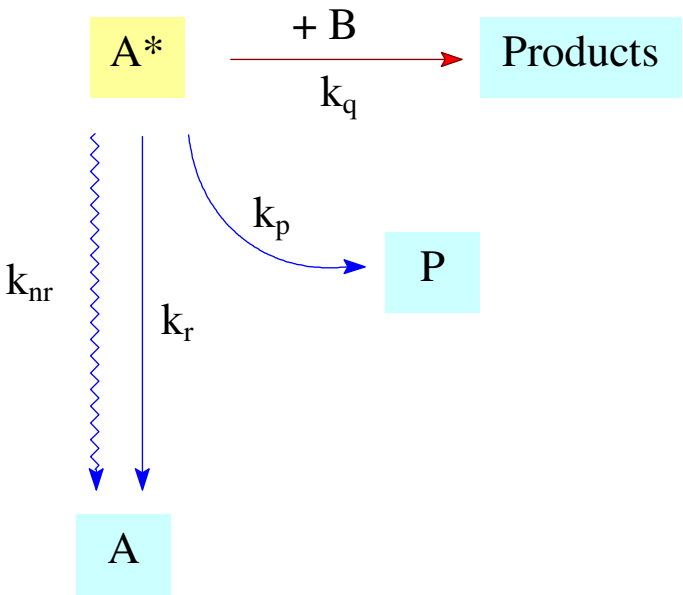
Excited-State Processes



Bimolecular Processes:

$A^* + B \rightarrow A + B^*$	energy transfer
$A^* + B \rightarrow A^+ + B^-$	electron transfer
$AH^* + B \rightarrow A^{-*} + BH^+$	proton transfer
…… ……	……

Acidity (basicity) of excited state vs ground state

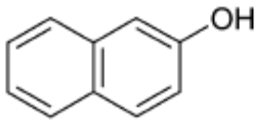
Same or different?

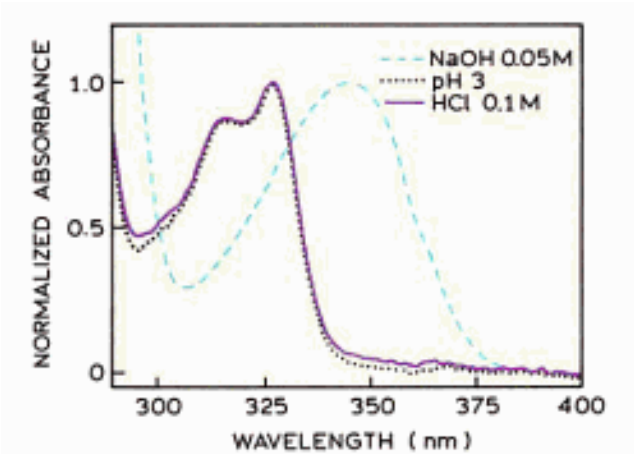
If different, in which direction?

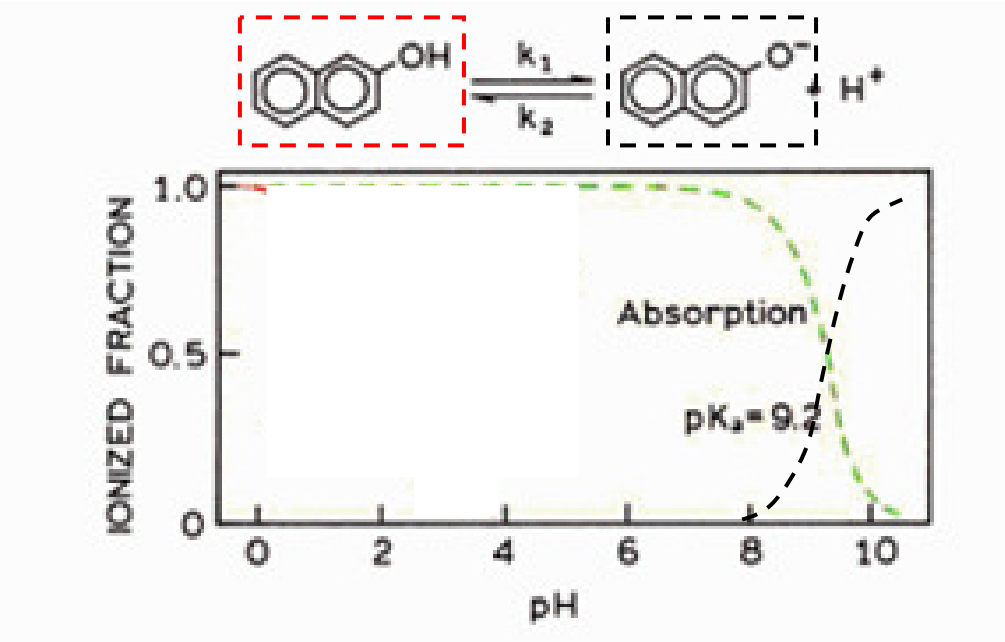
How can be measured ?

