Vibrational Stark Effect on CN mode

Soft matter optical spectroscopy

Seoncheol Cha

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Vibrational Stark Effects To Identify Ion Pairing and Determine Reduction Potentials in Electrolyte-Free Environments

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Identification of Ion-Pair Structures in Solution by Vibrational Stark Effects

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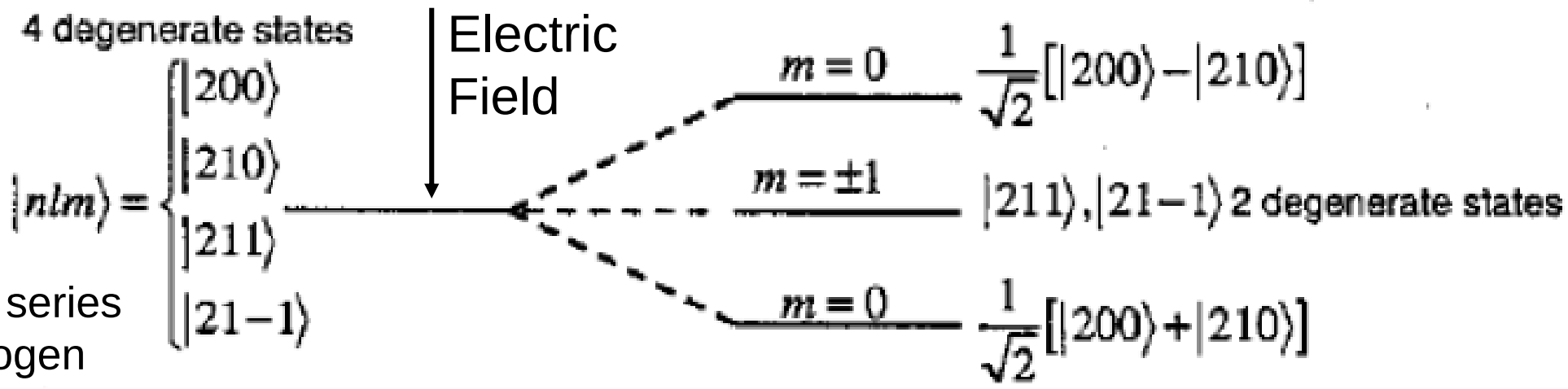
Stark Effect of Hydrogen Atom

