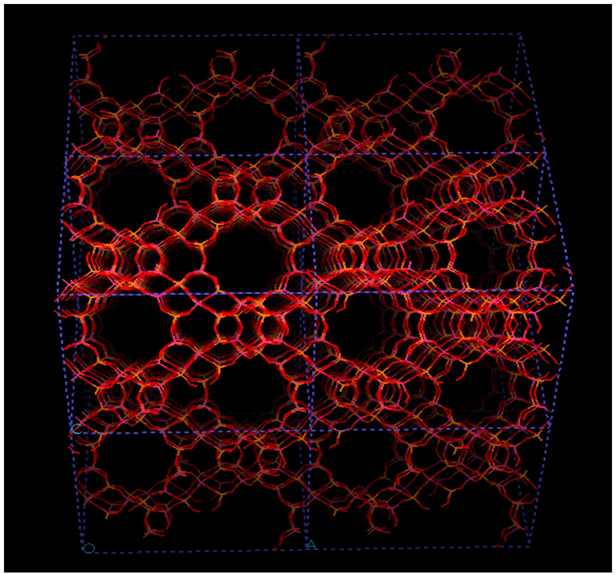
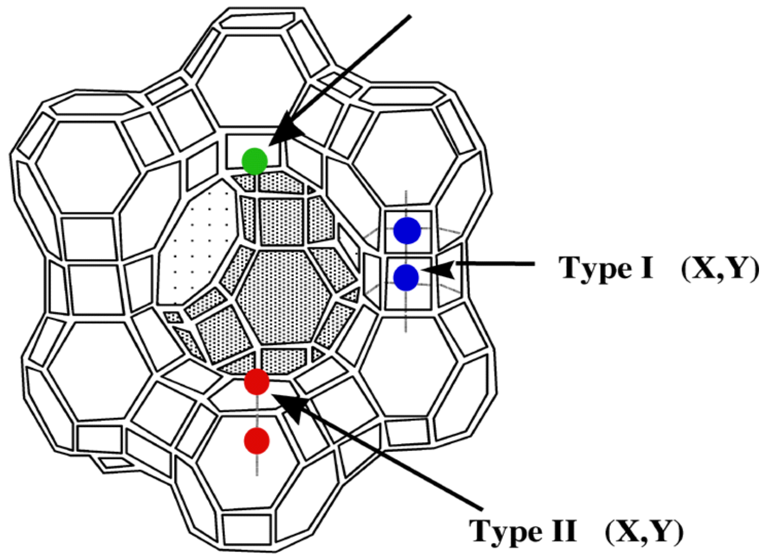
Chemistry in Confined Spaces

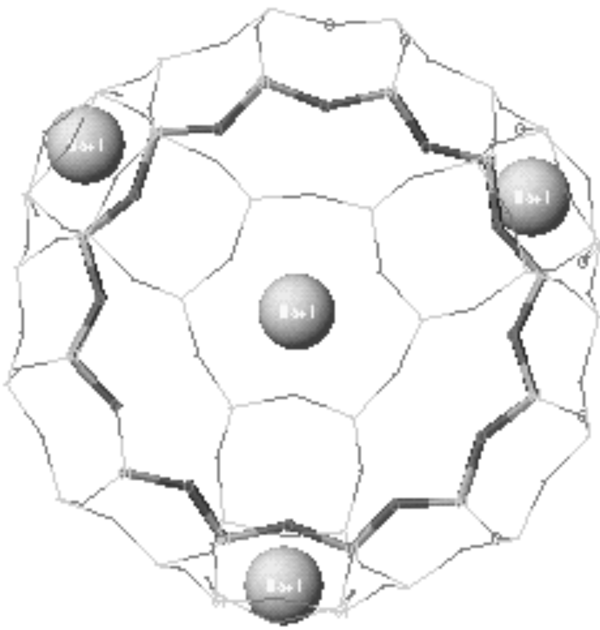
Characteristics of Faujasite Y Zeolite

$M_x(AlO_2)_x\ (SiO_2)_y.ZH_2O$

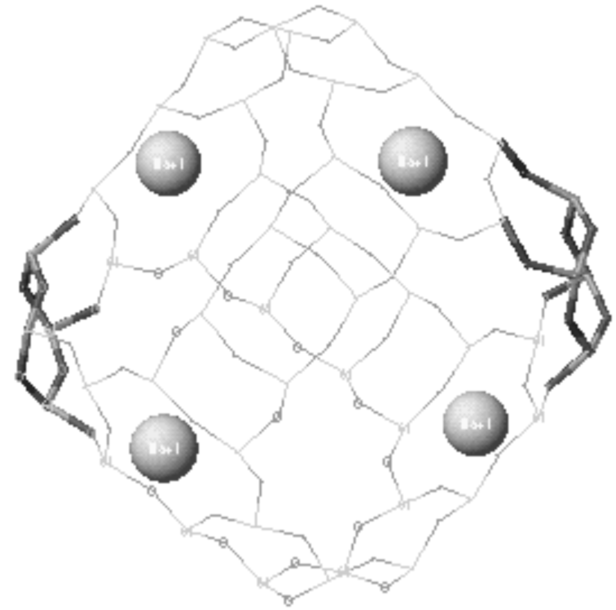




- Microporous solid
- Large surface area
- Well defined channels/cages
- Si/Al ratio = 2.4
- Type I - 4 cations /supercage
- Type II- 4 cations /supercage



7.4 A° Window



13.4 A° Supercage diameter

Zeolite X: $M_{86}[(AlO_2)_{86}(SiO_2)_{106}].264H_2O$

Zeolite Y: $M_{56}[(AlO_2)_{56}(SiO_2)_{136}].250H_2O$

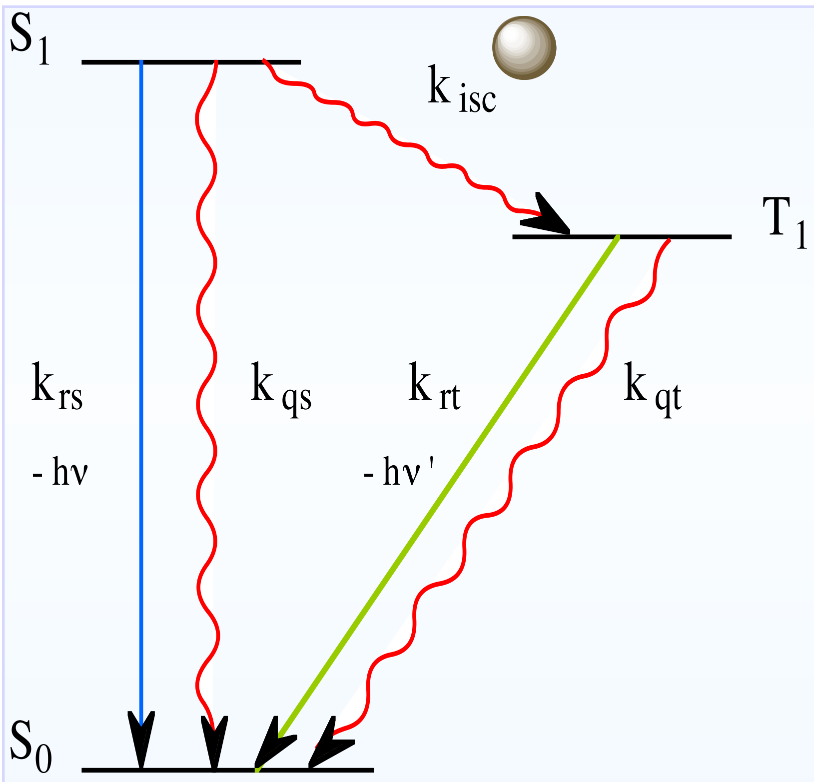
Alkali Ion Controlled Photochemistry

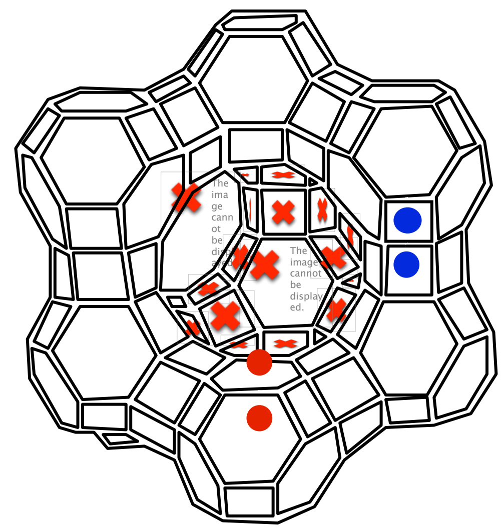
Alkali Ion-Organic Interactions

- **Alkali Ion-Organic Very Weak Interaction (Spin-Orbit coupling)**
- **Alkali Ion-Carbonyl Dipolar Interaction**
- **Alkali Ion-π (Alkenes) Quadrupolar Interaction**
- **Alkali Ion-π (Aromatics) Quadrupolar Interaction**

Alkali Ion Effect: Electron Spin Inversion

Heavy Cations Enhance S_1 to T_1 Crossing



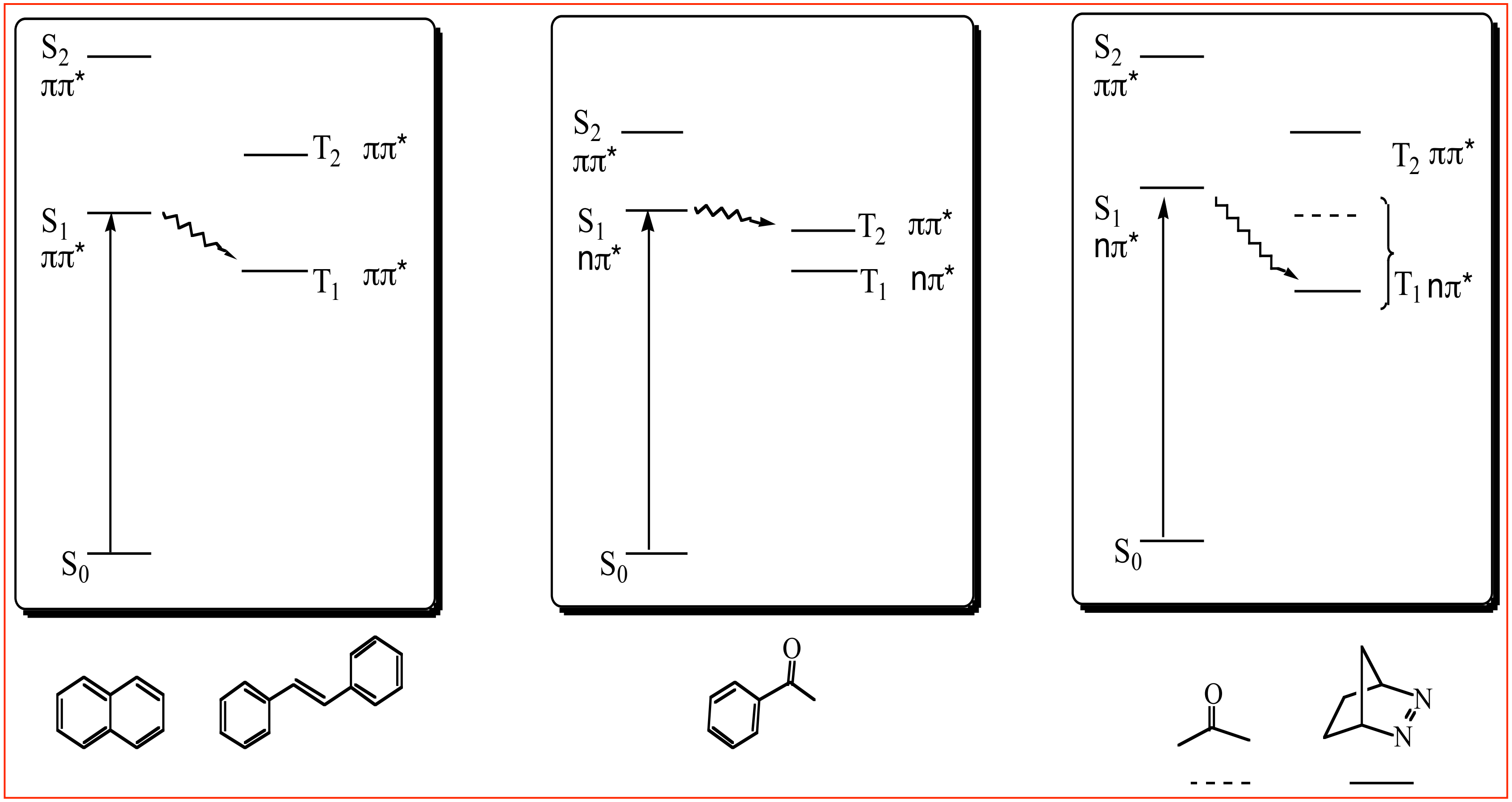


Ability of zeolite supercage to induce spin-orbit coupling depends on the SOC of the alkali ion

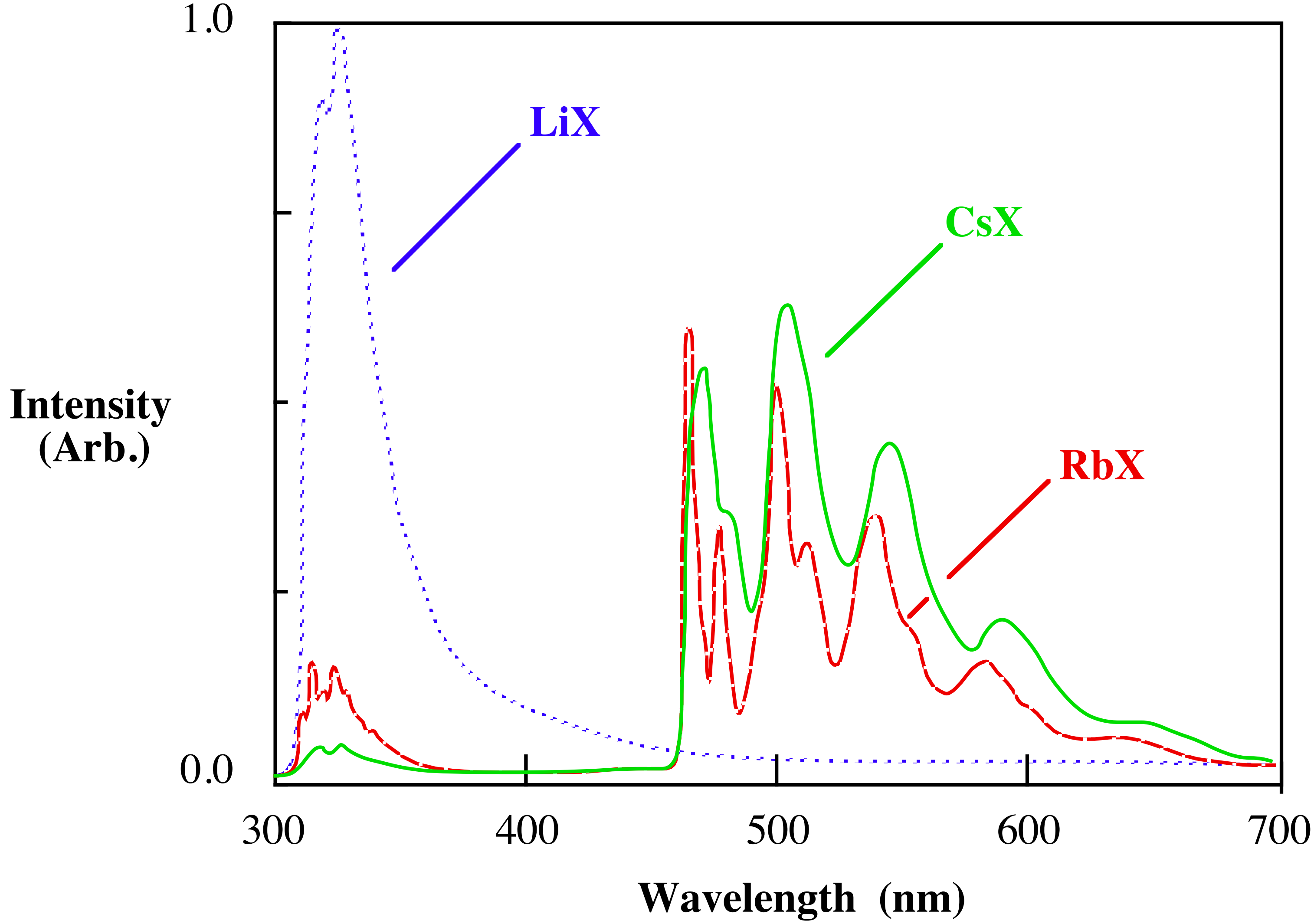
Atom	Ionic Radius of the Cation (Å)	Spin-Orbit Coupling ζ cm^{-1}
Li	0.86 (+)	0.23
Na	1.12	11.5
K	1.44	38
Rb	1.58	160
Cs	1.84	370
Tl	1.40	3410
Pb	1.33 (2+)	5089

Whether the Heavy Alkali Ion Could Influence the Intersystem Crossing Depends on the Electronic Configurations of the States Involved

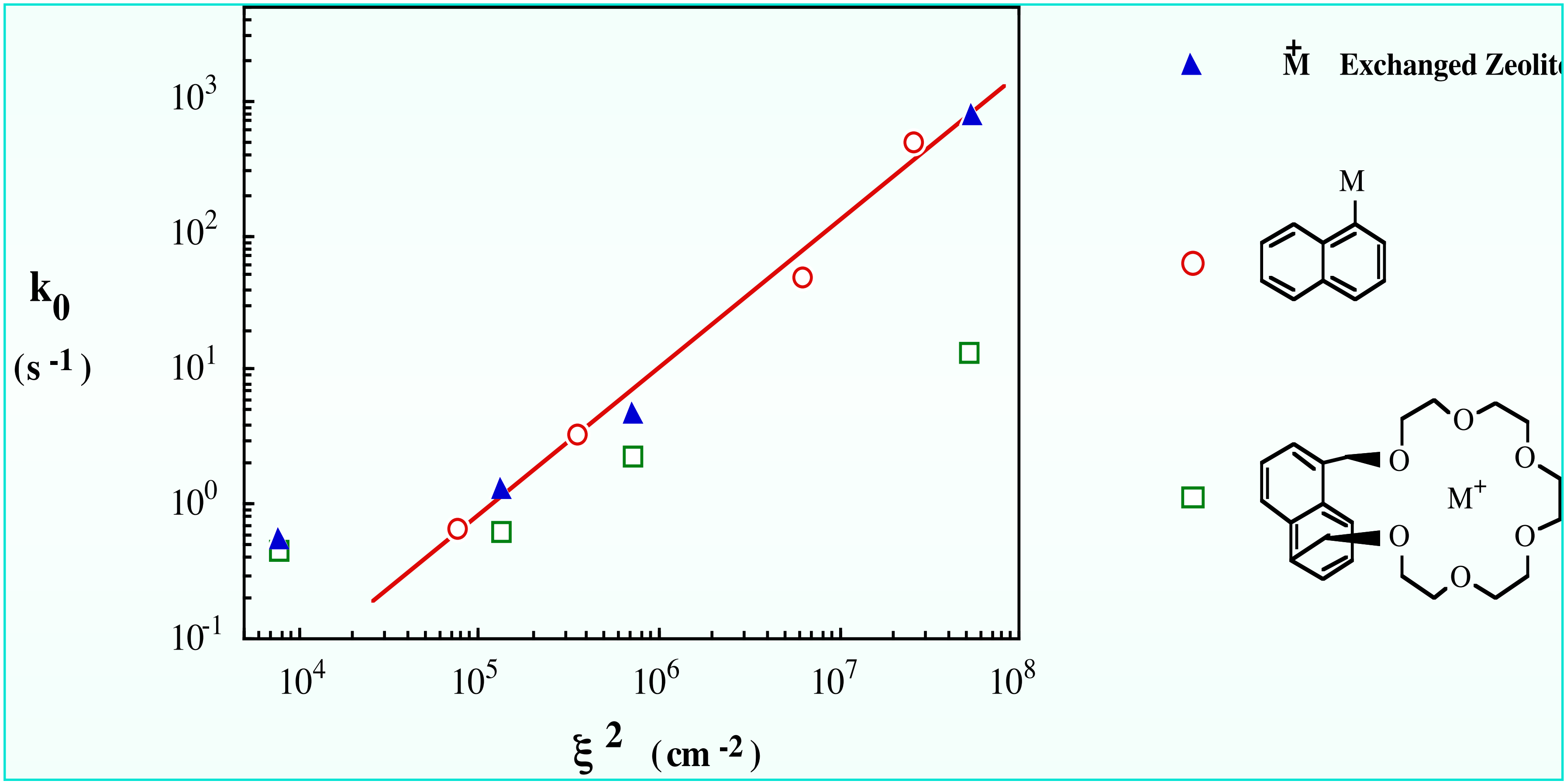
(El Sayed’s Rule)