Can be predicted?

Example:


OH


NaOH 0.05M
pH 3
HCl 0.1M
NORMALIZED ABSORBANCE
1.0
0.5
0
300
325
350
375
400
WAVELENGTH (nm)


OH
k_1
k_2
O^-
H^+
IONIZED FRACTION
1.0
0.5
0
Absorption
$pK_a = 9.2$
0
2
4
6
8
10
pH

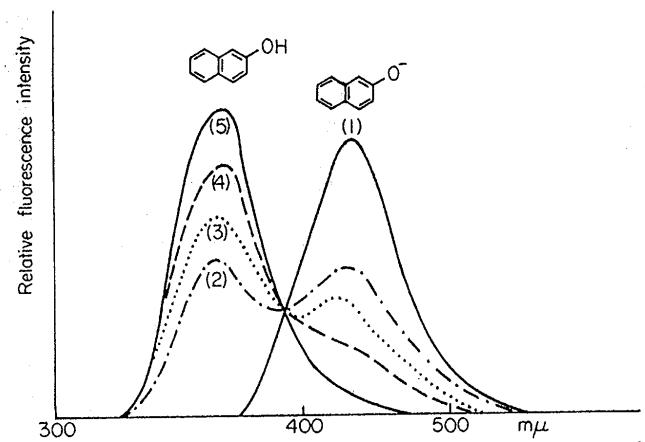
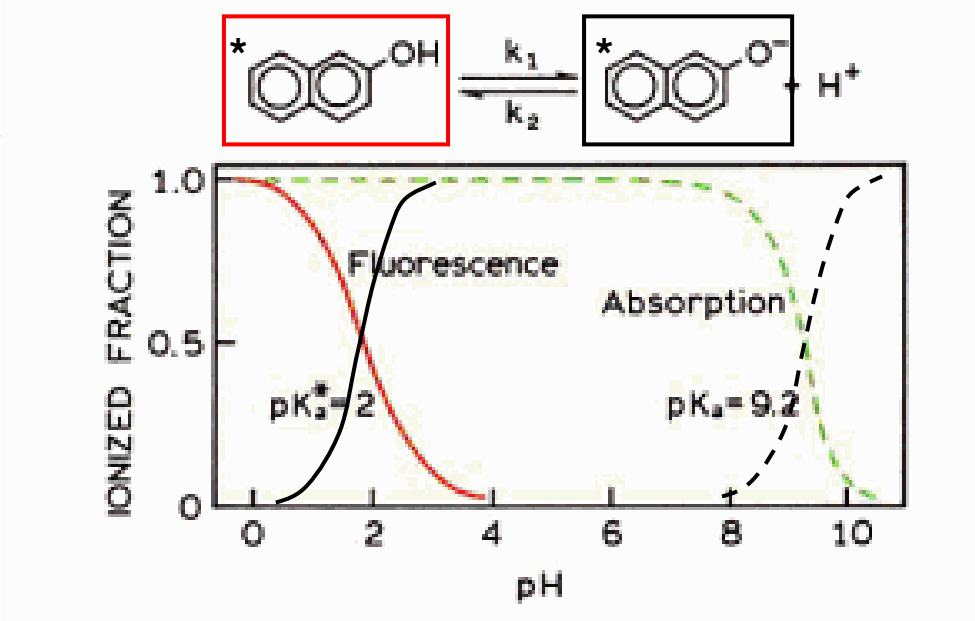
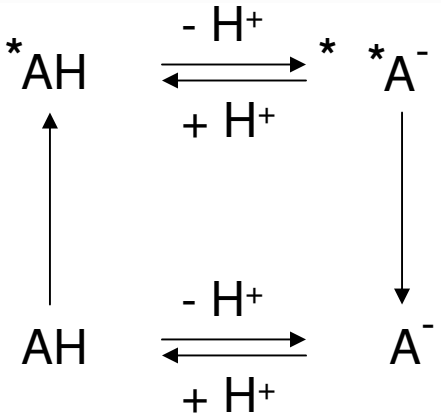
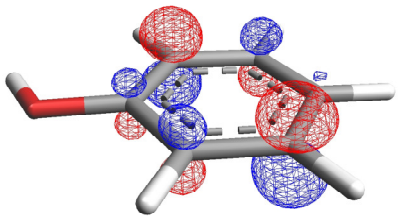