$$H_0 = \frac{p^2}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

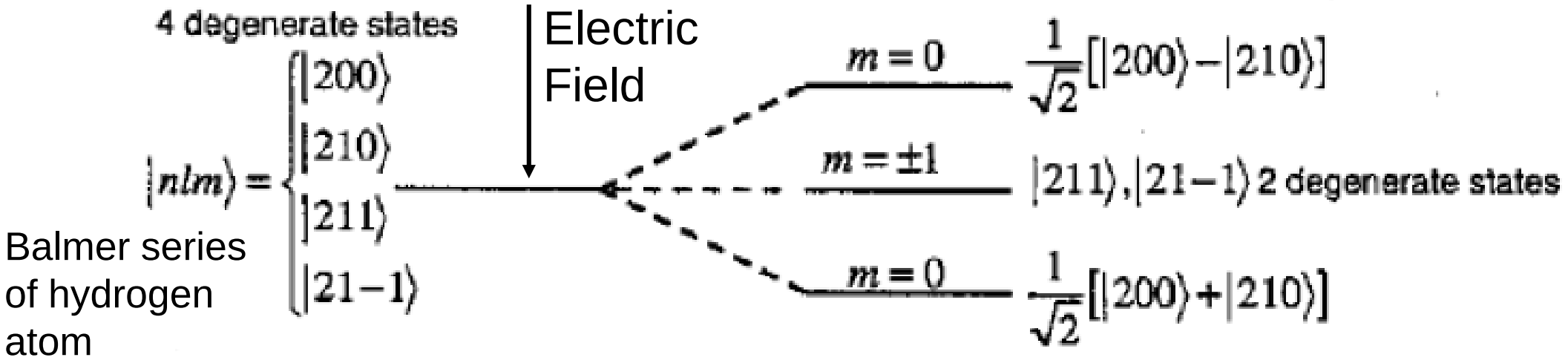
$$\lambda H_1 = e\mathrm{E}z$$

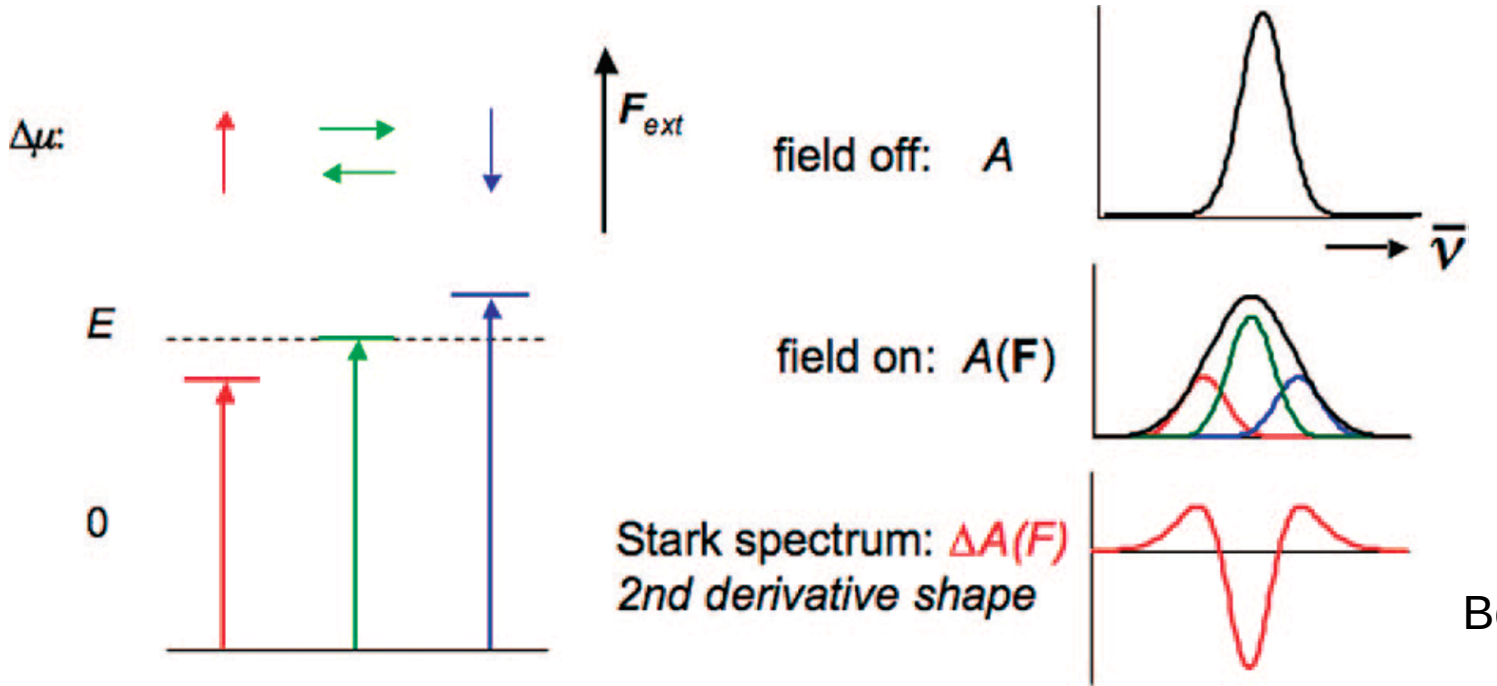
$$E_{100}^{(1)} = e\mathrm{E} < \phi_{100}|z|\phi_{100} >= e\mathrm{E}\int d^3r|\phi_{100}(r)|^2 z$$