Emission Spectra of Naphthalene Included in MY Zeolites
Dependence on the Alkali Ion: ππ*–ππ* Crossing



External Heavy Atom Effect on Triplet Decay Rates of Naphthalene

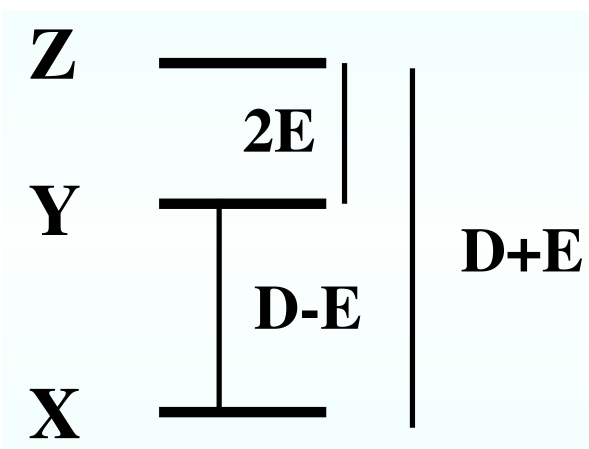


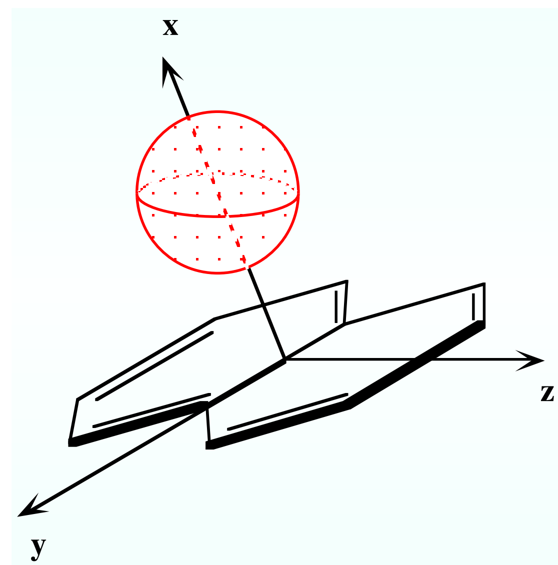
Heavy Atom Effect is Specific: ODMR Studies

Optical Detection of Magnetic Resonance (ODMR) -

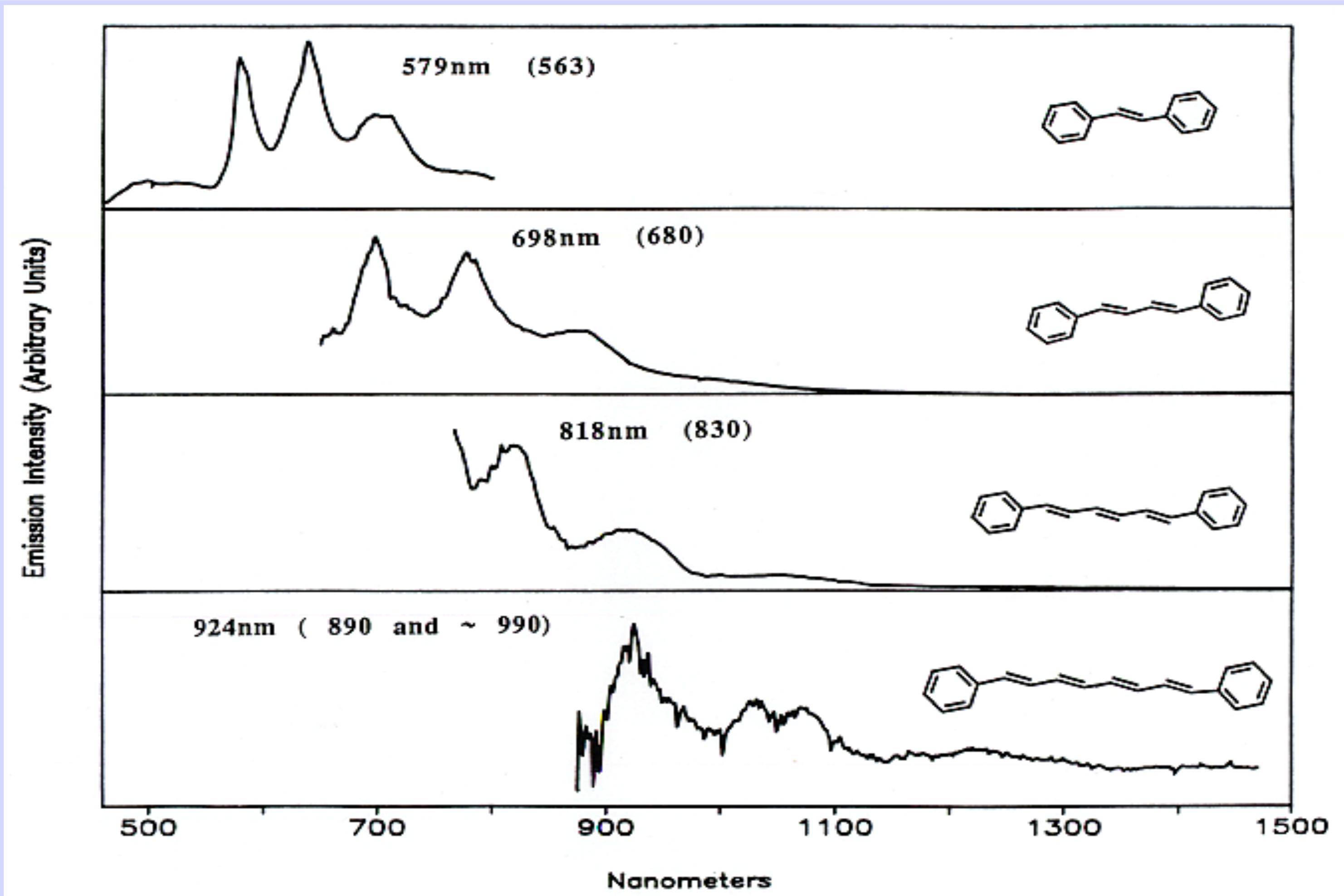
Triplet Sub-Level Specific Kinetics at 1.2 °K

- **Total decay constants from each sub-level**
- **Relative radiative rates from each sub-level**
- **Relative intersystem crossing rates to each sub-level**
- **Slow Passage ODMR Transitions**

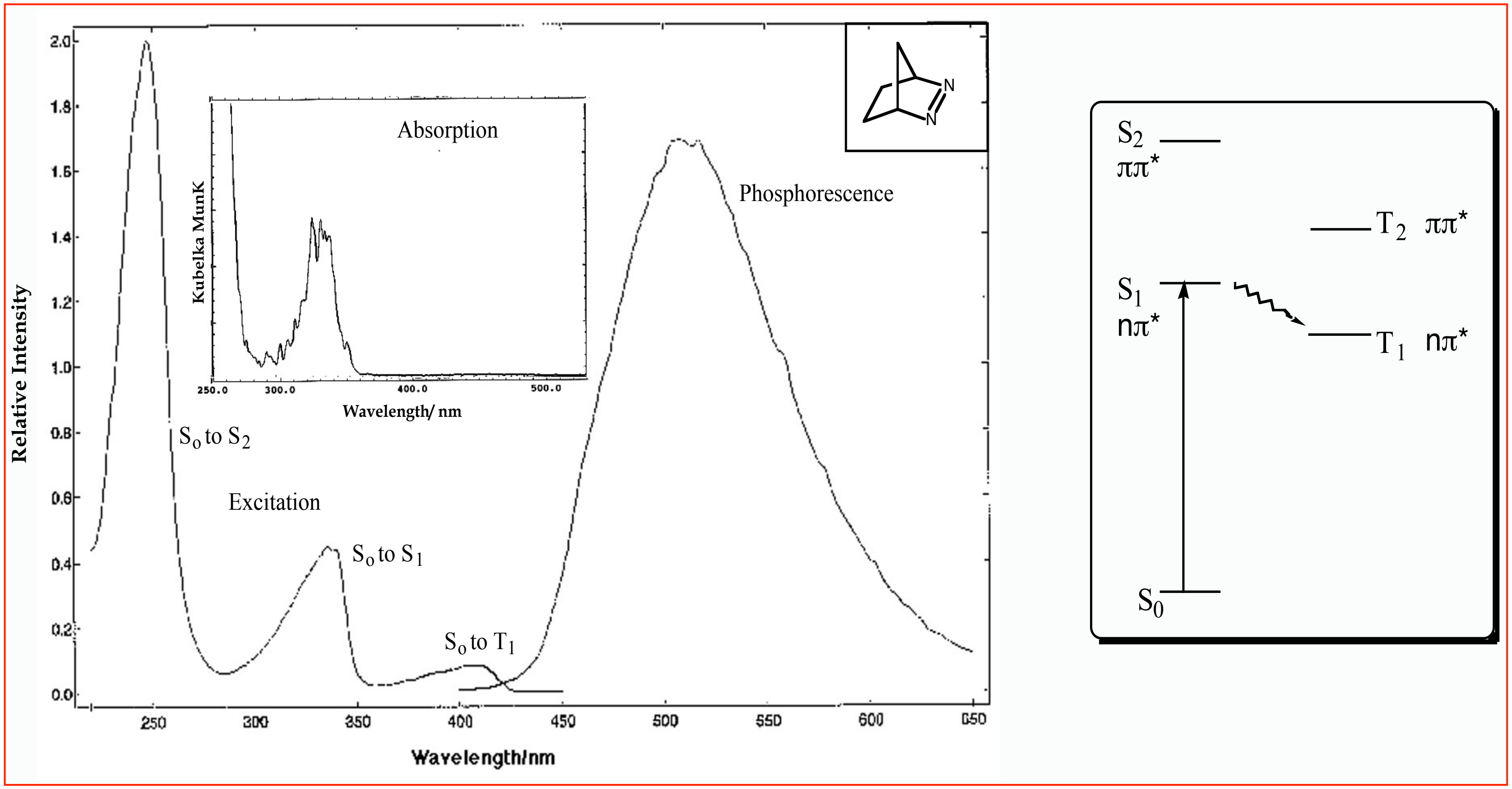




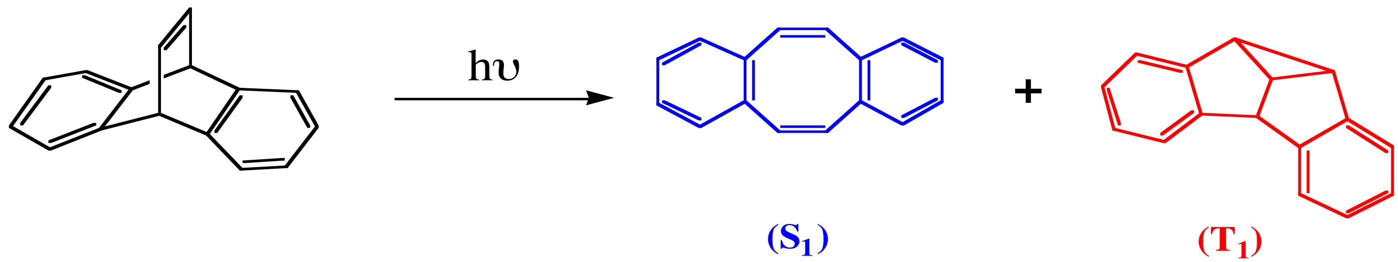
Phosphorescence From Diphenyl Polyenes: Unique to Zeolites



Phosphorescence from Azo Compounds in TlY at 77 K nπ*–nπ* crossing

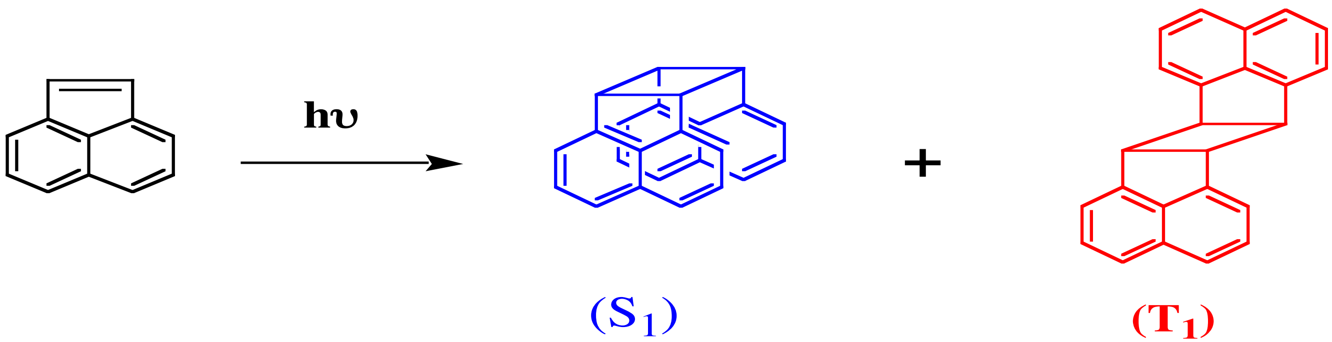


Photoproduct Distribution Influenced by Alkali Ions



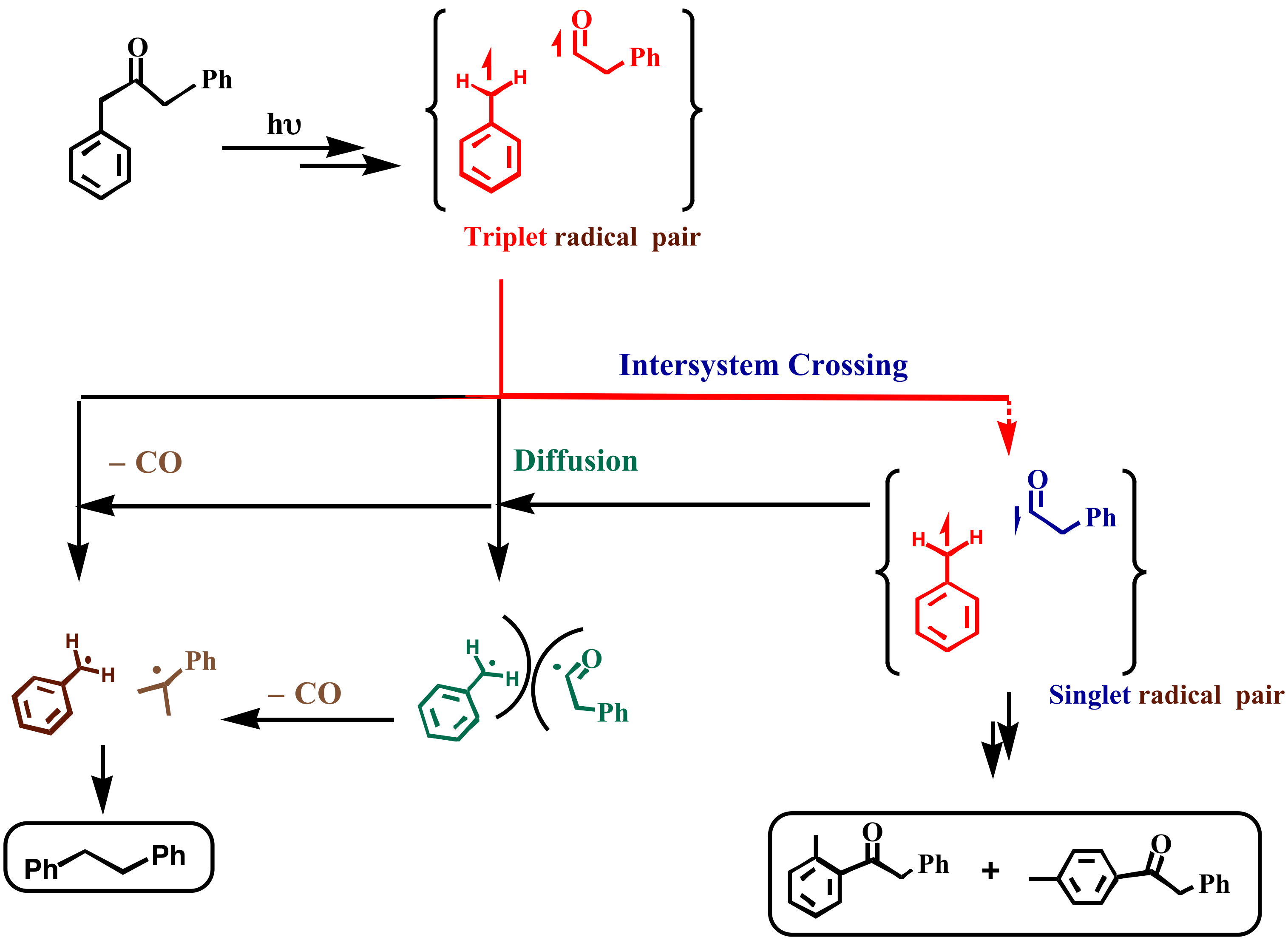
Acetonitrile	77	23
Acetone	-	100
KY(Hexane slurry)	75	25
RbY	35	65
CsY	28	72
TlY	1	99