Figure 3.11 Fluorescence spectrum of 2-naphthol in solutions of different pH (from ref. 34). (1) 0·02 *M* NaOH, (2) 0·02 *M* sodium acetate + 0·02 *M* acetic acid, (3) pH 5–6, (4) 0·004 *M* $HClO_4$, (5) 0·15 *M* $HClO_4$

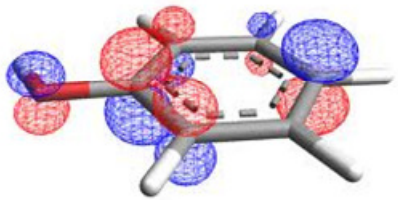




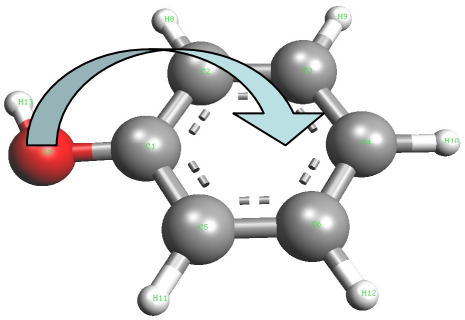
LUMO

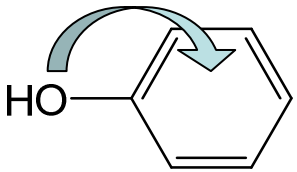


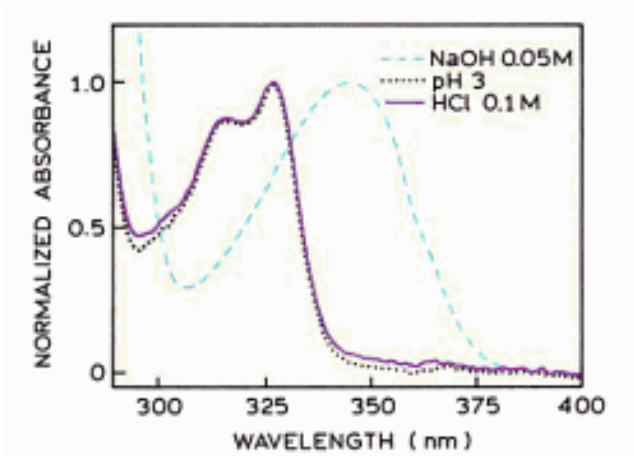
HOMO

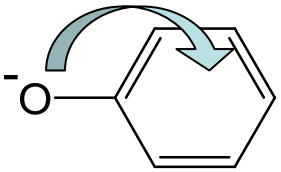


Excitation = charge transfer from O to ring