Balmer series of hydrogen atom

Stark Effect





Boxer, J.Phys.Chem.B (2009) 113 2972

Vibrational Stark Effect

TABLE 1: Bond Types, Frequencies, Intensities, and Stark Tuning Rates of Relevant Functional Groups[48] [a]

bond type	$\bar{\nu}$ range, cm^{-1}	intensity	Stark tuning rate, $\lvert\Delta\vec{\mu}\rvert$, $cm^{-1}/(MV/cm^{-1})$
—C—H	2850–3100	weak	0.2–0.6
—C—D	2000–2200	weak	0.4–1.5
—C—F	1100–1300	strong	0.4–0.9
carbonyl	1600–1750	strong	0.6–1.8
—C≡N	2050–2270	strong	0.4–2.9
azide	2080–2170	very strong	small
—N=C=O	2250–2300	very strong	small
nitro	1490–1600	strong	~1.3
—Si—H	2100–2200	medium	~2.3

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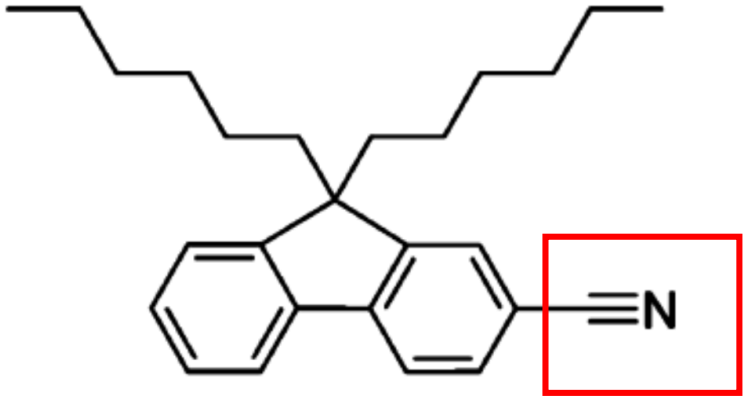
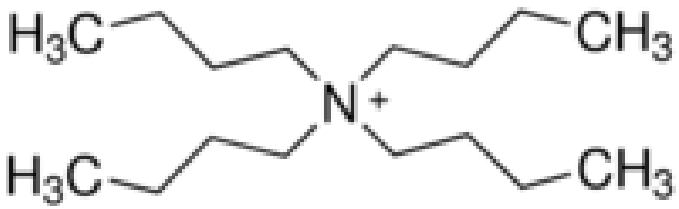
Sample