Photoproduct Distribution Influenced by Alkali Ions

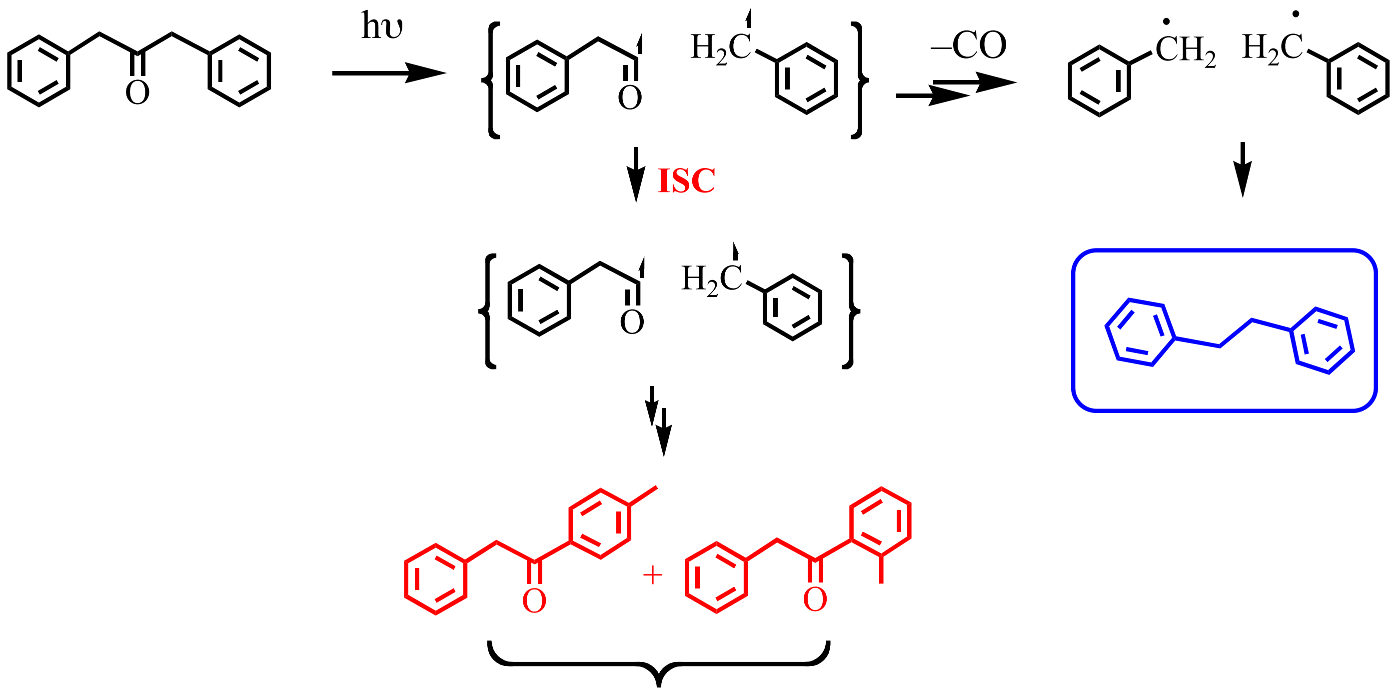


Zeolite	Cis/Trans
LiY	25
NaY	25
KY	2.3
RbY	1.5

Intersystem Crossing in Diradicals Influenced by Alkali Ions



Intersystem Crossing in Diradicals is also Influenced by Alkali Ions



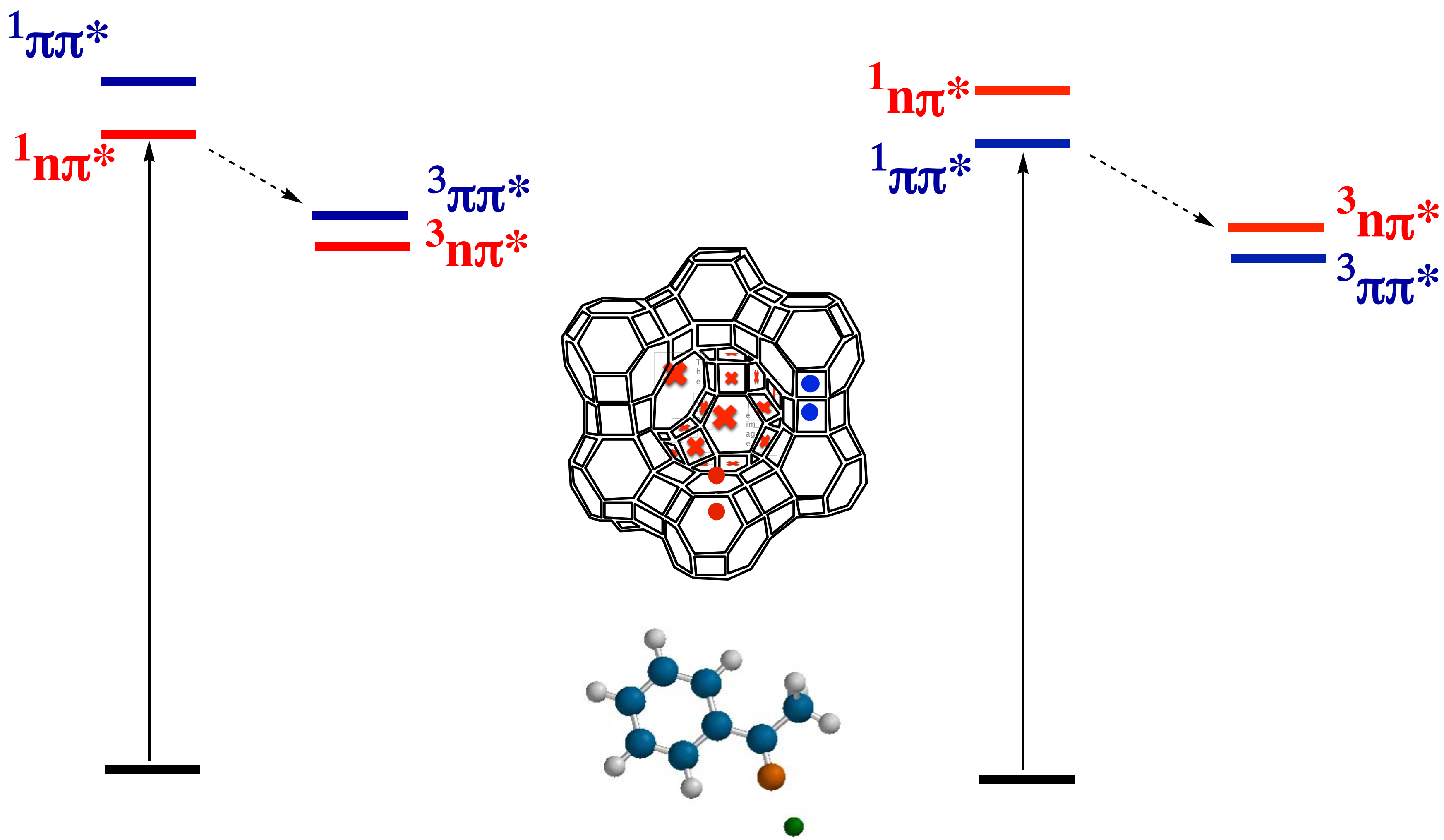
Hexane	**0**	**>99%**
KY (1.44Å)	**20**	**80**
RbY (1.58Å)	**30**	**70**
CsY (1.84Å)	**63**	**37**
TlY (1.40Å)	**76**	**23**

Alkali Ion Controlled Photochemistry

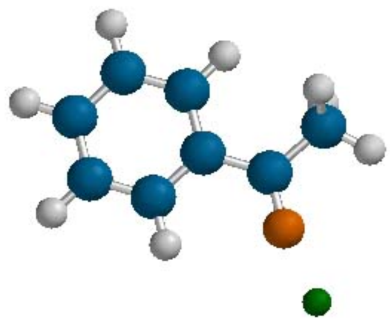
Alkali Ion-Organic Interactions

- **Alkali Ion-Organic Very Weak Interaction (Spin-Orbit coupling)**
- **Alkali Ion-Carbonyl Dipolar Interaction**
- **Alkali Ion-π (Alkenes) Quadrupolar Interaction**
- **Alkali Ion-π (Aromatics) Quadrupolar Interaction**

Alkali Ion Effect Induced State Switching

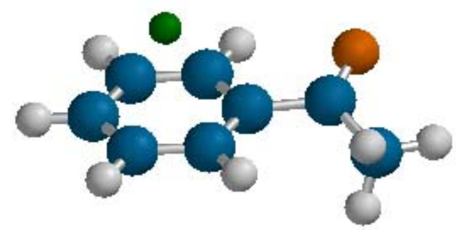


Binding Modes and Binding Affinities of Alkali Ions to Acetophenones



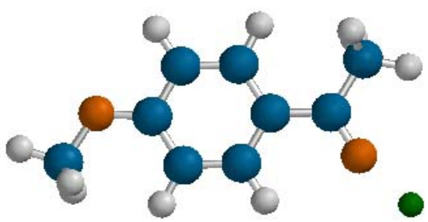
Acetophenone
Li^+ bound to carbonyl

BA: 55.28 kcal/mole



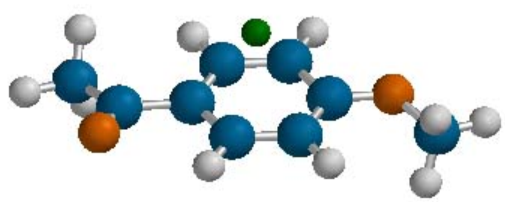
Acetophenone
Li^+ bound to the phenyl ring

BA: 37.77 kcal/mole



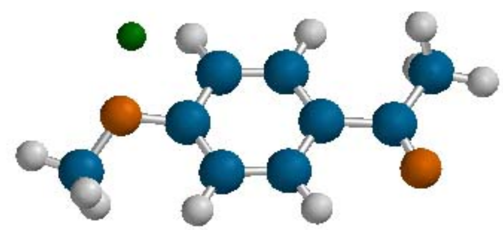
4’-Methoxyacetophenone
Li^+ bound to carbonyl

BA: 59.74 kcal/mole



4’-Methoxyacetophenone
Li^+ bound to the phenyl ring

BA: 40.35 kcal/mole



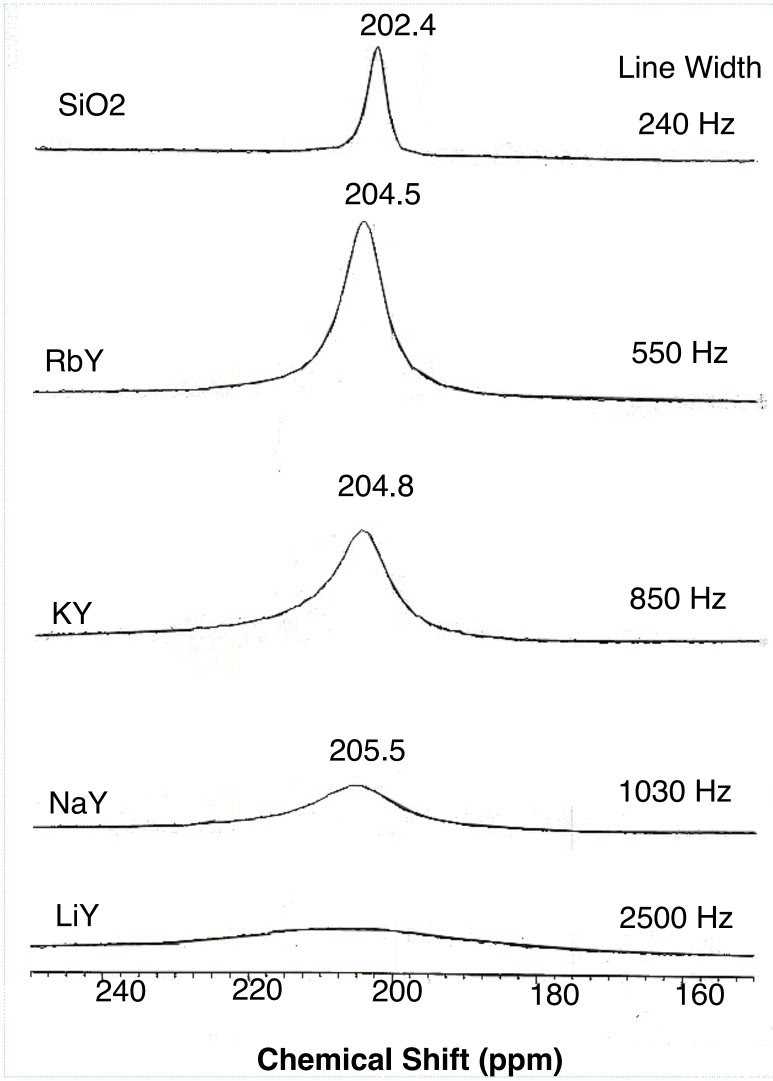
4’-Methoxyacetophenone
Li^+ bound to methoxy

BA: 38.46 kcal/mole

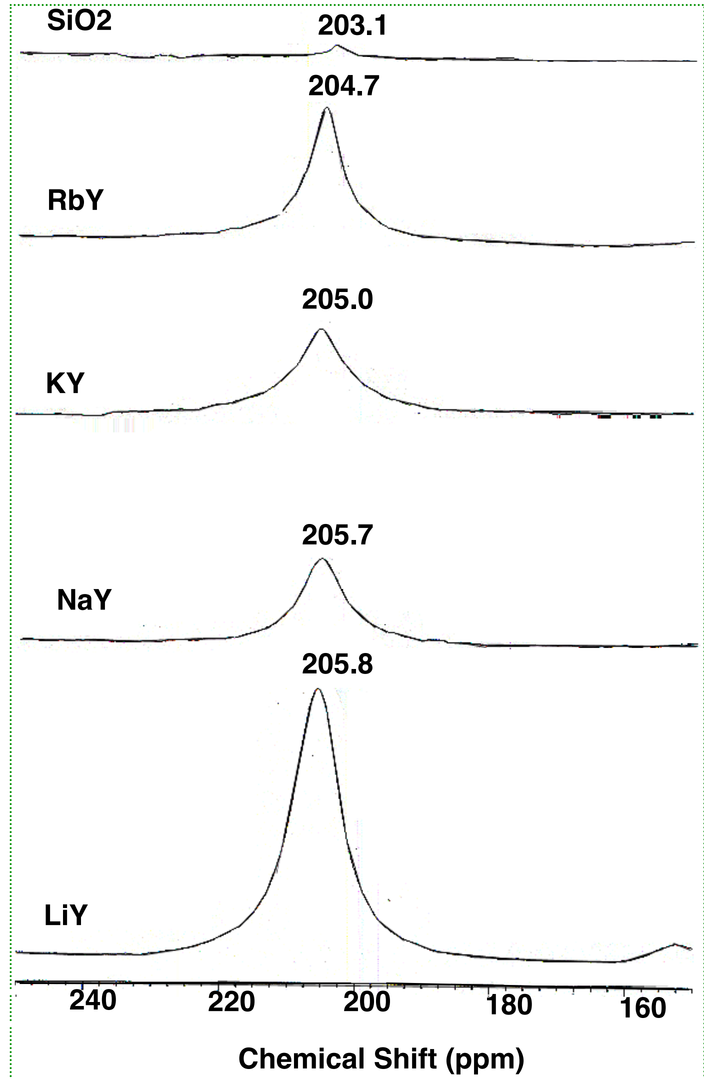
TITAN – ROB3LYP 6-31G*

^{13}C MAS NMR Studies of Acetophenone ($^{13}C=O$) Adsorbed in MY Zeolite

Static

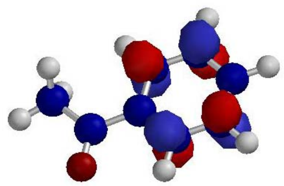
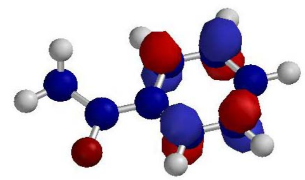
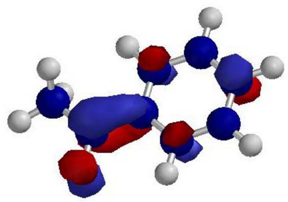
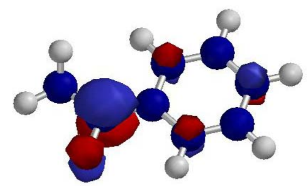
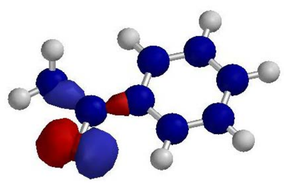
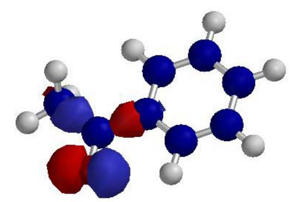
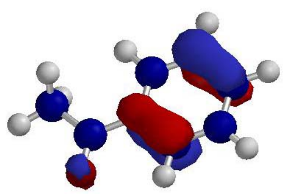
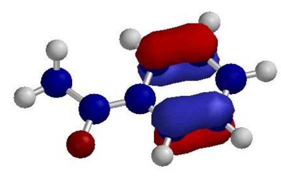
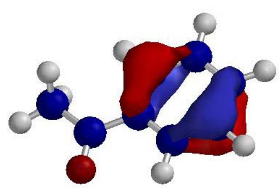
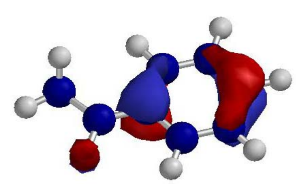


^{1}H ^{13}C CP MAS



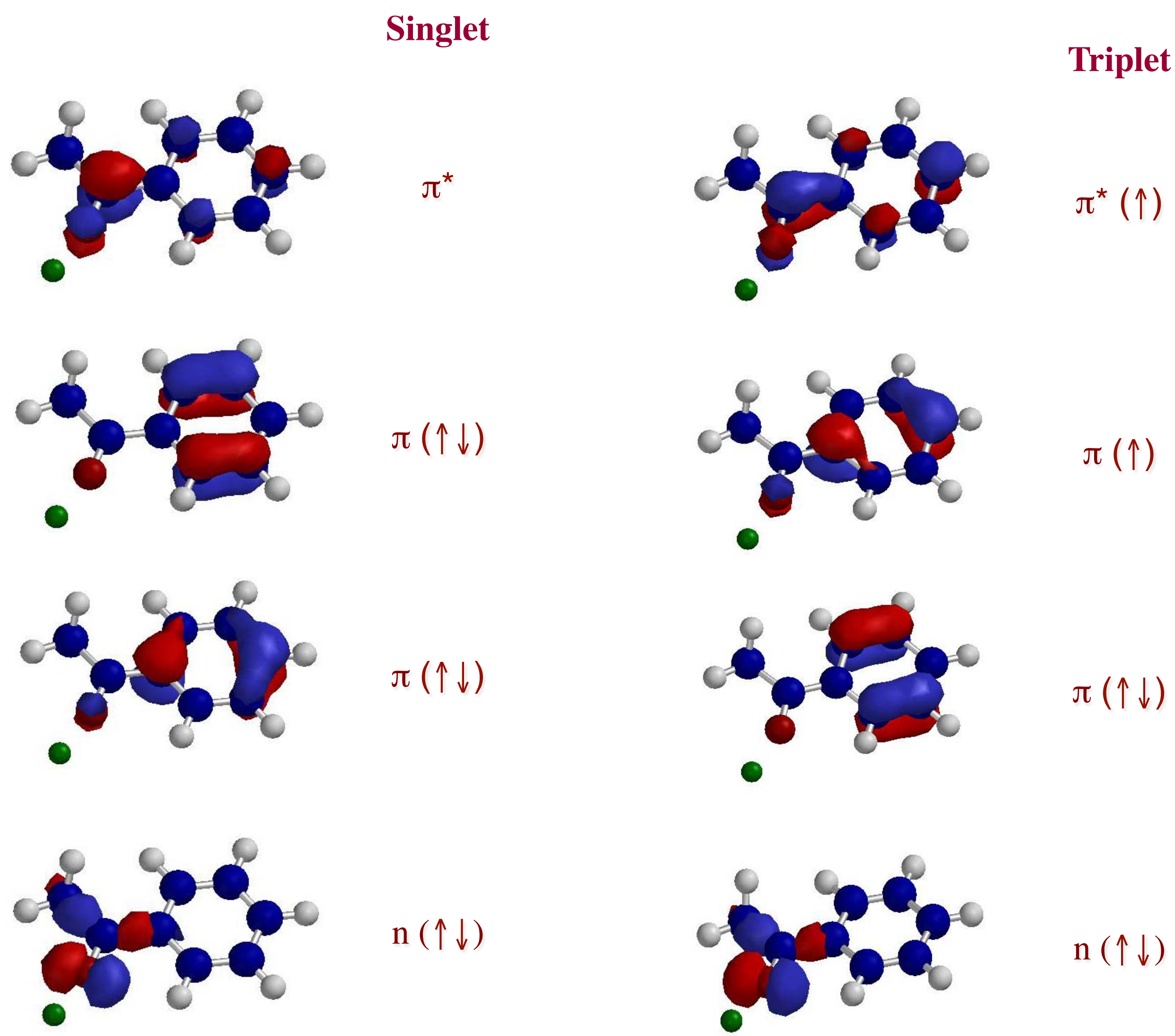
Orbital diagram - Nature of triplet excited state (T_1) - Acetophenone

(TITAN – ROB3LYP 6-31G*)

	Singlet		Triplet
	π^*		π^*
	π^*		π^* (↑)
	n (↑↓)		n (↑)
	π (↑↓)		π (↑↓)
	π (↑↓)		π (↑↓)

E_{S-T} = 71.60 kcal/mol

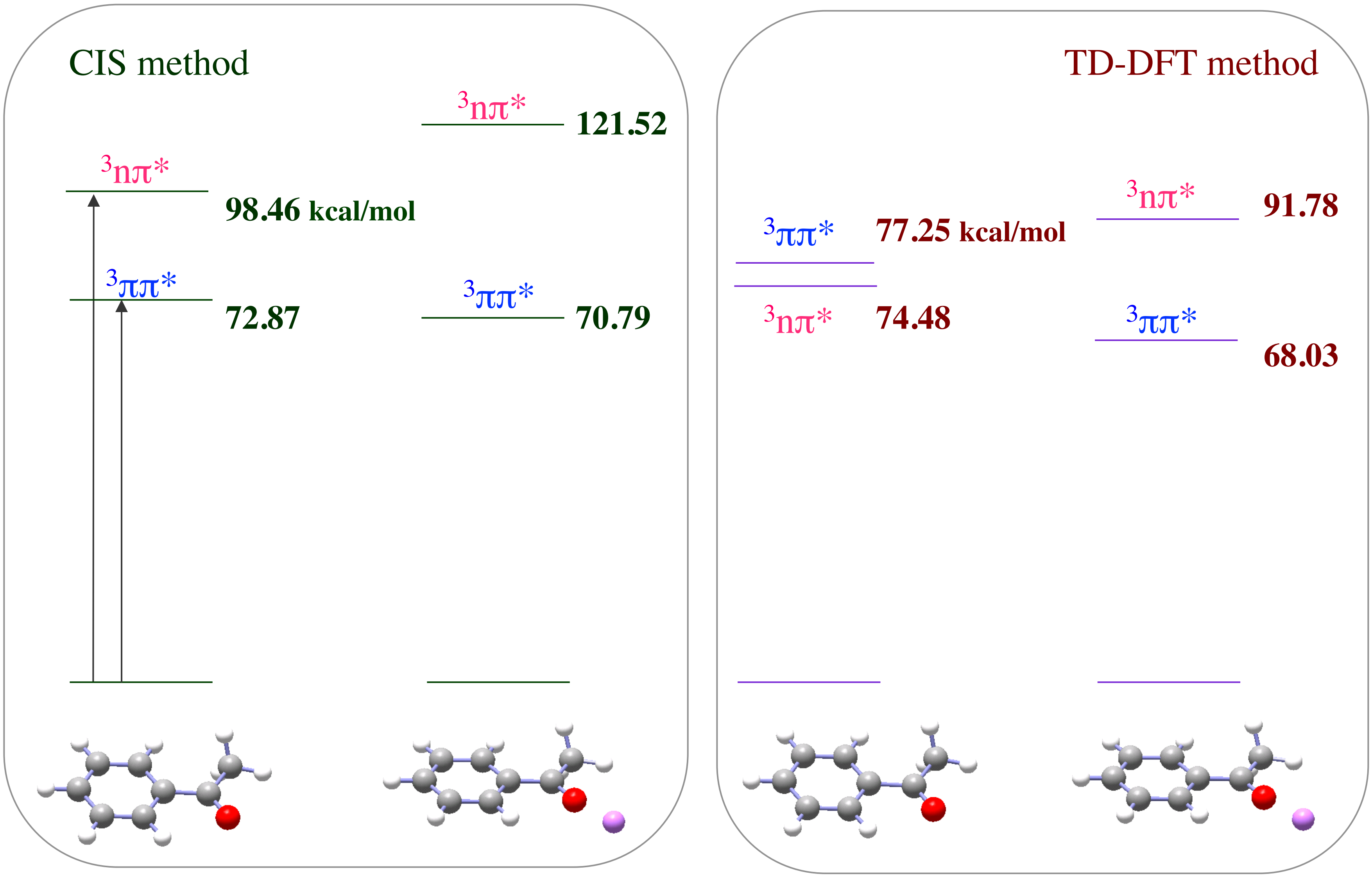
Orbital diagram – Nature of triplet excited state (T_1)
Acetophenone – Li^+ complex (C=O) (TITAN – ROB3LYP 6-31G*)