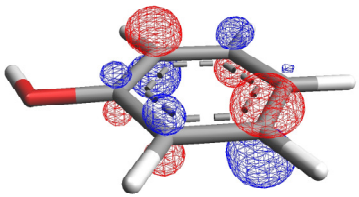




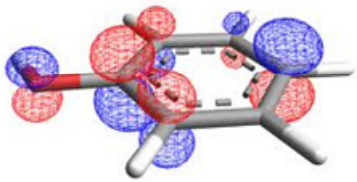


Spectral red shift: charge transfer easier when O is de-protonated

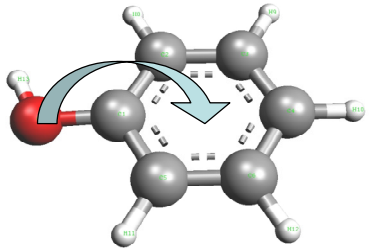
LUMO



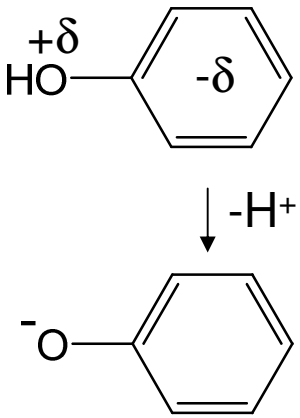
HOMO

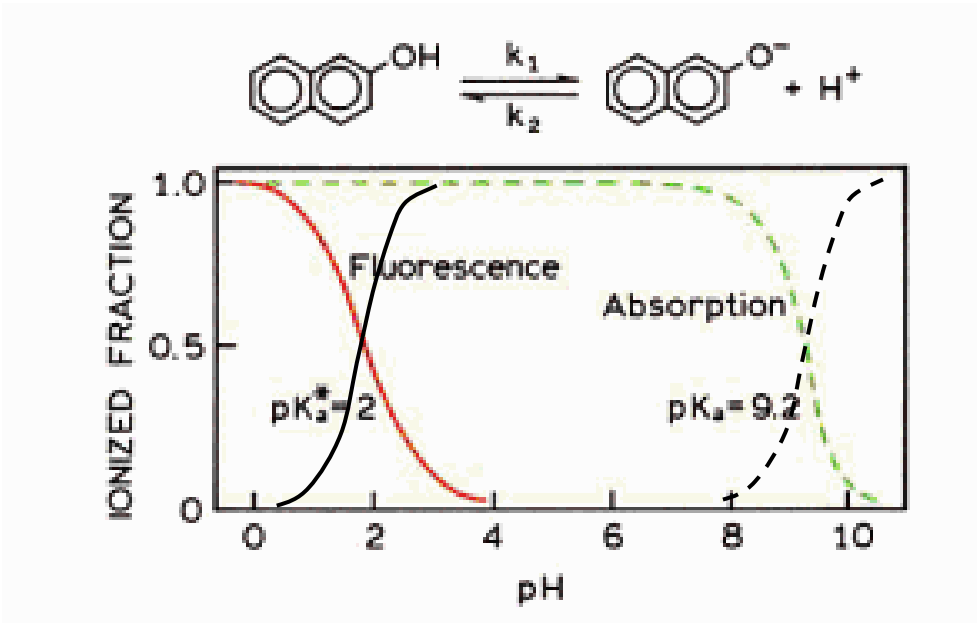


Excitation = charge transfer from O to ring

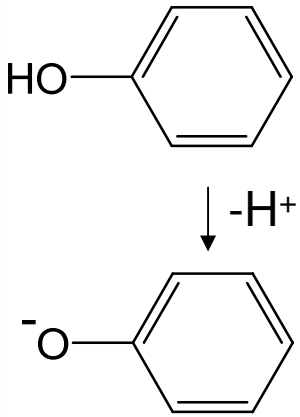


Exc. state





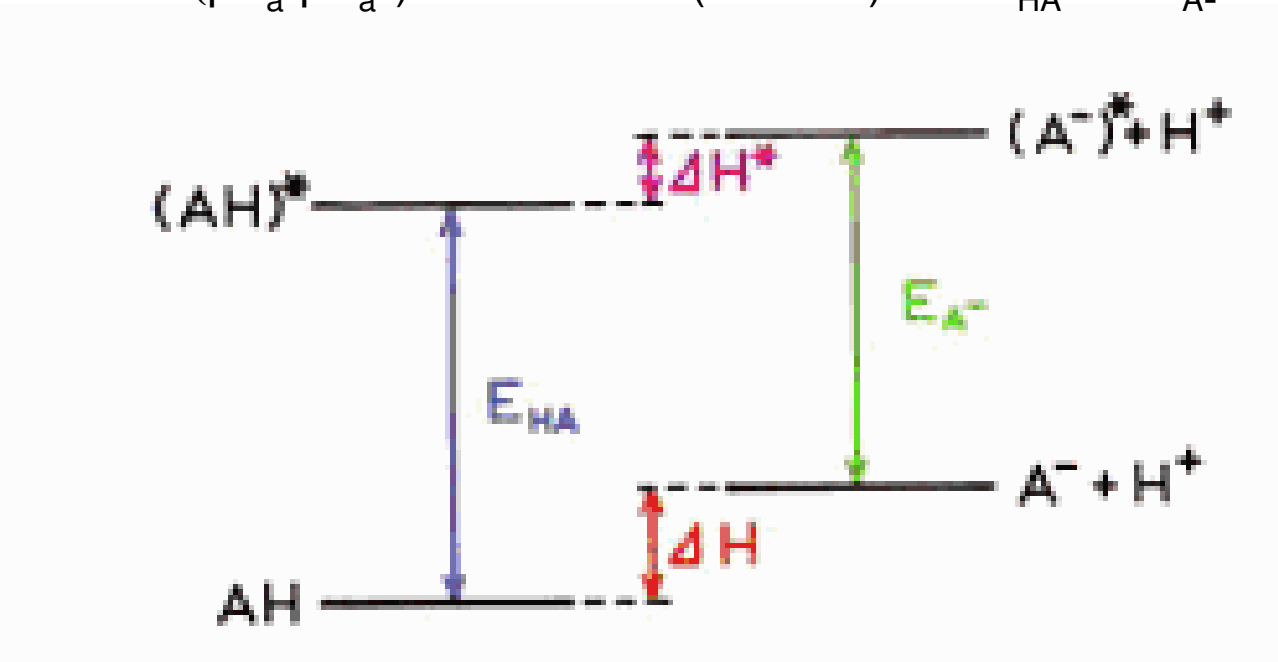
Ground state