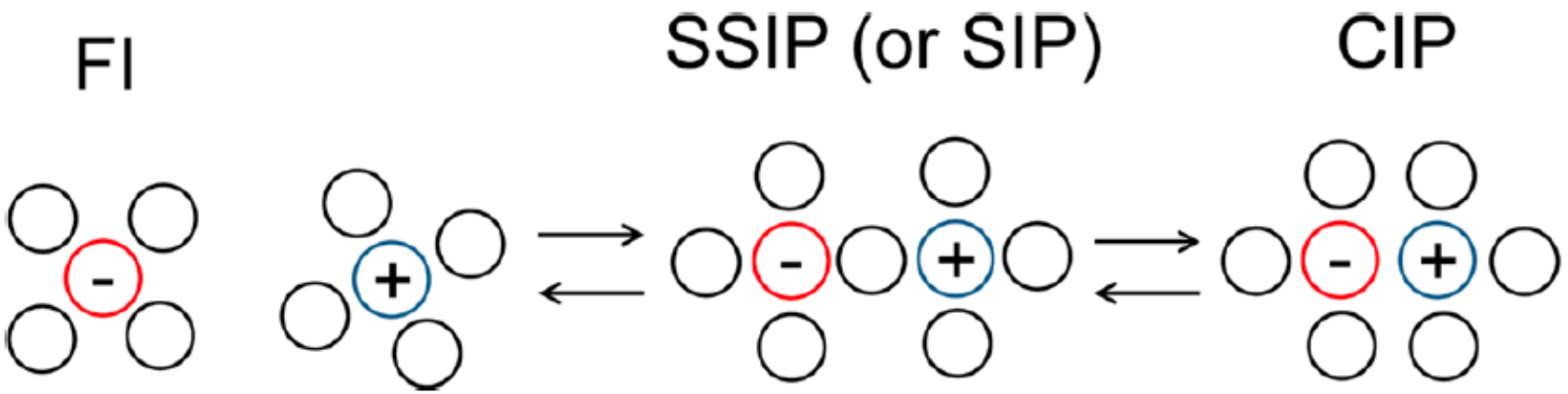
F_1CN



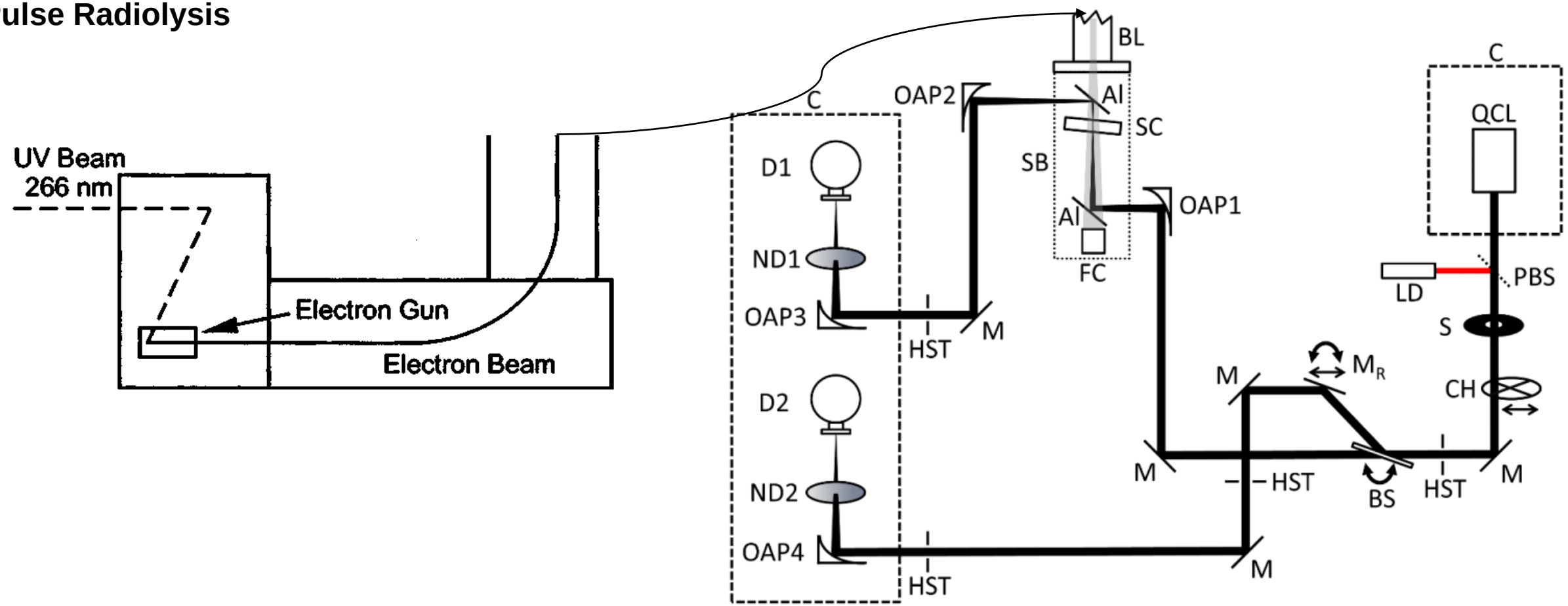
$TBA^+BF_4^-$



BF_4^-



Pulse Radiolysis

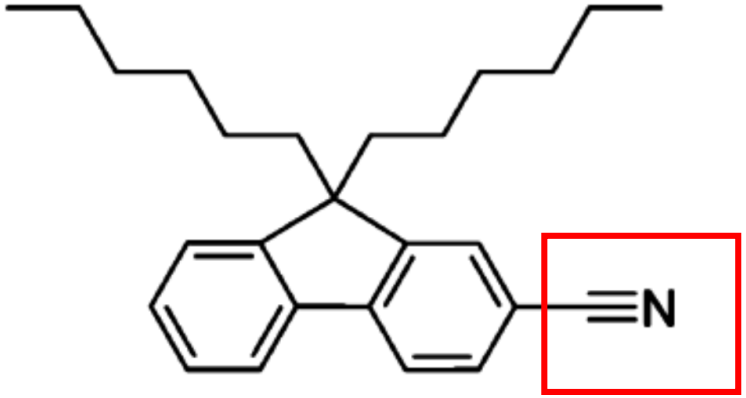


QCL : Quantum Cascade Laser
(tunable diode laser 2330 cm^{-1} to 1052 cm^{-1})

Wishart and coworkers, Rev. Sci. Instrum (2004) 75 4359
Wishart and coworkers, Rev. Sci. Instrum (2015) 86 044102