Similar results were obtained with Na^+

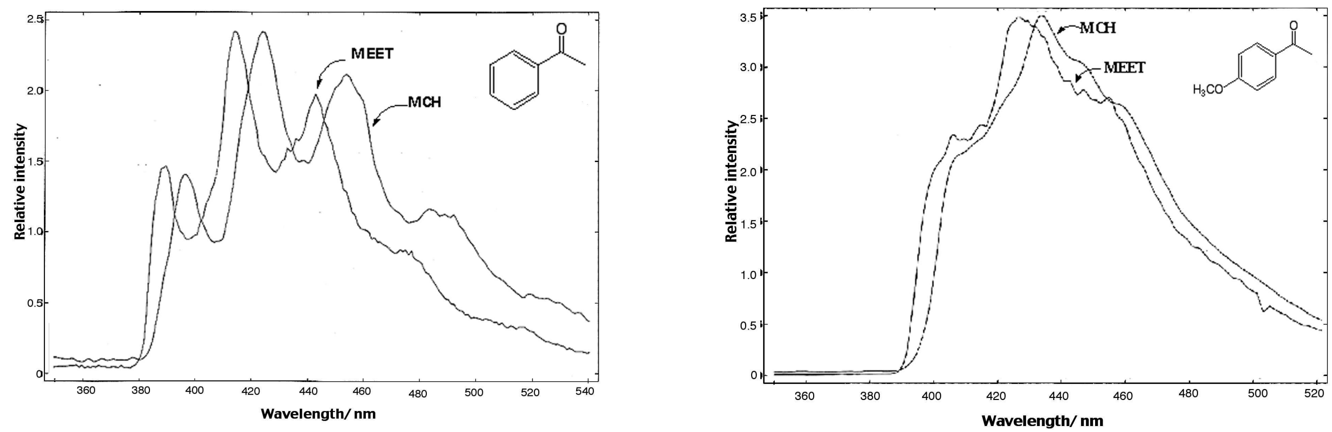
$E_{S\text{-}T}$ = 69.09 kcal/mol

Acetophenone and Acetophenone-Li$^+$ Complex

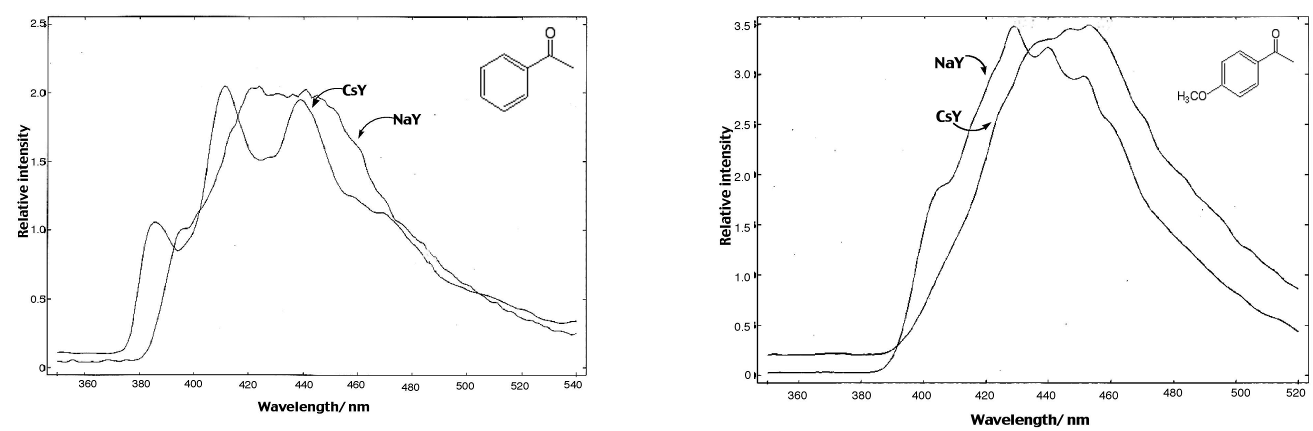


Gaussian - CIS/6-31+G* level and TD/6-31+G*

Steady State Emission

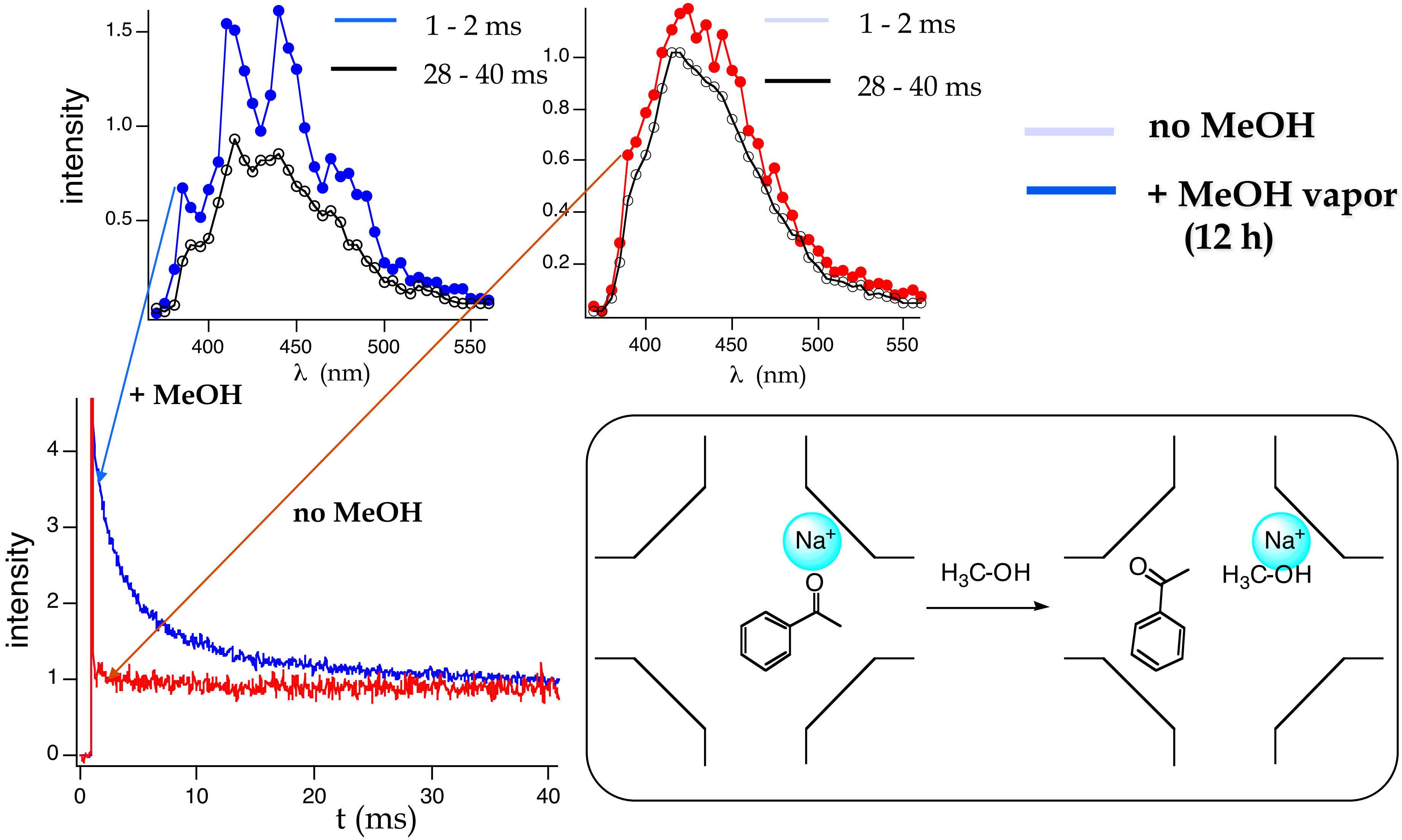


Phosphorescence emission spectra of acetophenone and 4’-methoxyacetophenone in methylcyclohexane glass and methanol/ethanol glass at 77°K

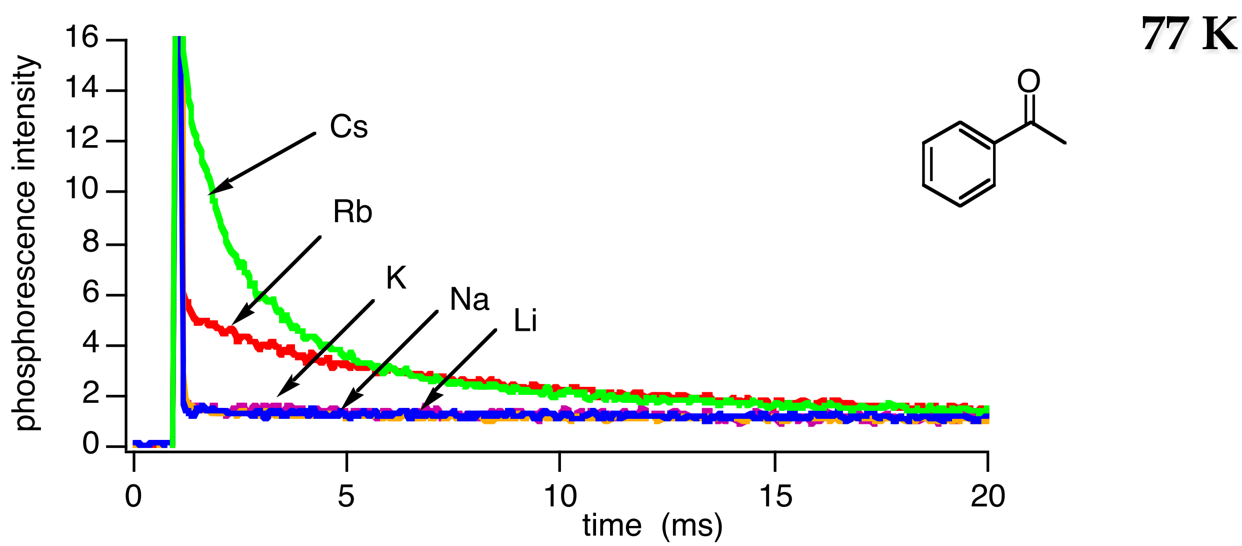


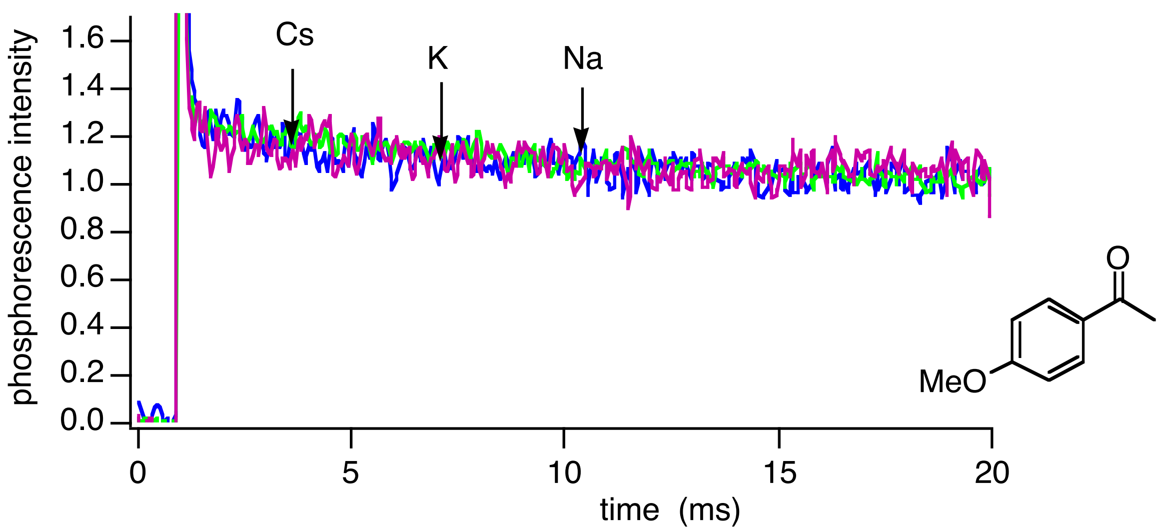
Phosphorescence emission spectra of acetophenone and 4’-methoxyacetophenone in NaY and CsY at 77°K

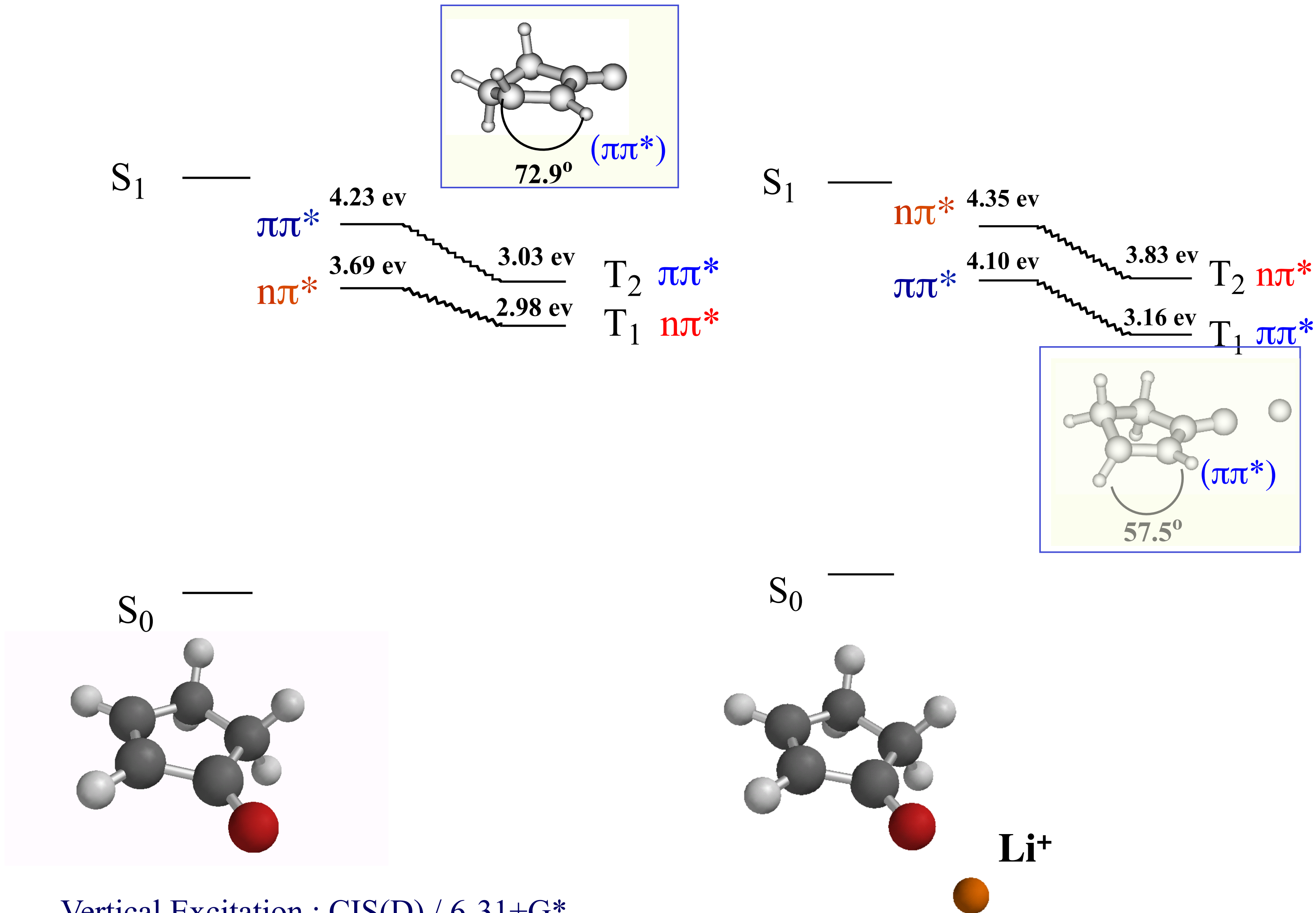
Acetophenone Emission Influenced by Zeolite
Time Resolved Studies



Triplet Lifetime Dependence on Alkali Ion

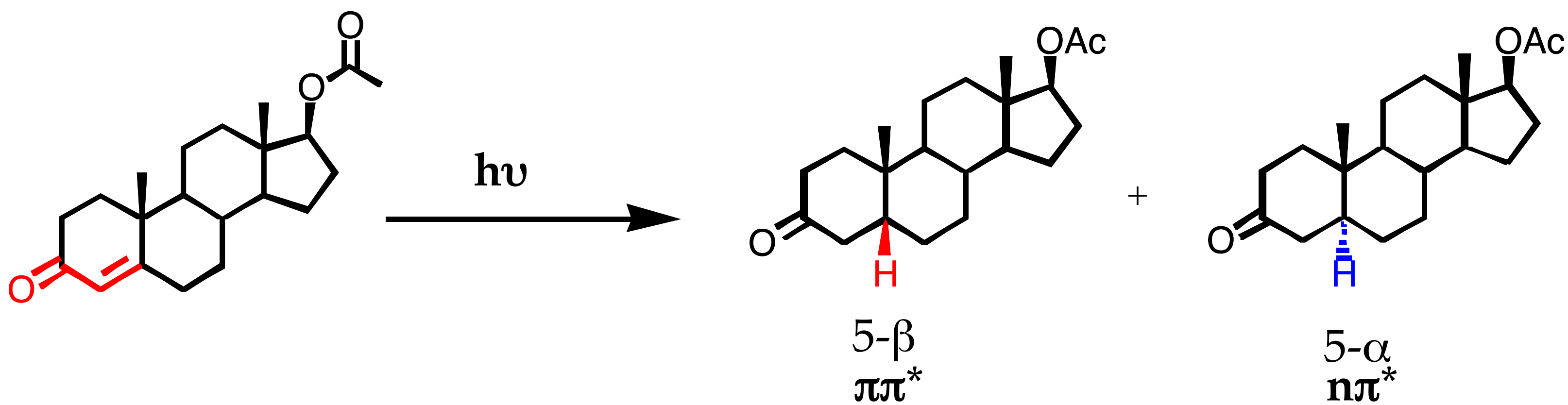






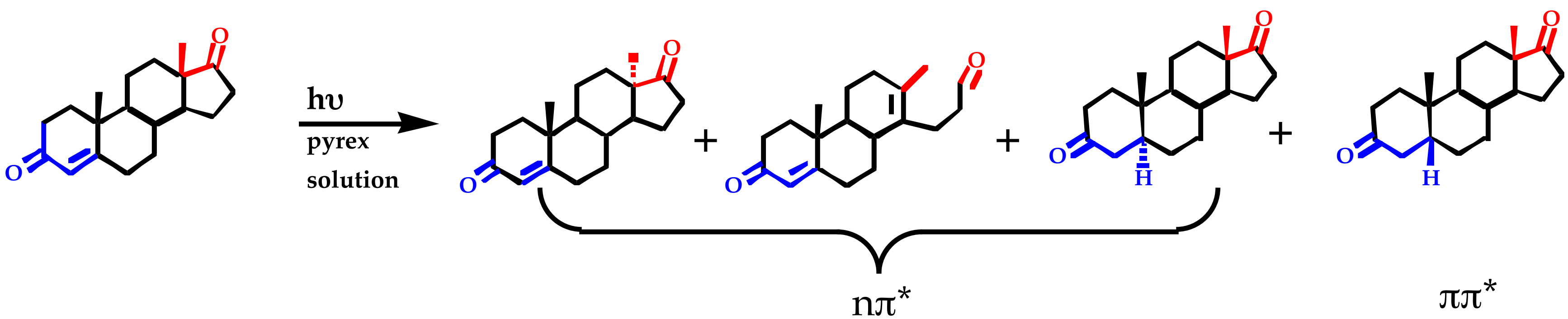
Vertical Excitation : CIS(D) / 6-31+G*
Relaxed Triplet : B3LYP / 6-31G*

