/mol	E_{S_2} , kcal/mol	ΔE , kcal/mol
	0.058	36.3	77.0	40.9
	0.031	40.9	80.9	40.0
	0.014	39.5	77.8	38.3
	0.0081	42.6	79.5	36.9
	0.0034	42.9	77.5	34.6
	$\sim 10^{-4}$	44.3	77.2	32.9

- (a) Why azulene's fluorescence quantum yield depends on the substituent?
 (b) Generally, in most molecules, from where does the fluorescence originate, S_1 , S_2 or S_3 ?

(2) The tabulated data below give considerable insight into the factors that control the radiationless process. Consulting the table answer the listed questions:

Molecule	k_F^0	k_{ST}	k_P^0	k_{TS}	Φ_F	Φ_P
Naphthalene	10^6	10^6	10^{-1}	10^{-1}	0.55	0.05
1-Fluoronaphthalene	10^6	10^6	10^{-1}	10^{-1}	0.84	0.06
1-Chloronaphthalene	10^6	10^8	10	10	0.06	0.54
1-Bromonaphthalene	10^6	10^9	50	50	0.002	0.55
1-Iodonaphthalene	10^6	10^{10}	500	100	0.000	0.70

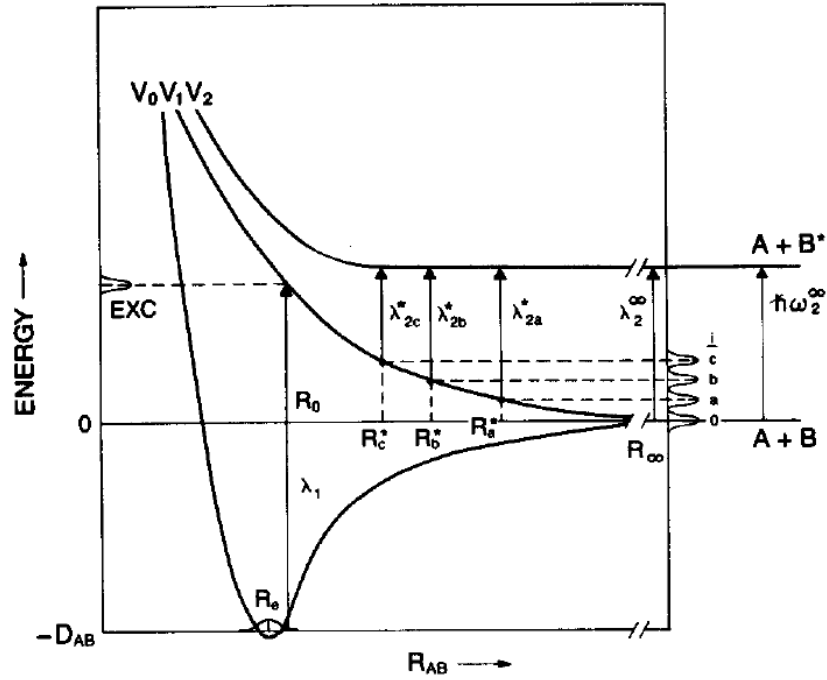
- (a) Why does the quantum yield of fluorescence decrease with the substituent---F, Cl, Br and I?
 (b) Why does the quantum yield of phosphorescence increase with the substituent---F, Cl, Br and I?
 (c) Although the quantum yield of fluorescence decreases with the substituent, why the rate constant of fluorescence does not change with the substituent---F, Cl, Br and I?

(3) (a) Why excited singlet (S_1) is higher in energy than the corresponding excited triplet (T_1) of the same electronic configuration?