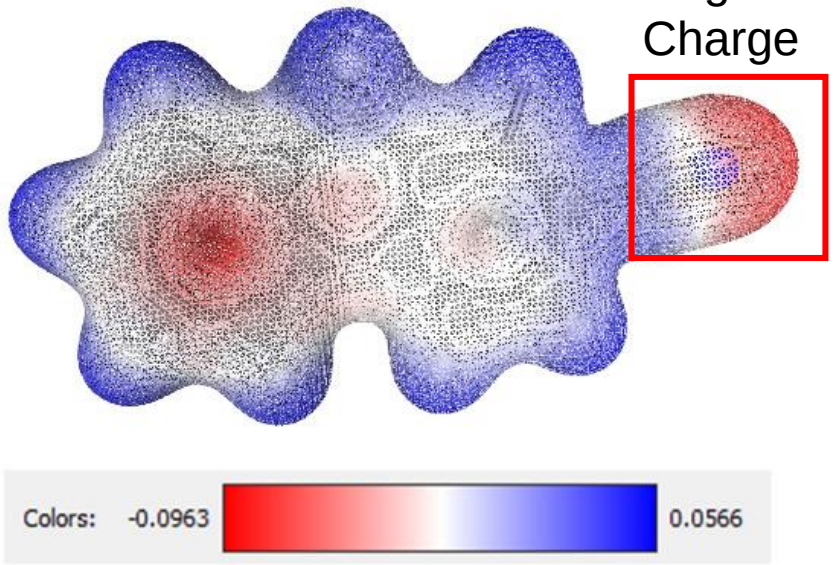
F1CN-●

F_1CN

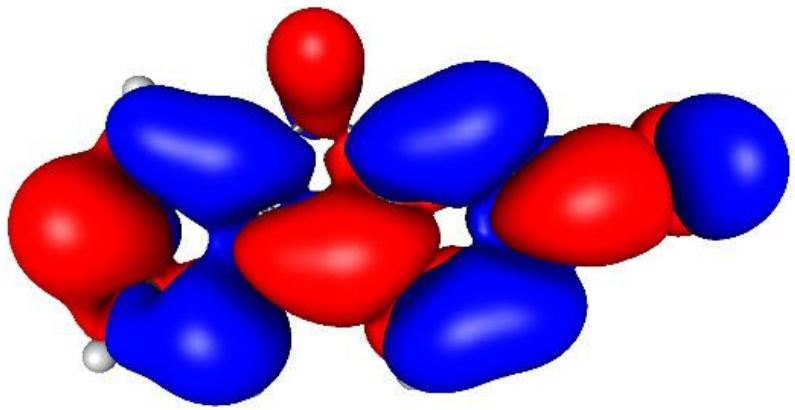