Reactivity Change Due to State Switching within Zeolites



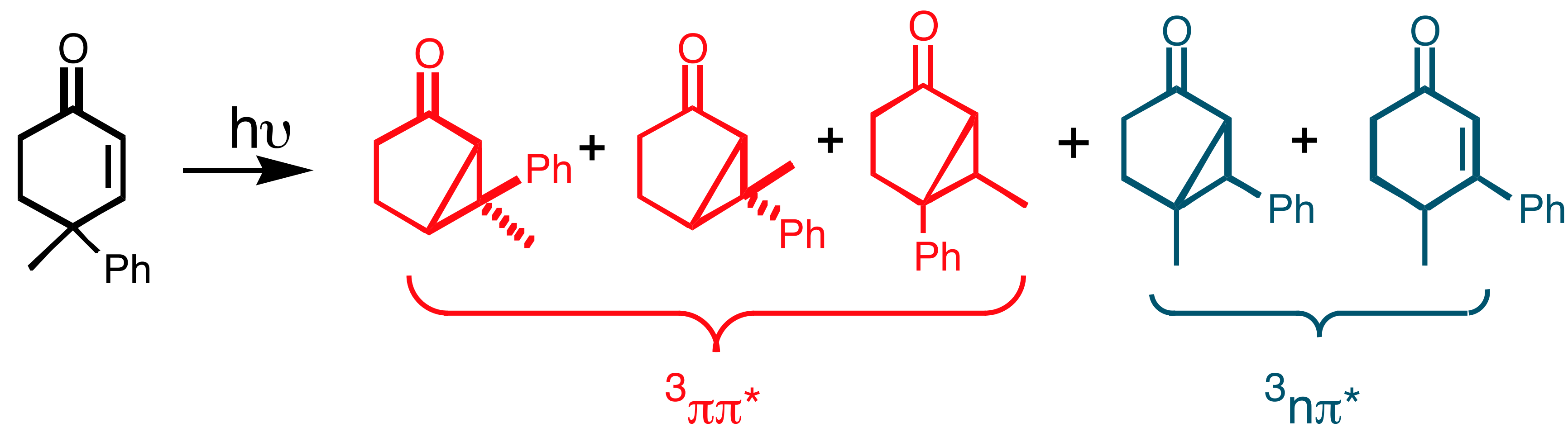
hexane	No reaction	
2-propanol	27 %	73 %
NaY (Si/Al: 2.5)	85	15
NaY (Si/Al: 300)	No reaction	

Reactivity Change Due to State Switching within Zeolites



Hexane	**40%**	**4%**	–	–
2-Propanol	**18**	**2**	**14**	–
Na Y (Si/Al: 2. 5)	–	–	**15**	**85**
High Silica Y (Si/Al: >285)	**30 %**	–	–	–

Reactivity Change Due to State Switching within Zeolites



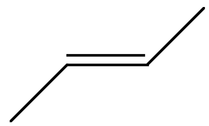
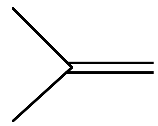
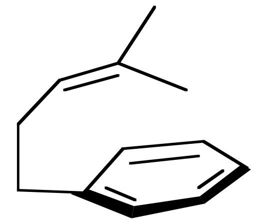
Benzene	**0 %**	**100%**
Ethanol	**33**	**67**
NaY/hexane	**70**	**30**

Alkali Ion Controlled Photochemistry

Alkali Ion-Organic Interactions

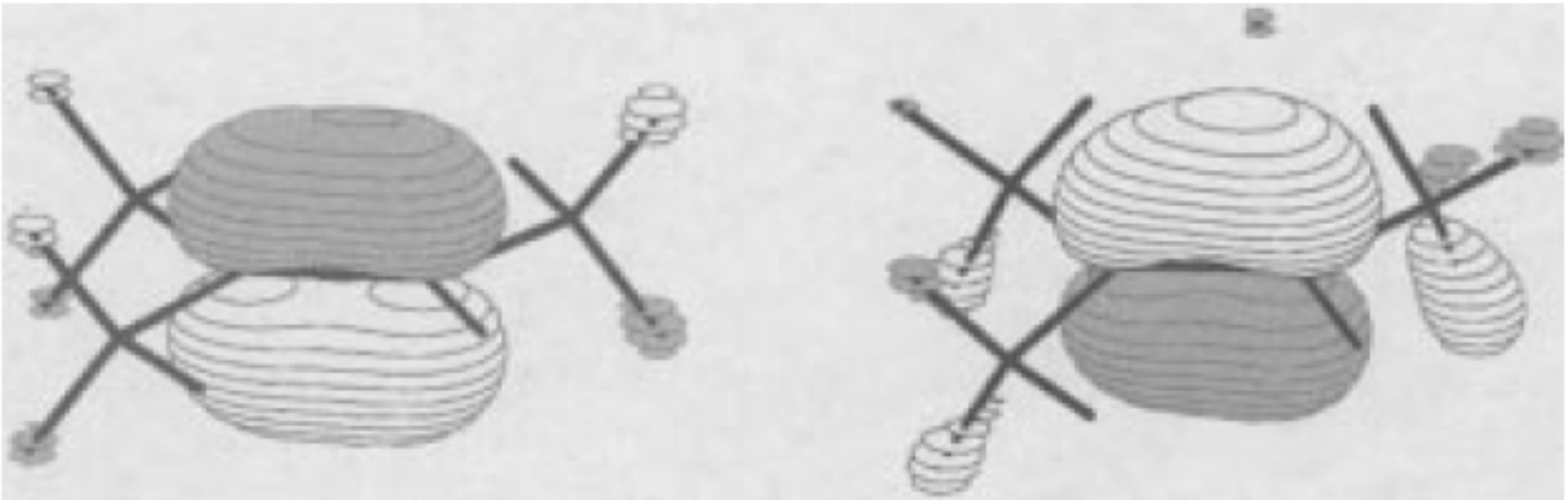
- Alkali Ion-Organic Very Weak Interaction (Spin-Orbit coupling)
- Alkali Ion-Carbonyl Dipolar Interaction
- **Alkali Ion-π (Alkenes) Quadrupolar Interaction**
- Alkali Ion-π (Aromatics) Quadrupolar Interaction

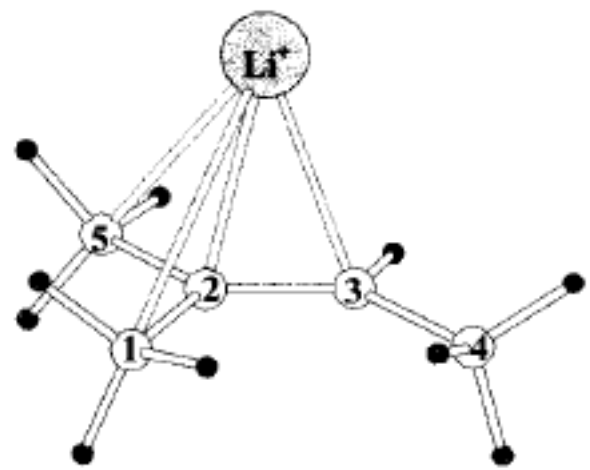
Theoretical Estimation of Alkali Ion-Olefin Binding Energy

				
	Li^+	-26.11 kcal/mol	-26.36 kcal/mol	-51.76 kcal/mol
	Na^+	-17.43	-17.67	-34.51
	K^+	-8.91	-9.61	-19.45
	Rb^+	-7.28	-7.83	-17.57
	Cs^+	-5.42	-5.84	-10.67

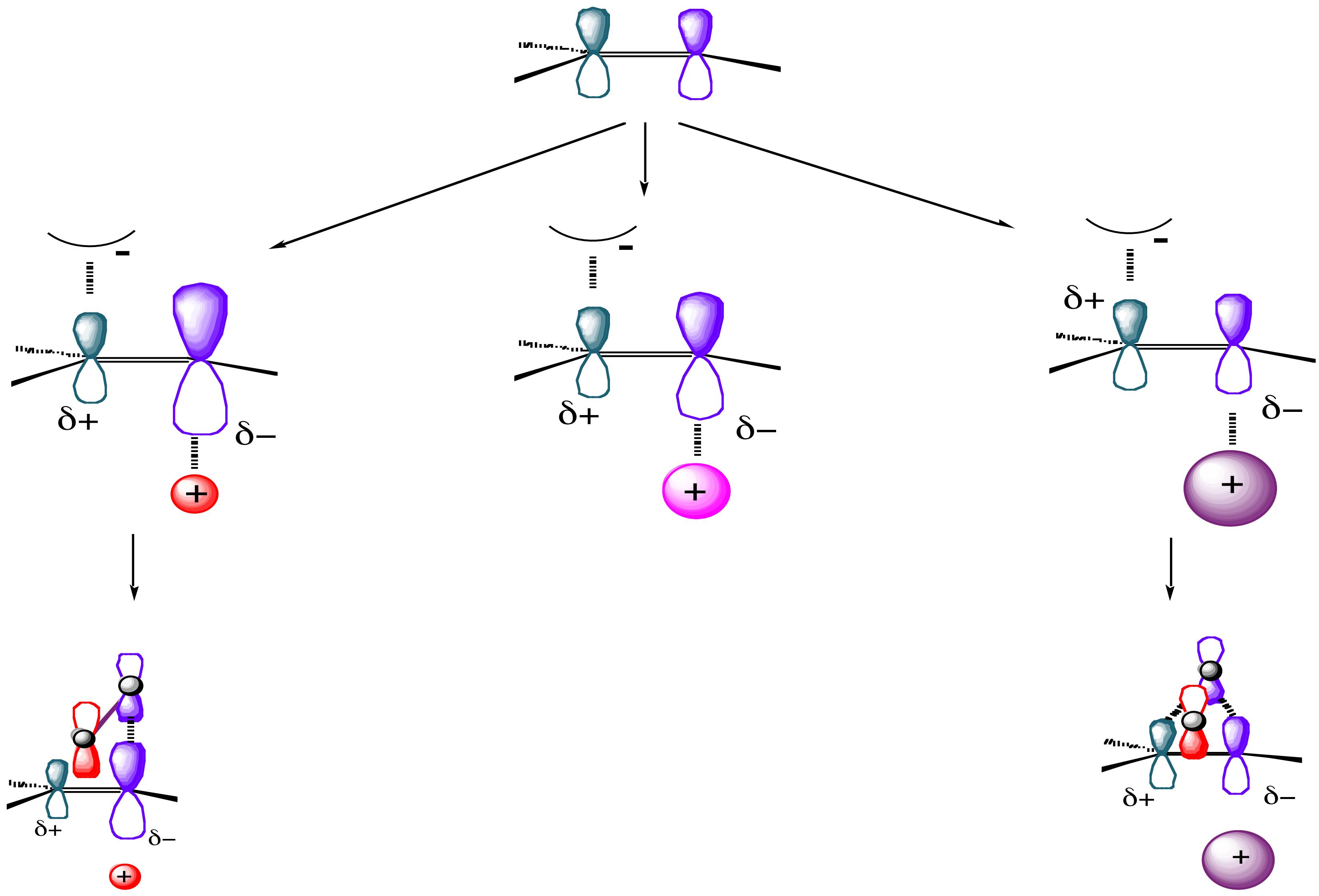
Hartree-Fock method/6-31G*

Cation dependent electron density distribution

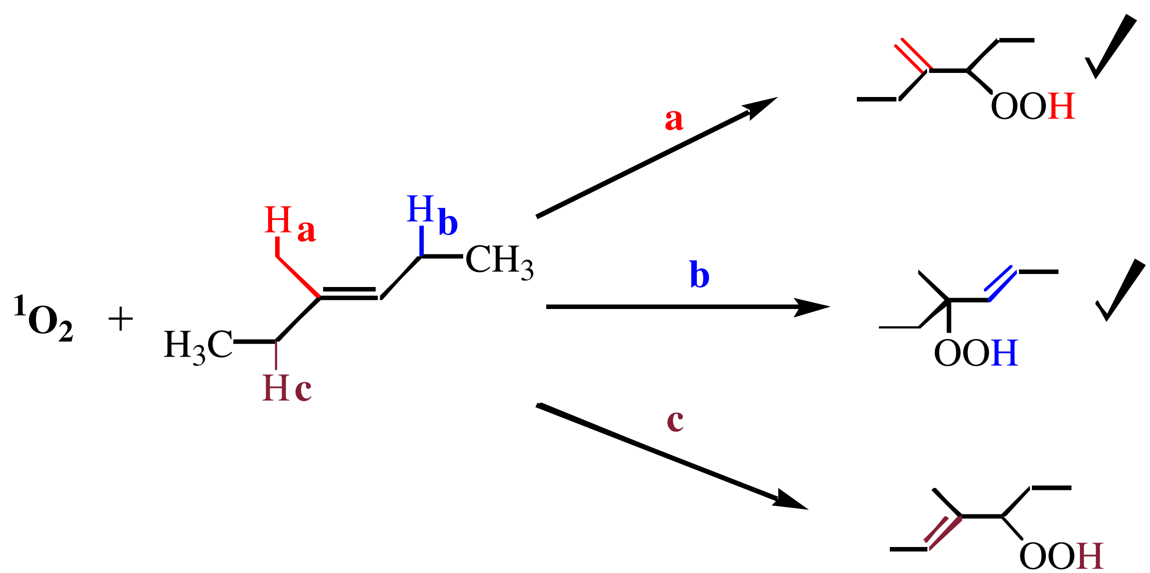




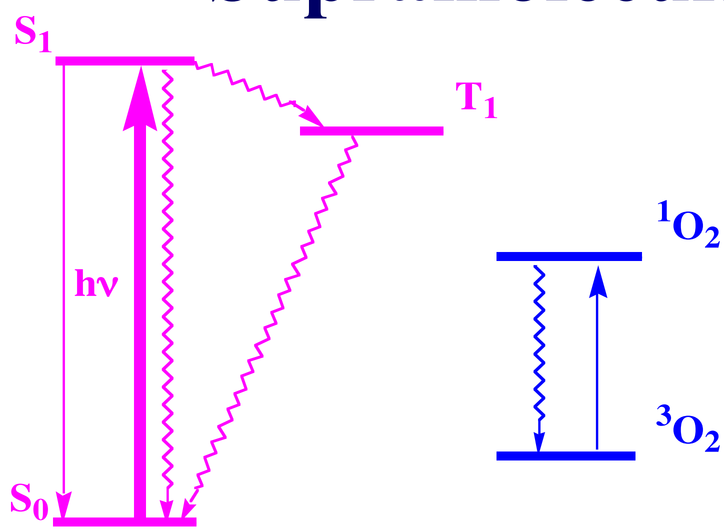
Electric Field May Polarize the Olefin

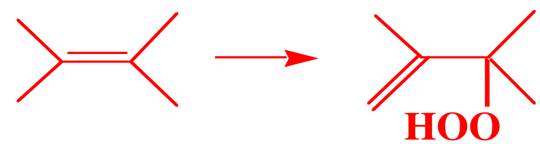


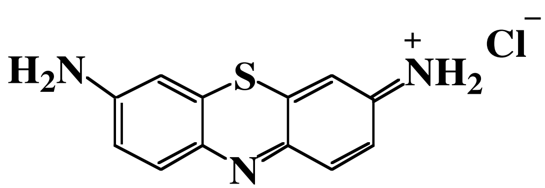
Regioselective Photo-Oxidation



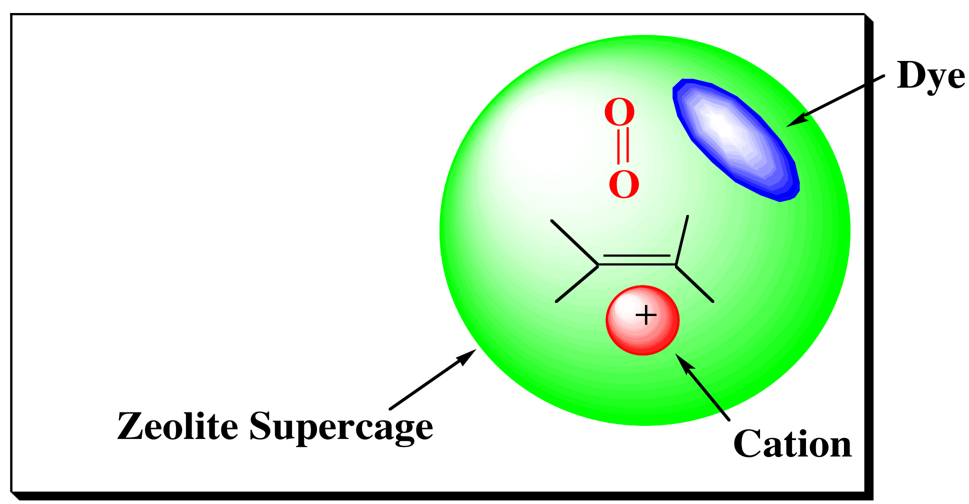
Supramolecular Assembly



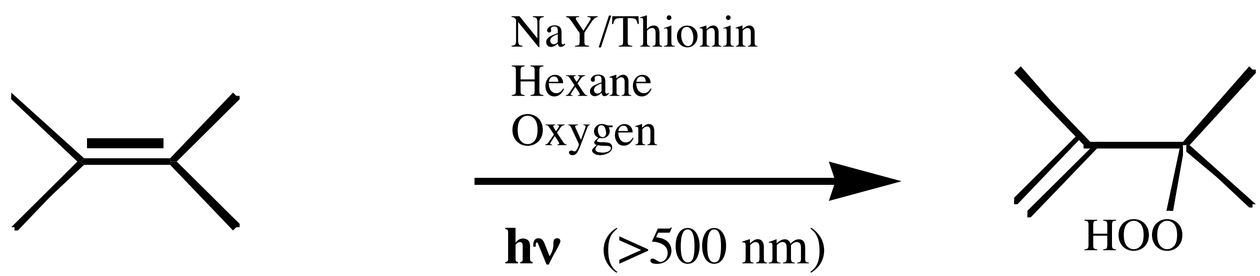


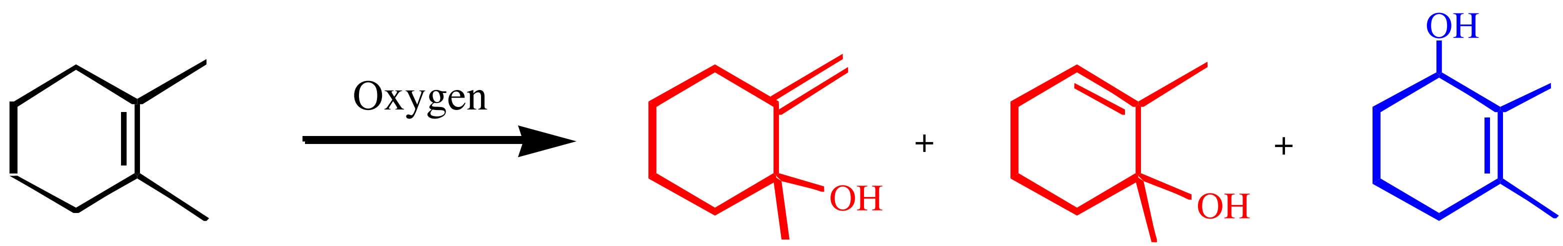


Thiazine dye: Thionin



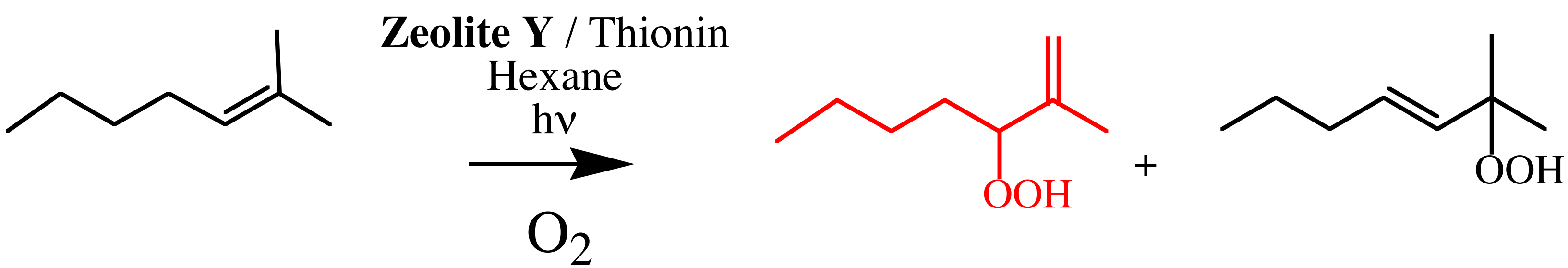
Evidence for Singlet Oxygen Generation within Zeolites—Reaction