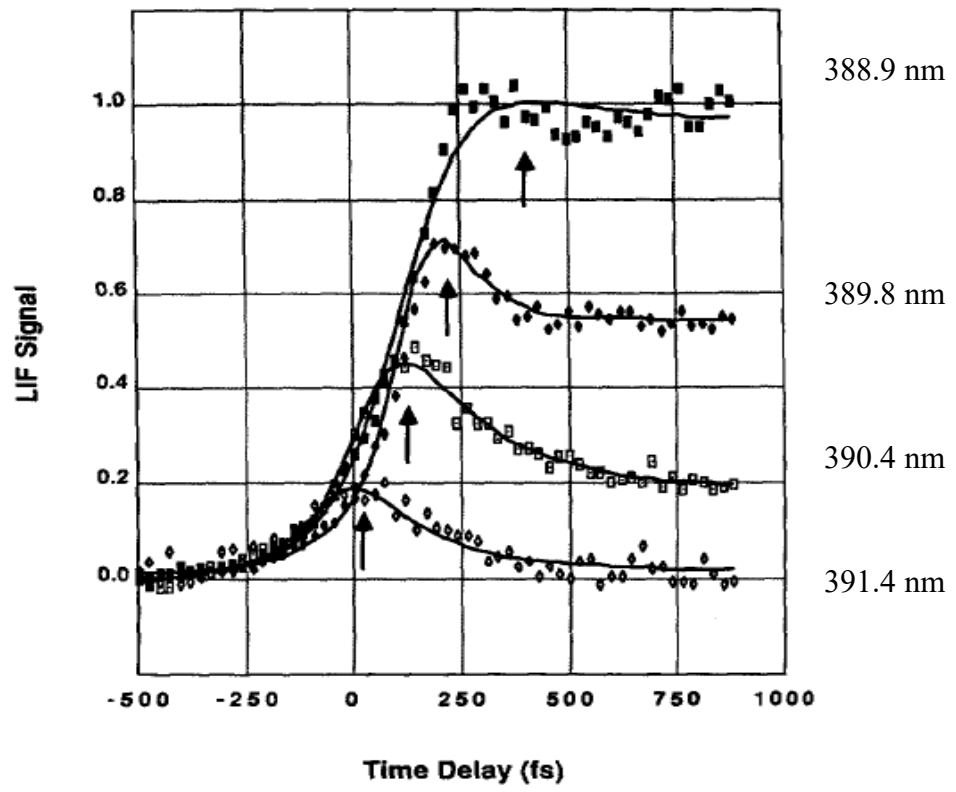
- (b) Between naphthalene and tetracene which one would have a smaller singlet–triplet gap?
 (c) Between benzophenone and stilbene which one will larger singlet–triplet gap?

(4) In one of pioneering studies, Zewail mapped the photodissociation surface of ICN. Needed information to answer the questions are included in the figures below.

- (a) How did Zewail monitor the photodissociation?
 (b) What information did he get by exciting the excited species with different wavelengths, 391.4, 390.4, 389.8 and 388.9 nm?
 (c) Why did he not observe the oscillation that he noted during the photodissociation of NaI



Rise and decay of laser induced fluorescence signal of CN^*

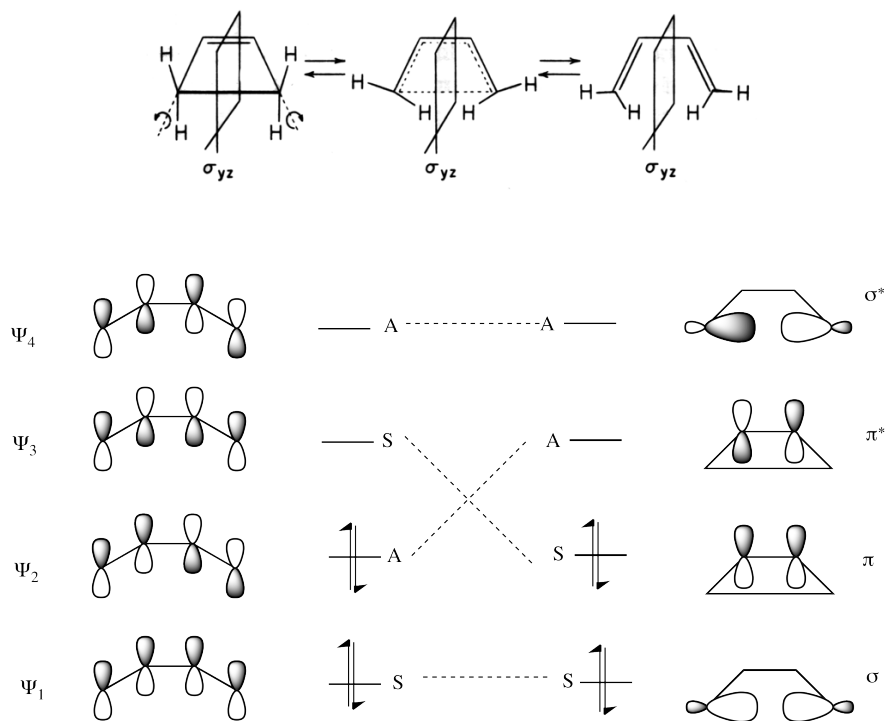


(5) The orbital correlation diagram for disrotatory ring opening of cyclobutene to butadiene is shown below.

(a) Using this construct a state correlation diagram.

(b) Using the state diagram and applying the concept of avoided crossings, build an energy surface that helps to track the reaction.

(c) In the above figure sketch the pathway an excited cyclobutene would take to reach butadiene.



(6) The emission spectrum of pyrene with two distinct bands is shown below.

(i) Explain with the help of a potential energy diagram (ground & excited state) why the emission at longer wavelength is structureless?

(ii) There is a delay in the appearance of the longer wavelength emission compared to the shorter wavelength emission. Why?