pK_a change: H^+ dissociation easier from positively charged oxygen in the excited state

Förster Cycle: pK_a^* can be calculated sfrom spectral shifts

$$(pK_a - pK_a^*)\ 2.303\ RT = (\Delta H - \Delta H^*) = E^{0\text{-}0}_{HA} - E^{0\text{-}0}_{A^-}$$

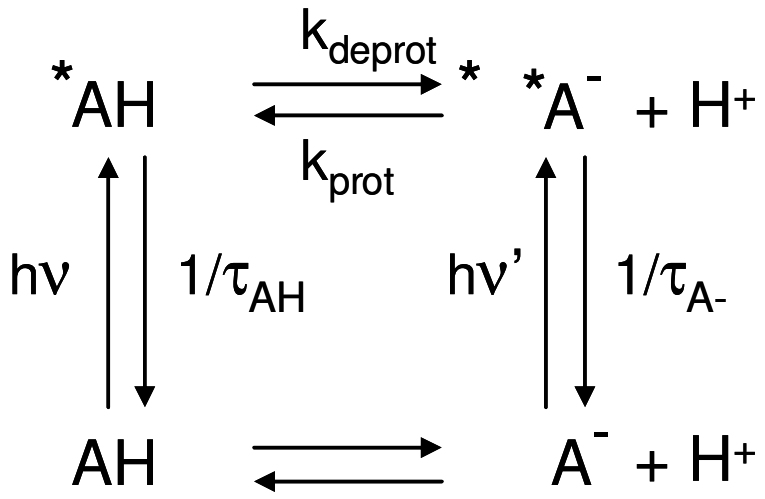


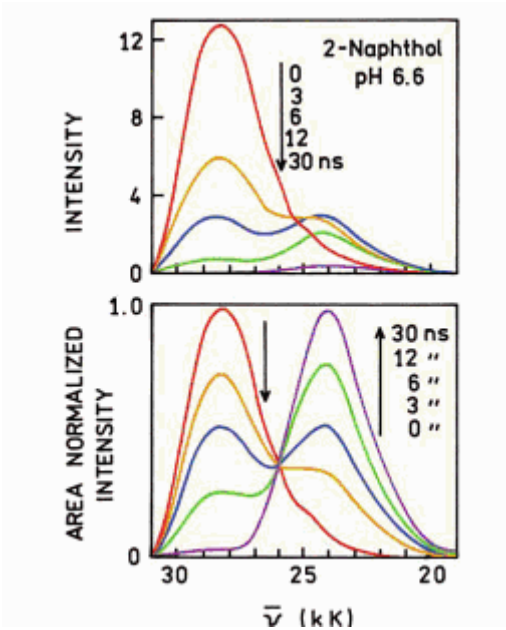
Enthalpy cycle equivalent to free cycle

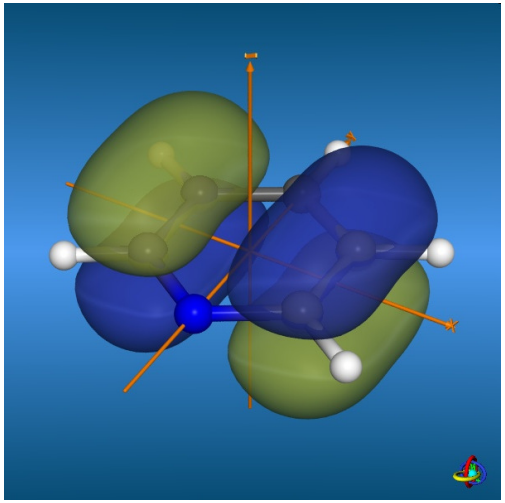
$$\Delta(\Delta H - \Delta H^*) = \Delta(\Delta G - \Delta G^*), \text{ as } \Delta S = \Delta S^*$$