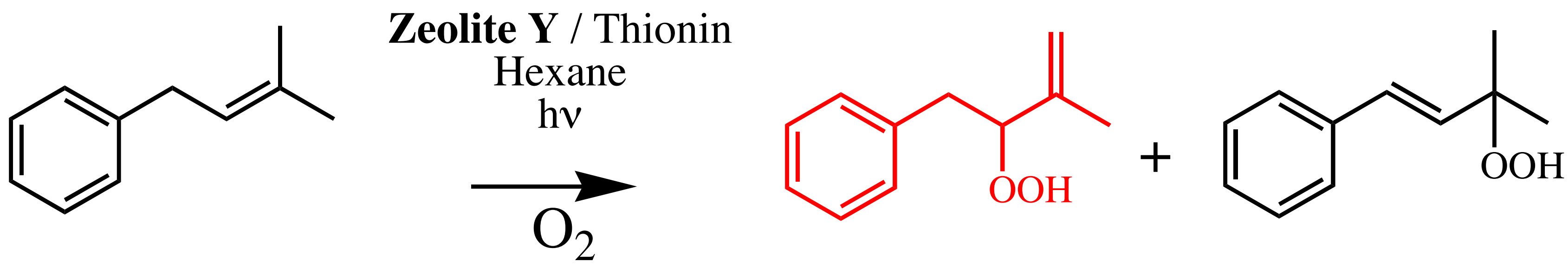
Rose Bengal /CH_3CN	89	11	0
Thionin/Na Y/Hexane	90	10	0
Autoxidation	6	39	54

Effect of Alkali Ions on Product Selectivity



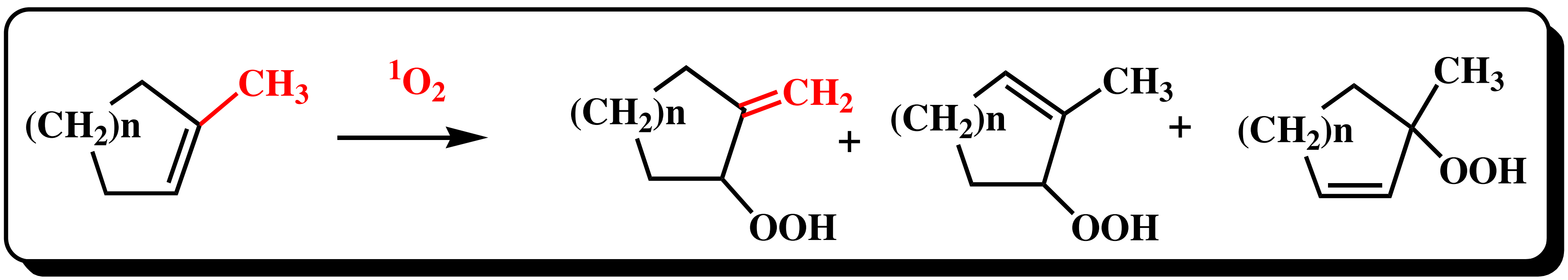
Cation	Cation radius	2°	3°
Acetonitrile/RB		**49**	**51**
LiY / Thionin	**0.76 Å**	**74**	**26**
NaY / Thionin	**1.02**	**74**	**26**
RbY / Thionin	**1.52**	**59**	**41**
CsY / Thionin	**1.67**	**50**	**50**

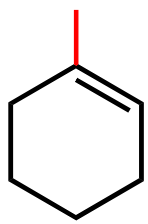
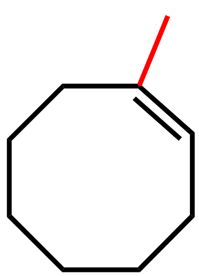
Effect of Alkali Ions on Product Selectivity



Cation	Cation radius	2°	3°
Acetonitrile /RB		**51**	**49**
LiY / Thionin	0.76 Å	**95**	**5**
NaY / Thionin	1.02	**90**	**10**
RbY / Thionin	1.52	**70**	**30**
CsY / Thionin	1.67	**55**	**45**

Effect of Alkali Ions on Product Selectivity



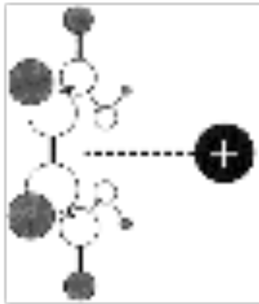
	Thionin/CH_3CN	40	15	45
	Thionin/NaY/Hexane	88	2	10
	RB/CH_3CN	27	42	31
	Thionin/NaY/Hexane	76	18	6

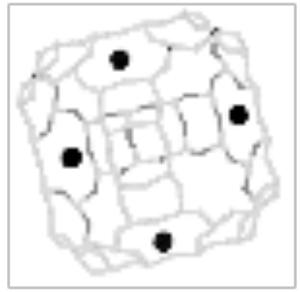
Alkali Ion Controlled Photochemistry

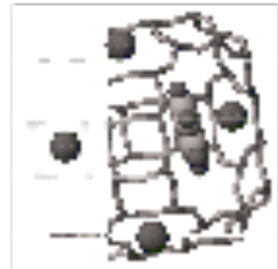
Alkali Ion-Organic Interactions

- Alkali Ion-Organic Very Weak Interaction (Spin-Orbit coupling)
- Alkali Ion-Carbonyl Dipolar Interaction
- Alkali Ion-π (Alkenes) Quadrupolar Interaction
- **Alkali Ion-π (Aromatics) Quadrupolar Interaction**

Computed Interaction Energies (kcal/mole)



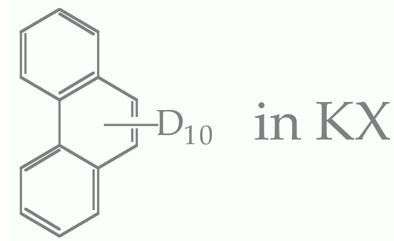


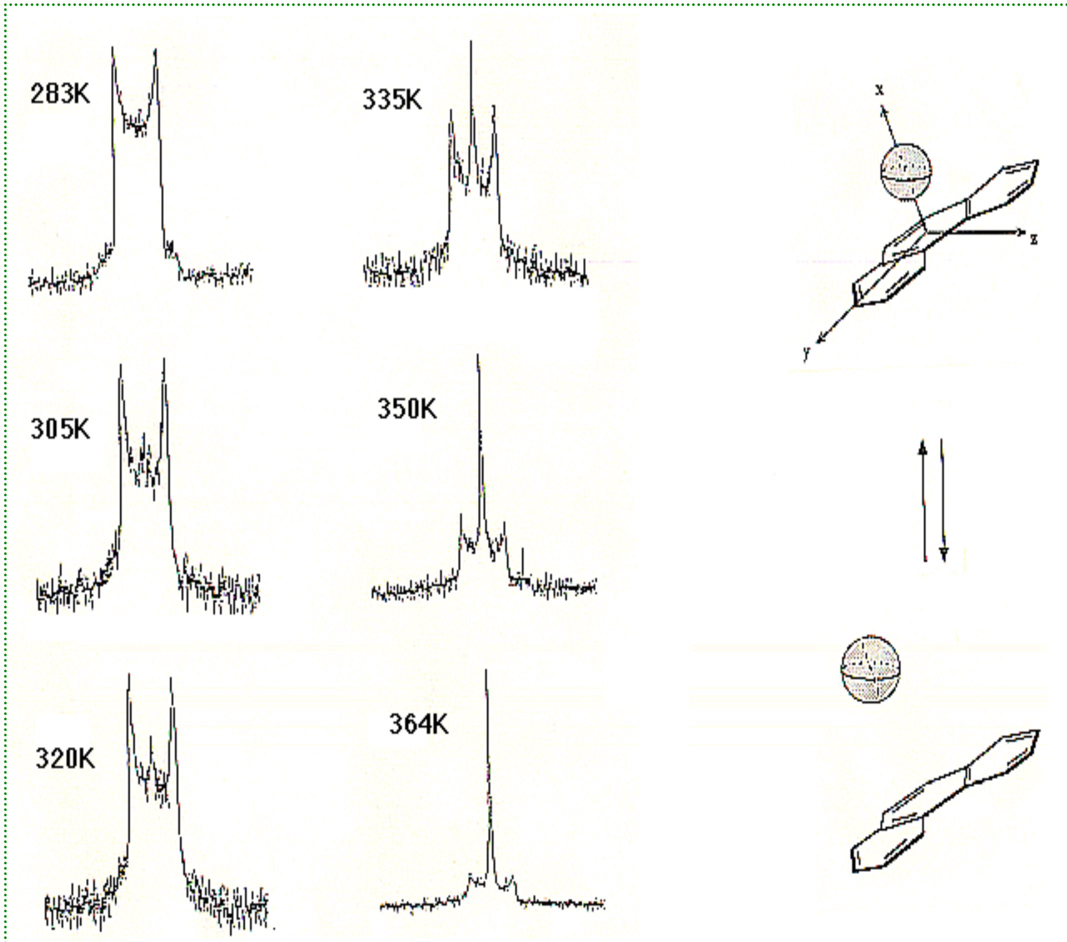


Metal ion	**M^+..Bz**
Li	-43.8
Na	-29.7
K	-16.7
Rb	-14.6
Cs	-11.9

All the values are computed at MP2 level of theory with a 6-31G* basis set for C, H, Li and Na. Hay-Wadt effective core potential with valence functions are employed for the heavier metal ions such as K, Rb and Cs.

Cation-π interaction
Variable temperature NMR





NaX

ΔH= –14.9 kcal/mole

ΔS= 52.5 cal/K.mole^{-1}

ΔF_{300} = 0.85 kcal/mole

KX

ΔH= –11.0 kcal/mole

ΔS= 29.9 cal/K.mole^{-1}

ΔF_{300} = 2.03 kcal/mole

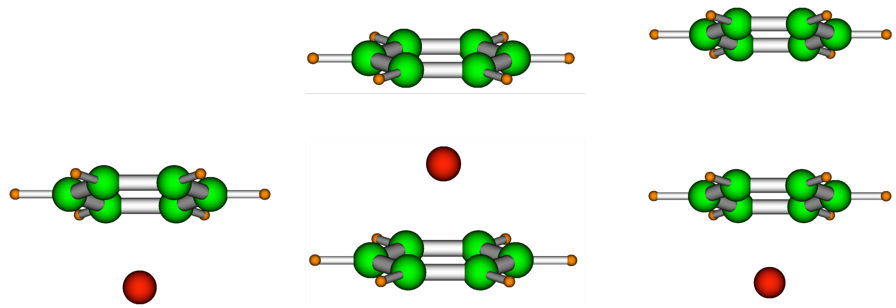
CsX

ΔH= –7.9 kcal/mole

ΔS= 22.7 cal/K.mole^{-1}

ΔF_{300} = 1.1 kcal/mole

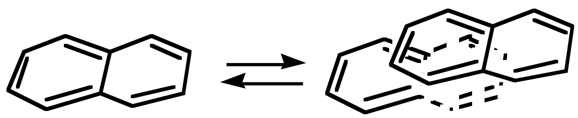
Computed Interaction Energies (kcal/mole)

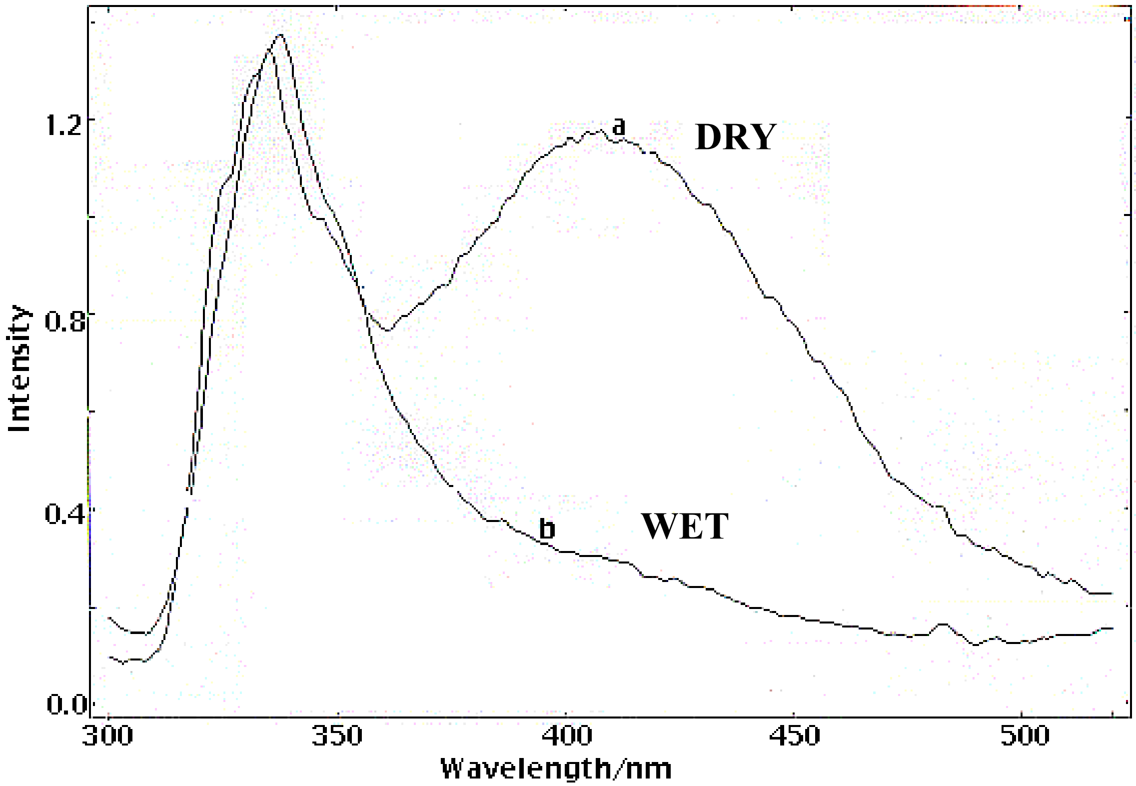


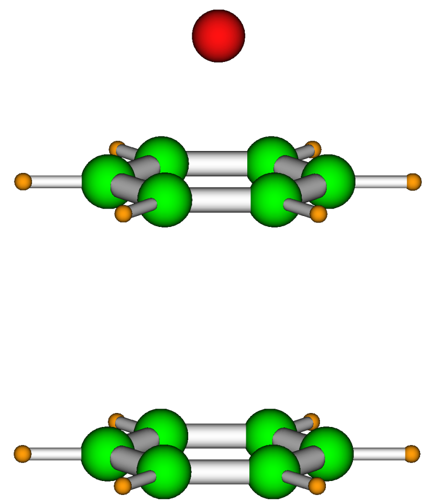
Metal ion /System	M^+..Bz	Bz..M^+..Bz	[M^+..Bz]..Bz
Li	-43.8	-81.1	-6.93
Na	-29.7	-56.2	-5.77
K	-16.7	-32.3	-5.03
Rb	-14.6	-27.7	-4.50
Cs	-11.9	-22.6	-4.19

All the values are computed at MP2 level of theory with a 6-31G* basis set for C, H, Li and Na. Hay-Wadt effective core potential with valence functions are employed for the heavier metal ions such as K, Rb and Cs.

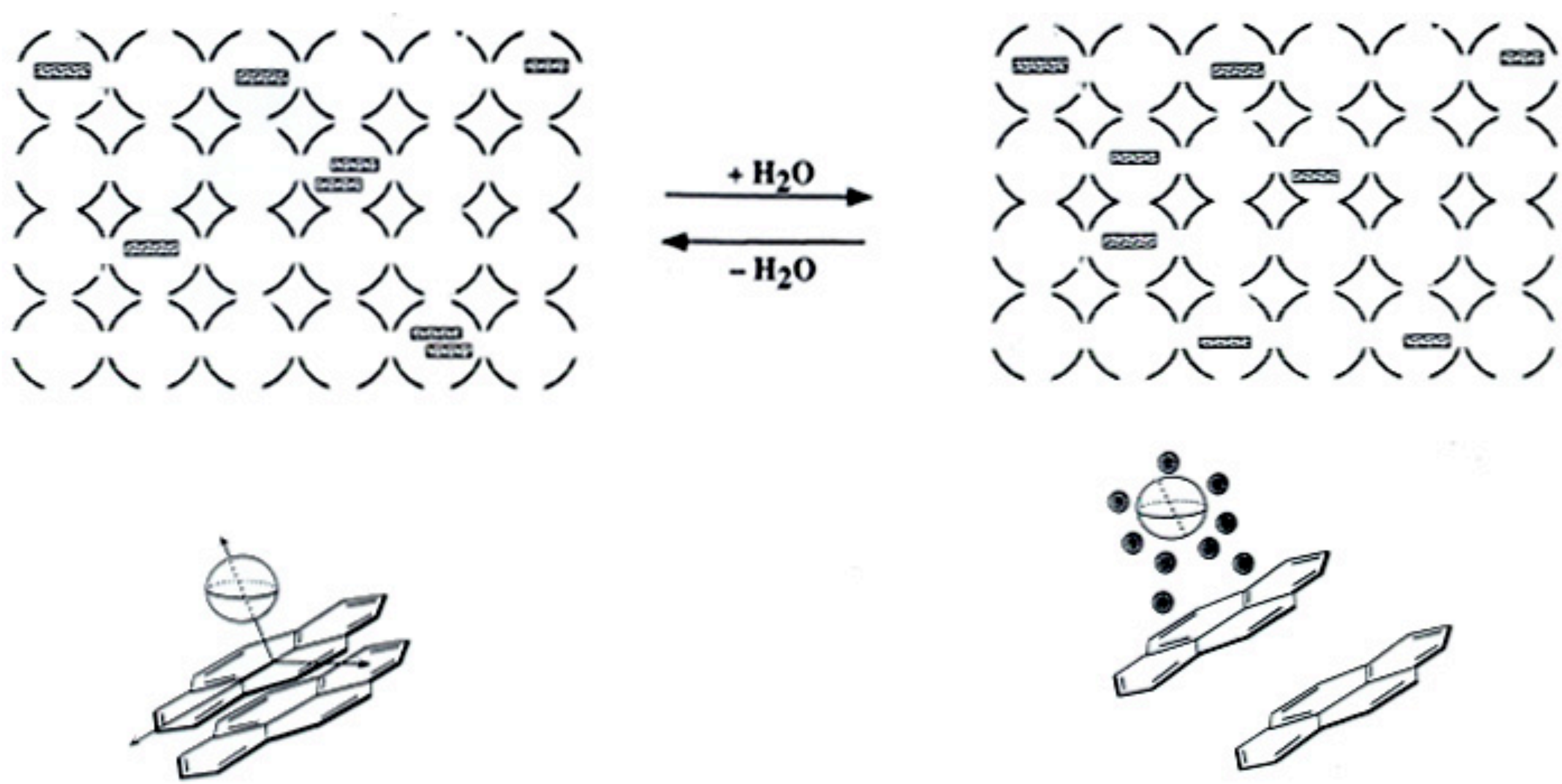
Alkali Ion Controlled Aggregation of Aromatic Molecules



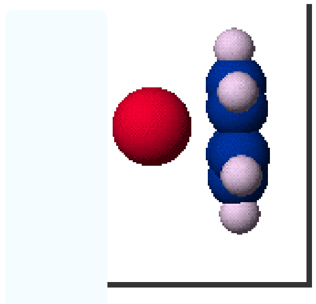


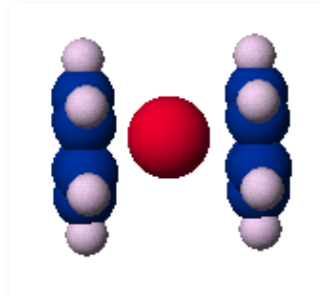


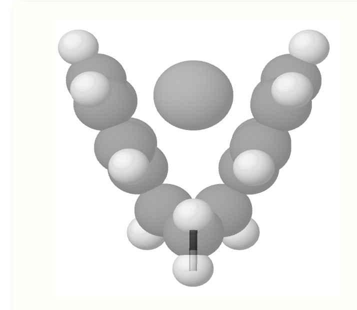
Aggregation of Aromatic Molecules Prompted by Alkali ion-π (Aromatic) Interaction



Computed Interaction Energies (kcal/mole)

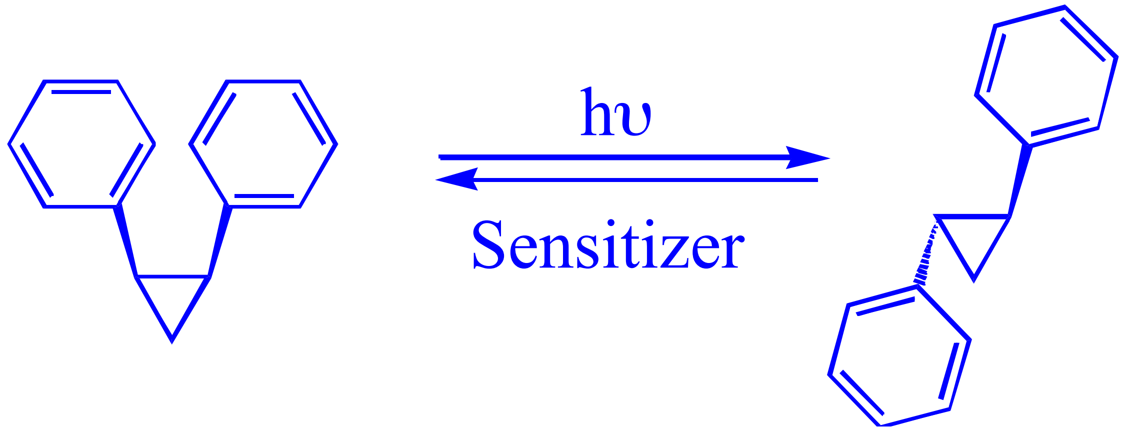


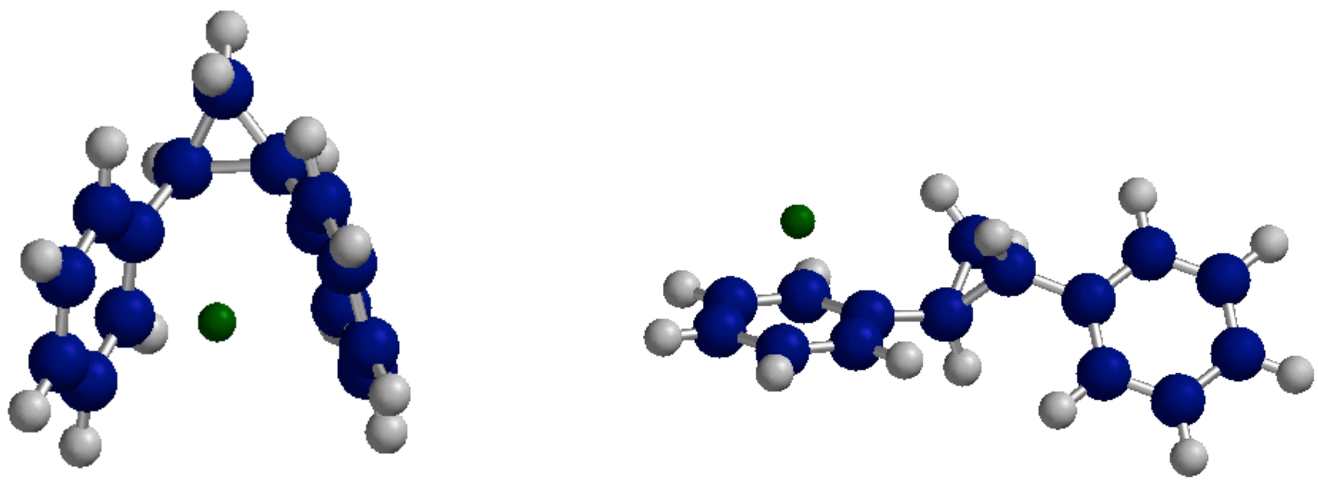




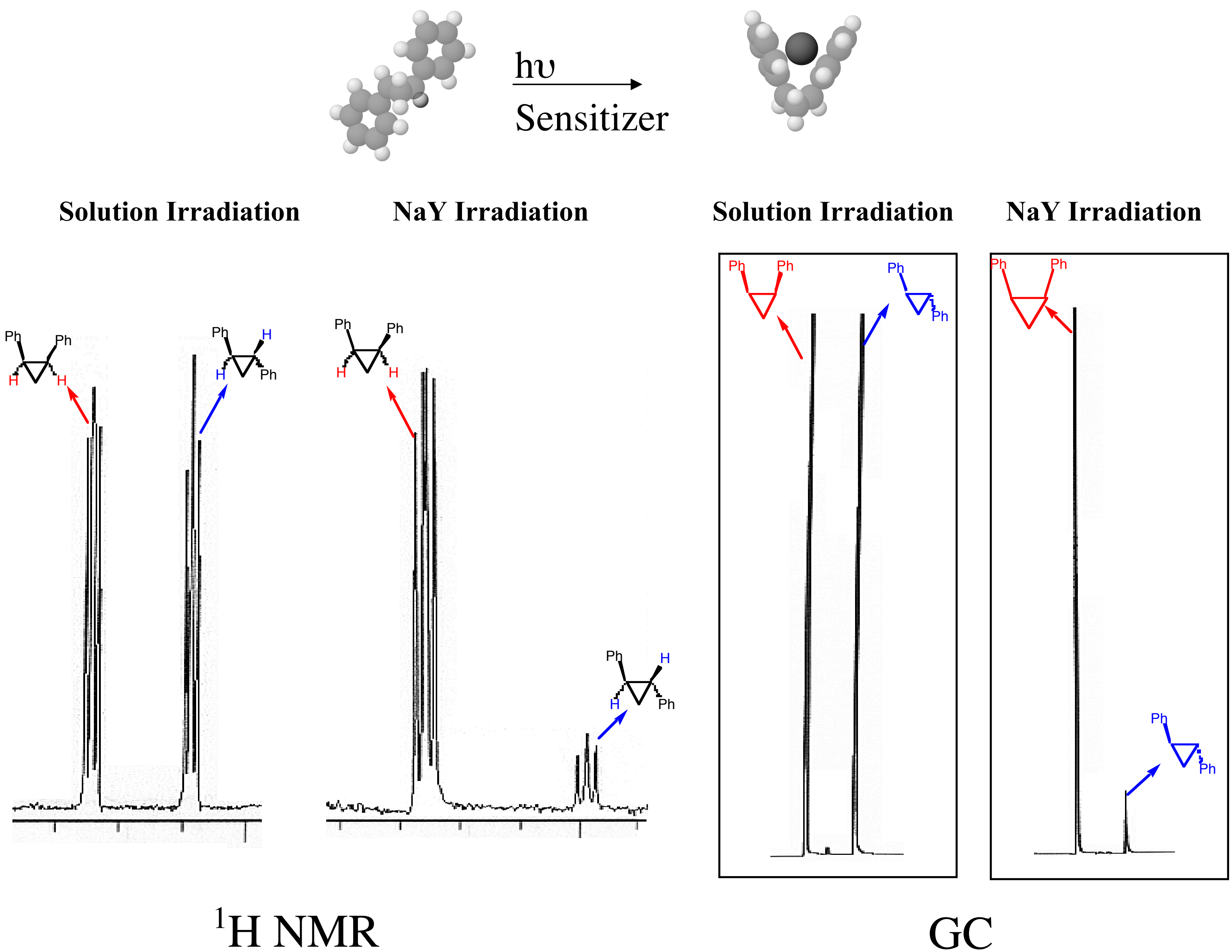
Metal ion /System	M^+..Bz	Bz..M^+..Bz	*cis*-DPC..M^+
Li	-43.8	-81.1	-75.8
Na	-29.7	-56.2	-53.9
K	-16.7	-32.3	-32.6
Rb	-14.6	-27.7	-28.2
Cs	-11.9	-22.6	-22.7

All the values are computed at MP2 level of theory with a 6-31G* basis set for C, H, Li and Na. Hay-Wadt effective core potential with valence functions are employed for the heavier metal ions such as K, Rb and Cs.

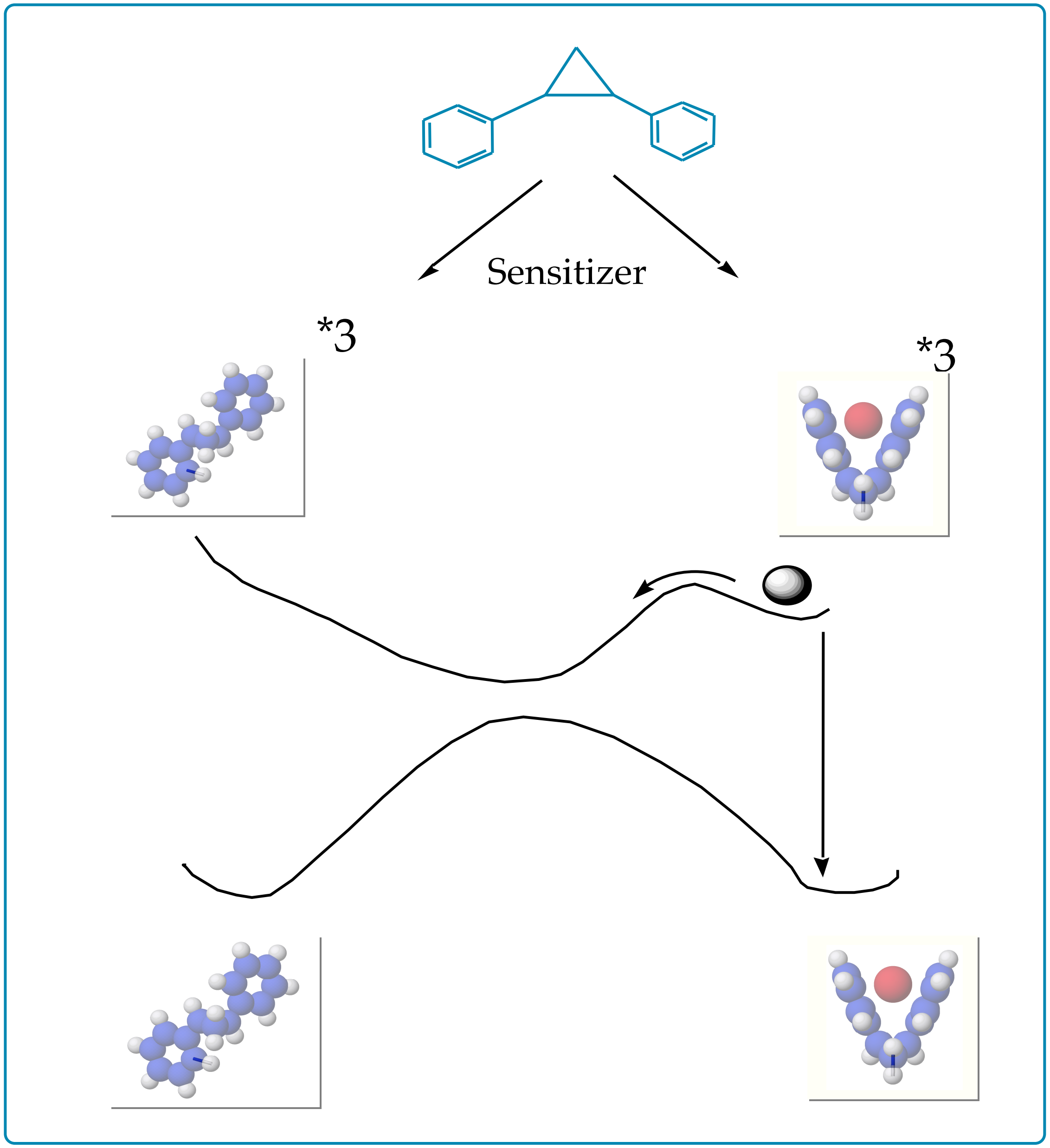




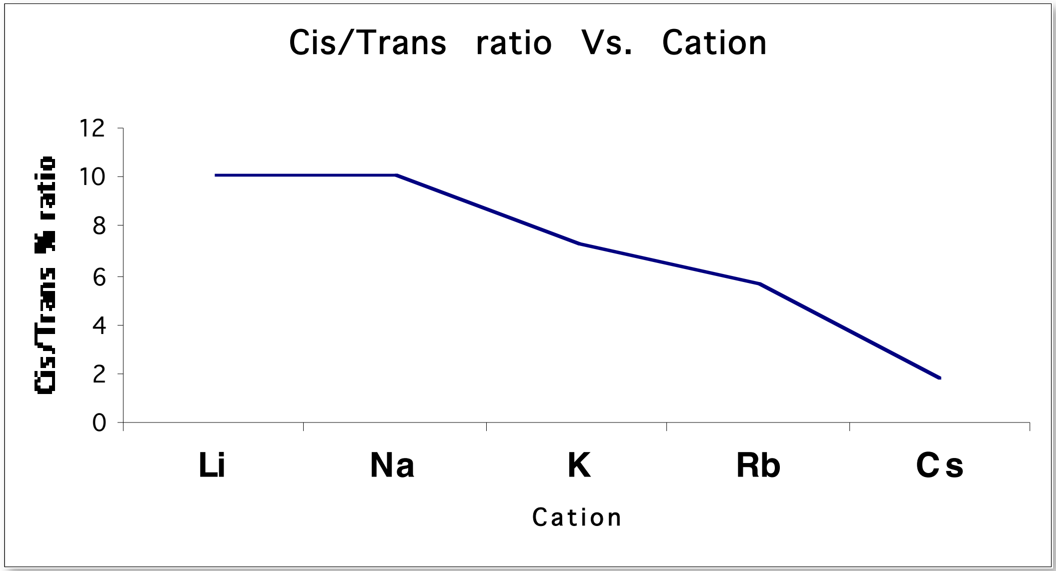
BE (kcal/mol) **-75.82** **-43.80**

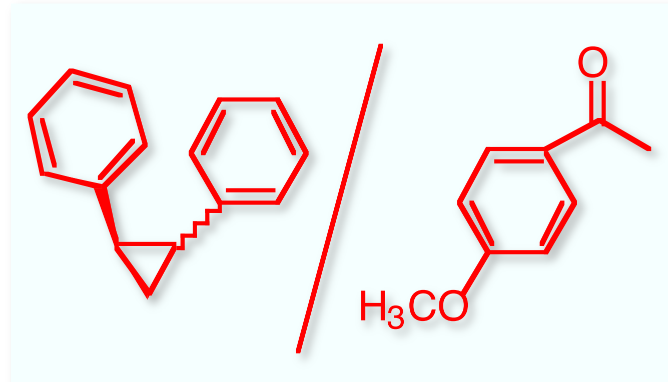

hυ
Sensitizer
Solution Irradiation
NaY Irradiation
Solution Irradiation
NaY Irradiation
Ph
H
¹H NMR
GC

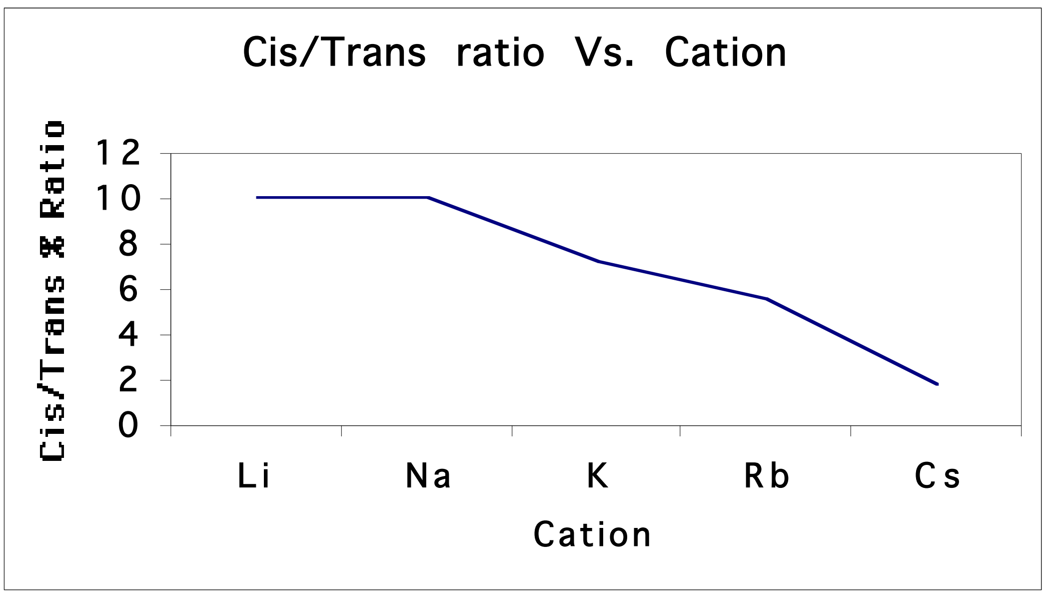
Cation Binding May Influence Excited State Chemistry

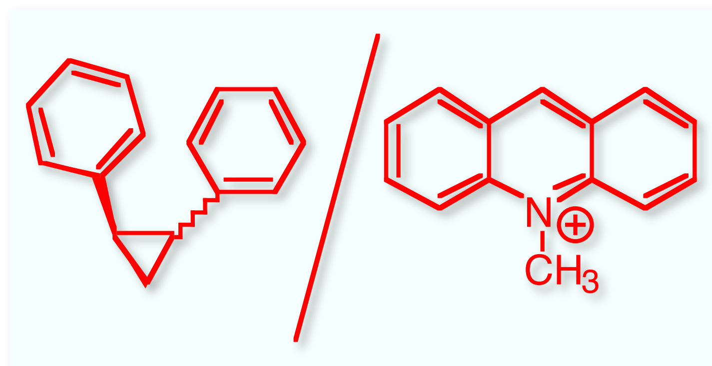


Cation Effect (dry condition)...

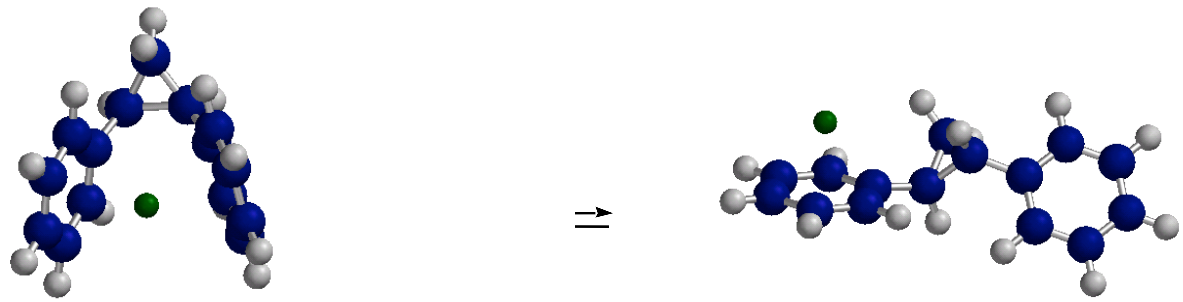






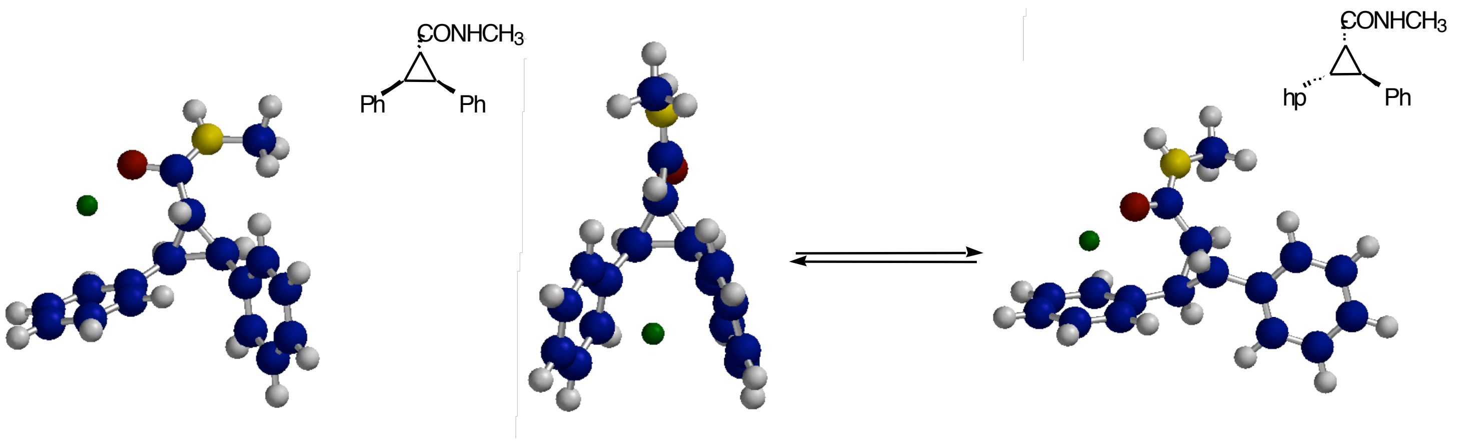


Alkali ion effect could be switched off by changing the binding site



BE (kcal/mol) **-75.82** **-43.80**

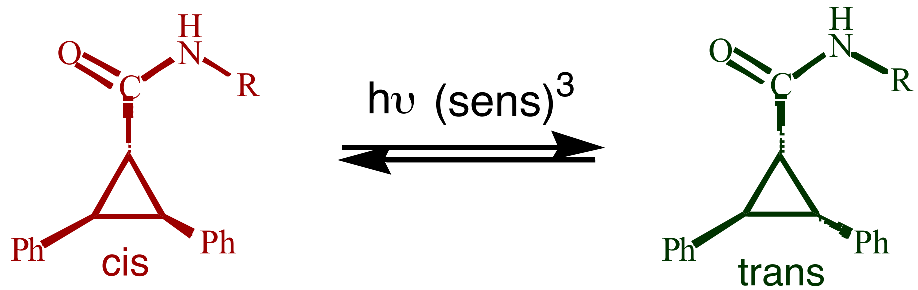
MP2/6-31 G* basis set



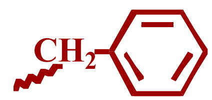
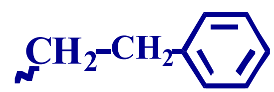
BE (kcal/mol) **-74.73** **-70.82** **-96.19**