Kinetic conditions for equilibrium to be established in the excited state

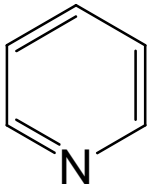
$$K_{deprot} > 1/\tau_{AH}\ ,\ k_{prot}[H^+] > 1/\tau_{A^-}$$



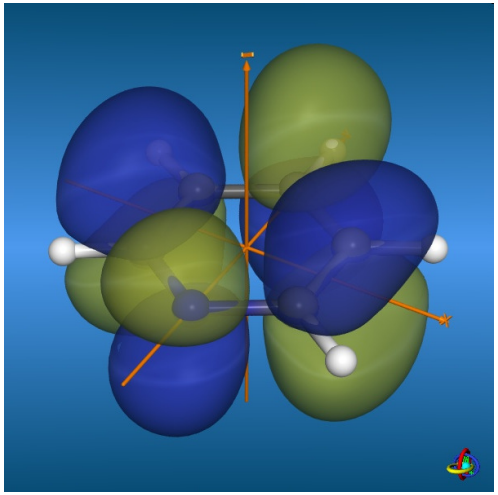


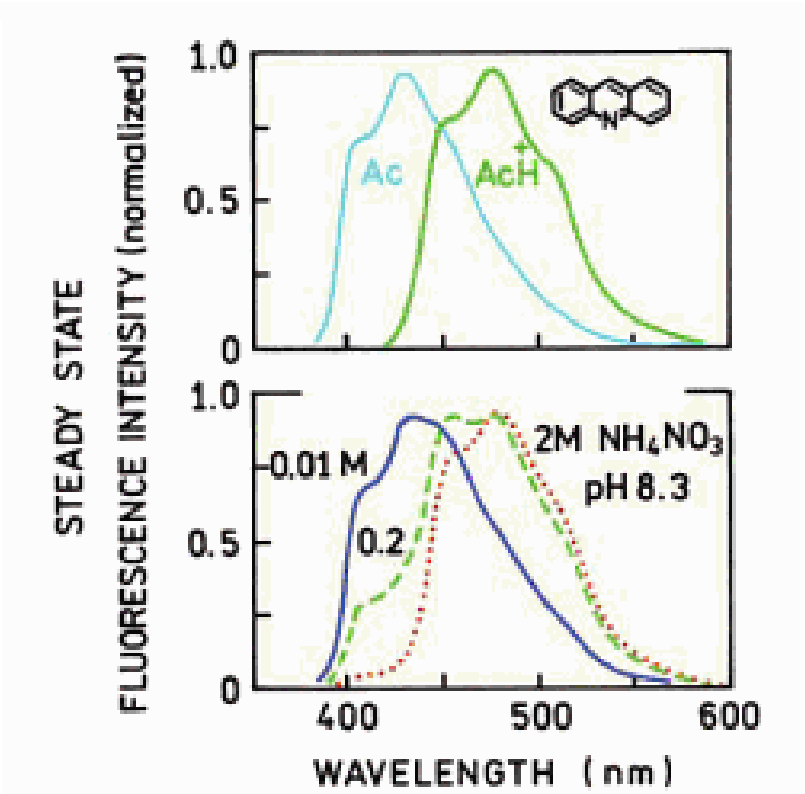


HOMO



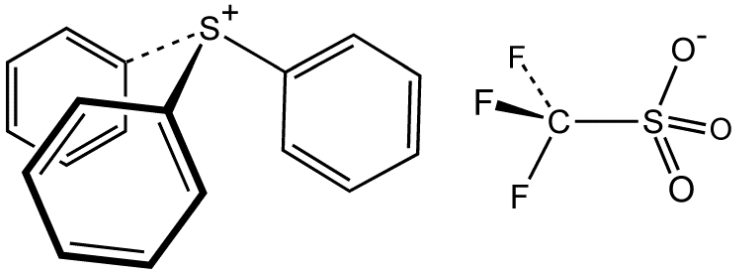
LUMO





$pK_a^* > pK_a$

Photoacids (Photolithography)



$$[(C_6H_5)_3S^+][CF_3SO_3^-] + h\nu \rightarrow [(C_6H_5)_2S^{+\cdot}][CF_3SO_3^-] + C_6H_5^{\cdot}$$

$$[(C_6H_5)_2S^{+\cdot}][CF_3SO_3^-] + C_6H_5^{\cdot} \rightarrow (C_6H_5C_6H_4)(C_6H_5)S + CF_3SO_3H$$