HF/3-21G* basis set

No Alkali Ion Influenced Cis Enrichment in Amides of Diphenylcyclopropane Carboxylic Acids



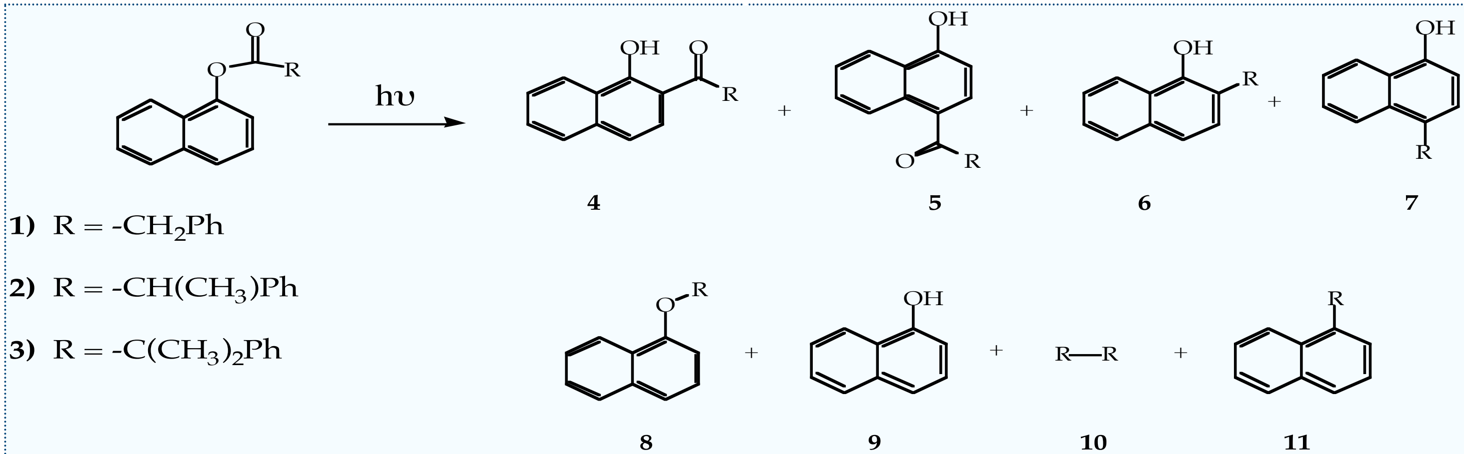
Photostationary state cis:trans ratio

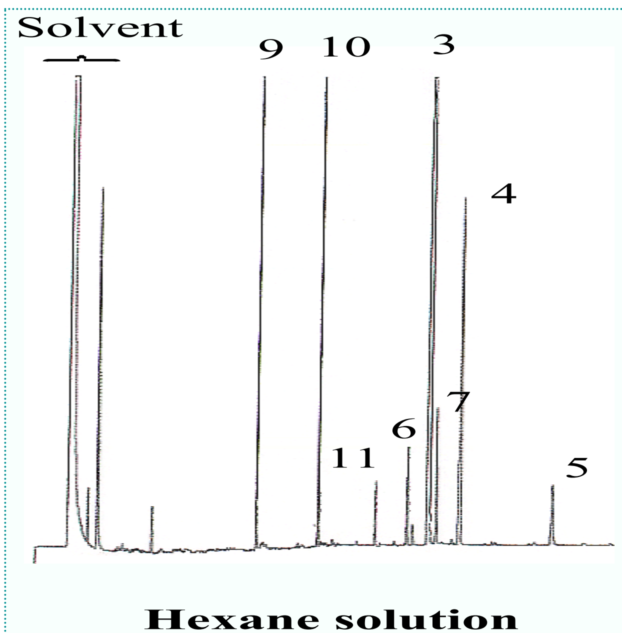
Medium	$CH_2CH_2CH_2CH_3$		
Solution	48:52	50:50	35:65
LiY	12:88	11:89	10:90
NaY	40:60	35:65	21:79
KY	35:65	58:42	38:62
RbY	33:67	55:45	40:60
CsY	55:45	56:44	41:59

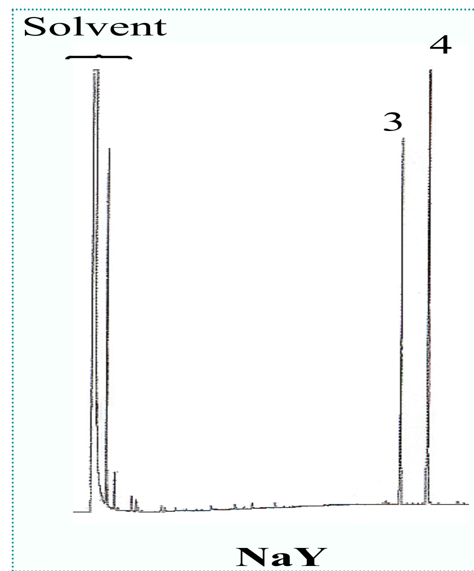
Alkali Ion Controlled Photochemistry

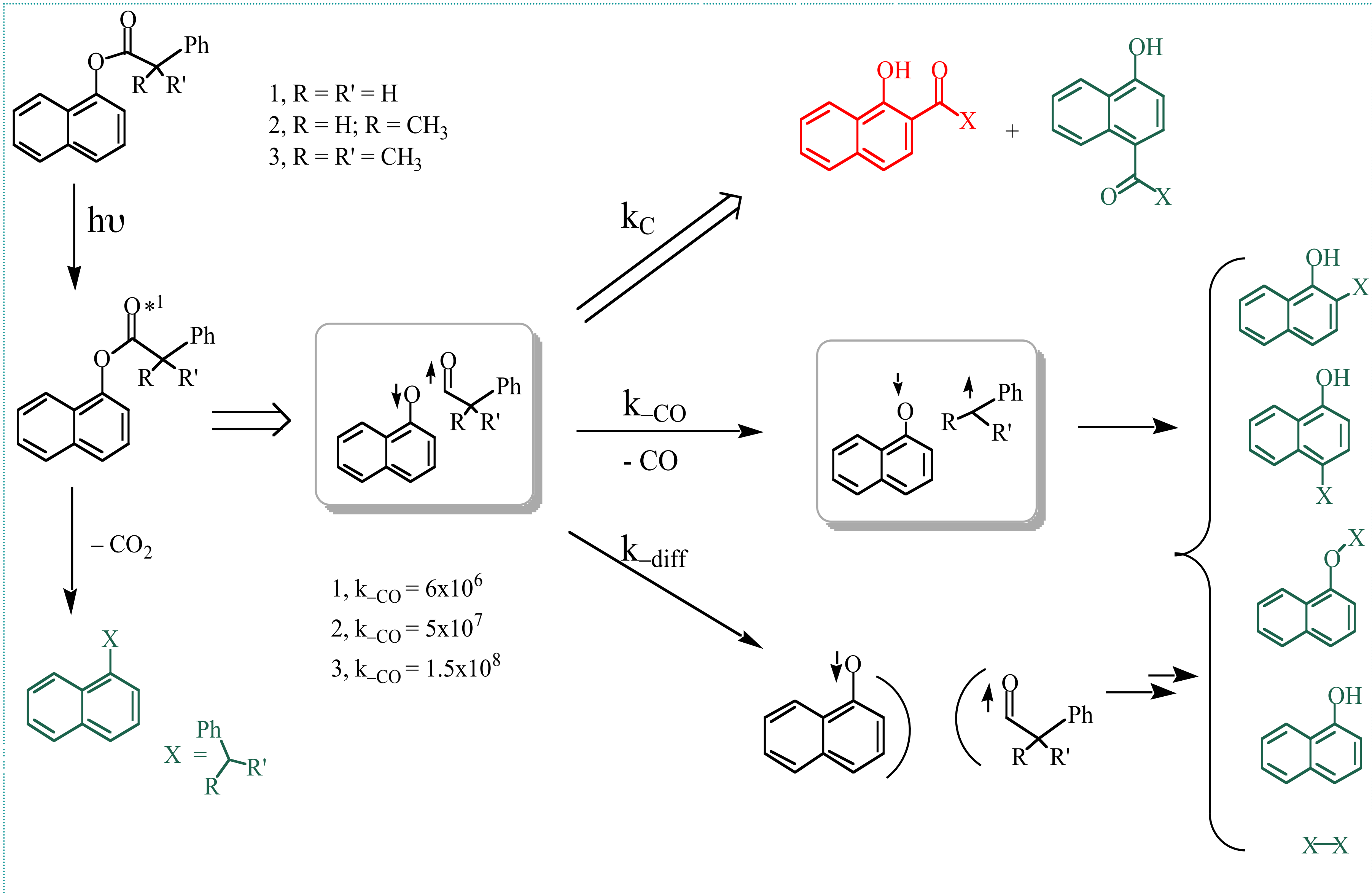
Alkali Ion-Organic Interactions
Making Use of Multiple Binding

- **Alkali Ion-Carbonyl Dipolar Interaction**
- **Alkali Ion-π (Alkenes) Quadrupolar Interaction**
- **Alkali Ion-π (Aromatics) Quadrupolar Interaction**

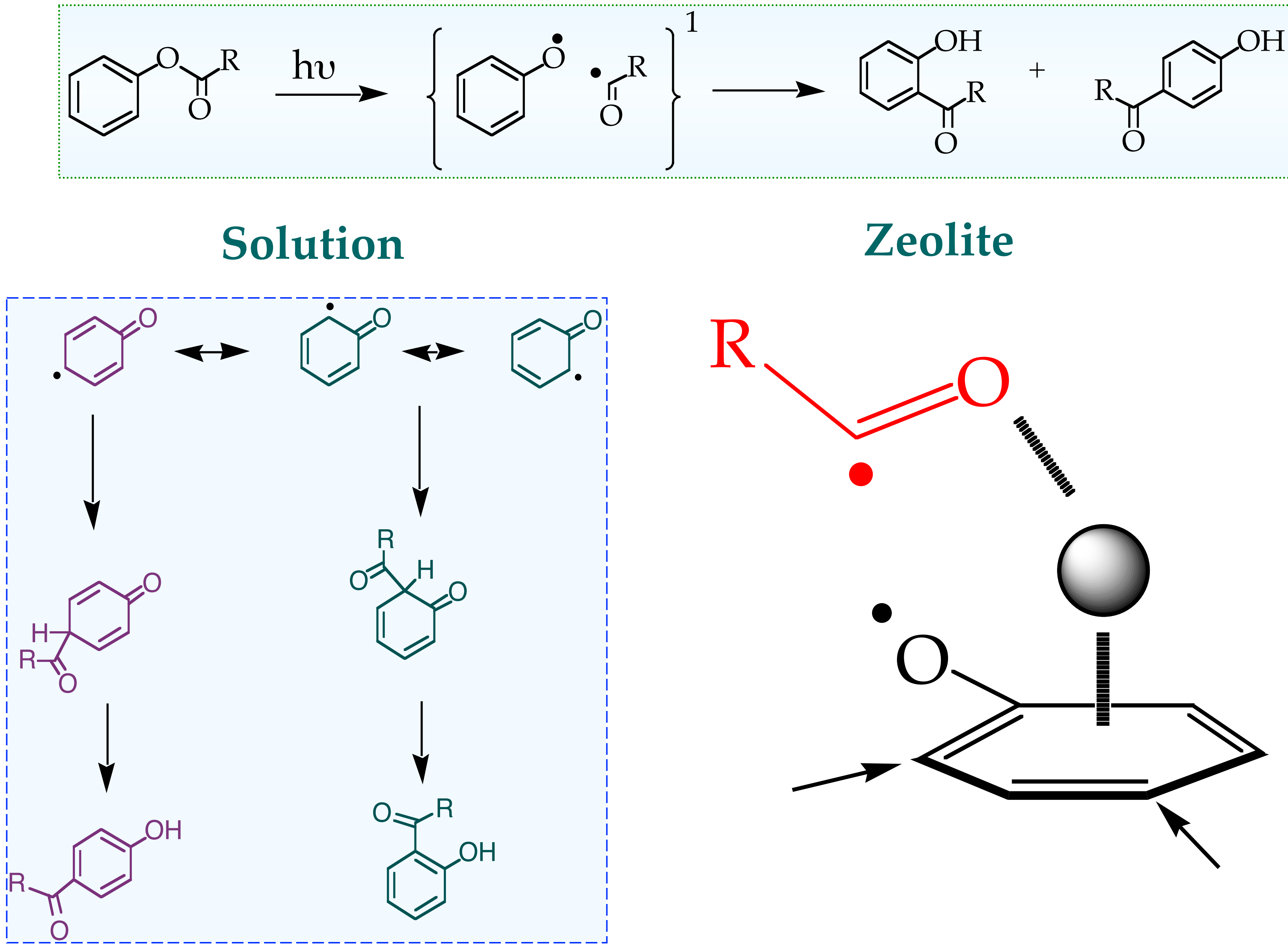

hυ
1) R = -CH2Ph
2) R = -CH(CH3)Ph
3) R = -C(CH3)2Ph
4
5
6
7
8
9
10
11


Solvent
9
10
3
4
7
6
11
5
Hexane solution

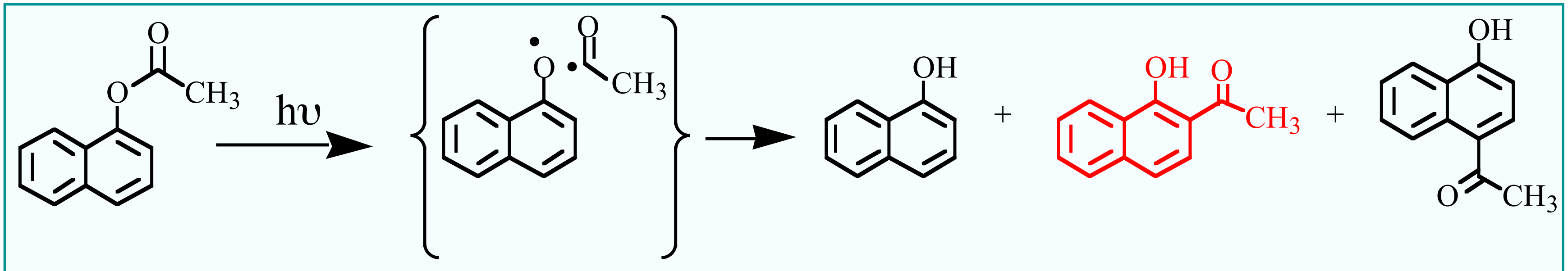

Solvent
4
3
NaY

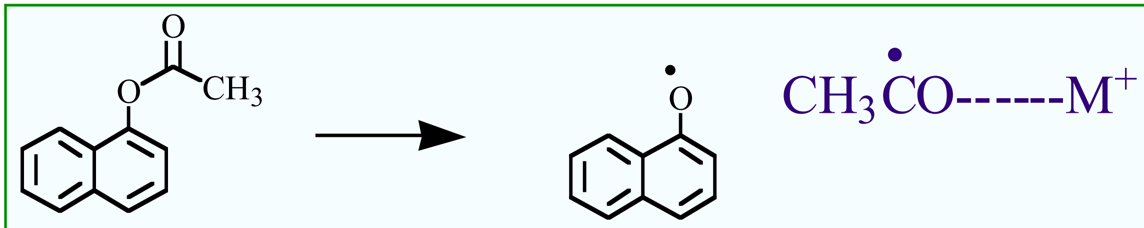


1, R = R' = H
2, R = H; R = CH3
3, R = R' = CH3
hυ
– CO2
X = Ph R R'
kC
k–CO
- CO
k–diff
1, k–CO = 6x10^6
2, k–CO = 5x10^7
3, k–CO = 1.5x10^8
X–X



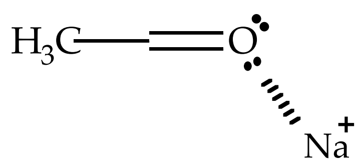
hυ
1
OH
R
O
+
Solution
Zeolite





TIME RESOLVED
STEP SCAN IR
H. FREI, JACS, 1998

- Acetyl radical (CH_3CO) is detected by IR (2127 cm^{-1})
- The absorption of CH_3CO radical within NaY is shifted by 285 cm^{-1} to the blue with respect to the argon matrix value of 1842 cm^{-1}
- Probable structure of CH_3CO radical within NaY is suggested to be



- The CH_3CO radical has a lifetime of ~75 μs within NaY

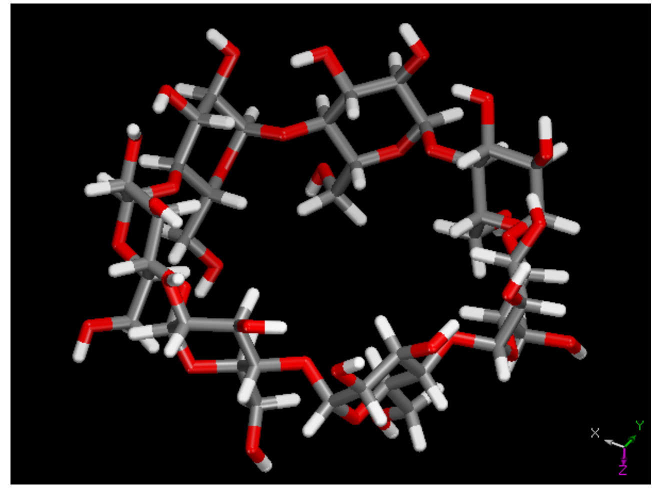
The Crow and the Pitcher

Cations are more than inert fillers

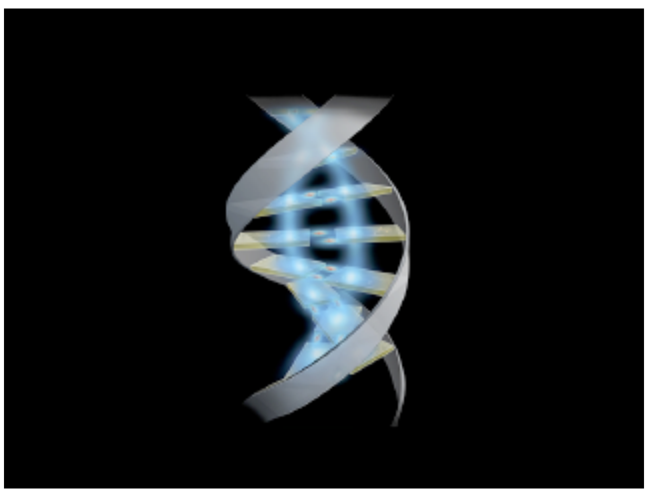
Cation-organic interactions could be used to influence various photochemical and photophysical events

Confined Media

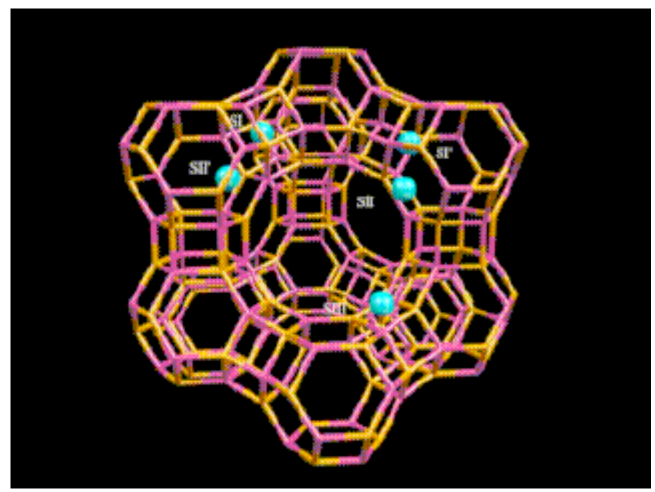
Crystals



Cyclodextrins



DNA

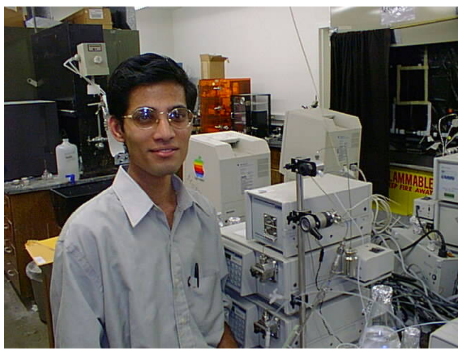


Zeolite

J. Shailaja

Sundar

A. Pradhan

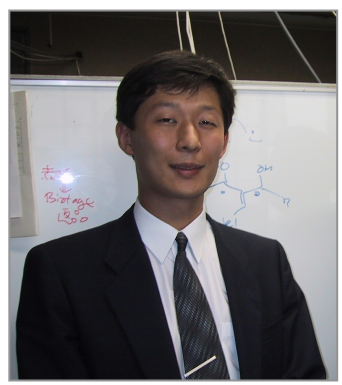


J. Sivaguru

JC

Sireesha

PH



S. Takagi

Manoj

Thanks for financial support

National Science Foundation

WHERE DISCOVERIES BEGIN

SCIENCE THAT MATTERS

U.S. Department of Energy

Science for America's Future