F1CN-●

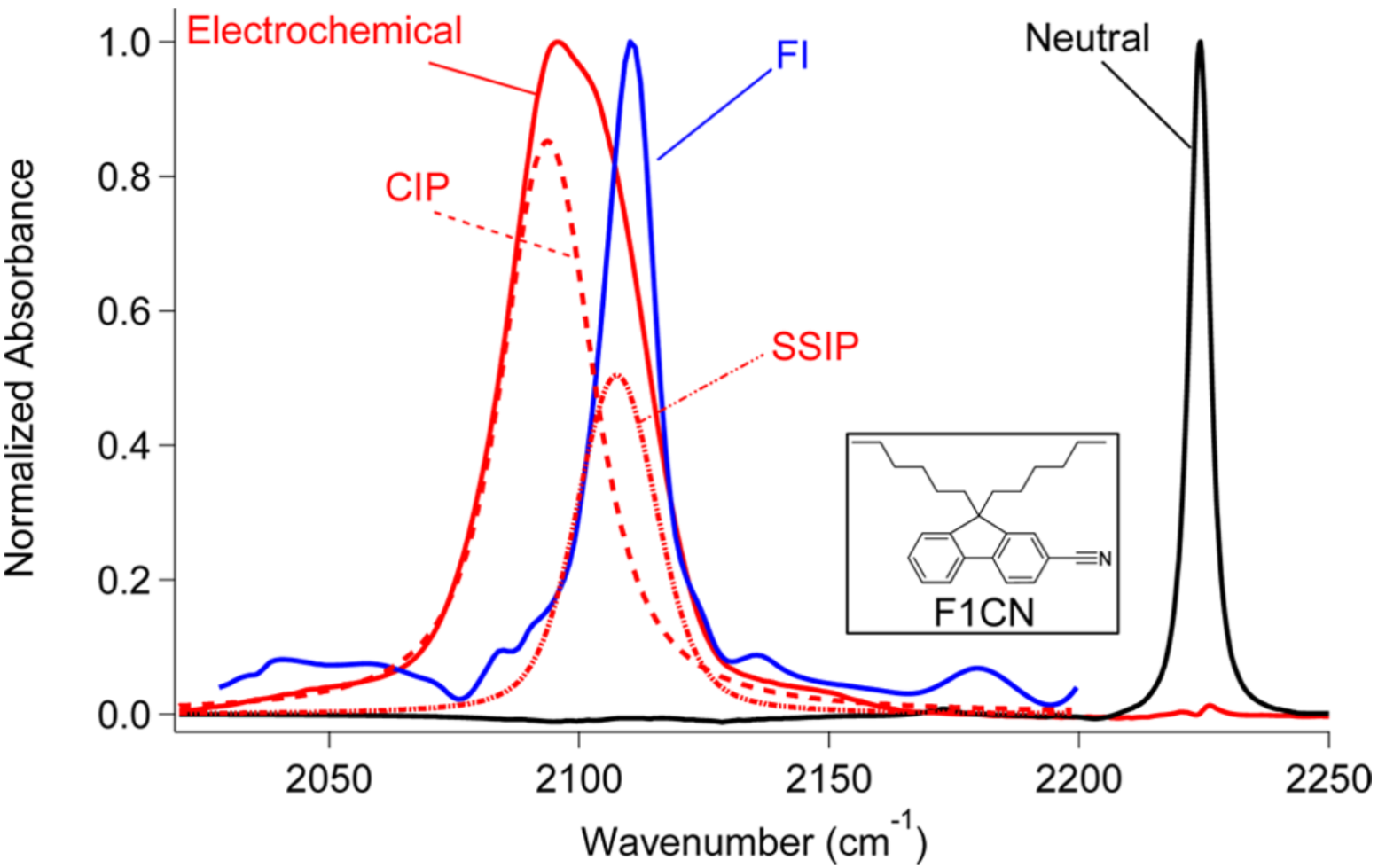
a



b



Experiments I.



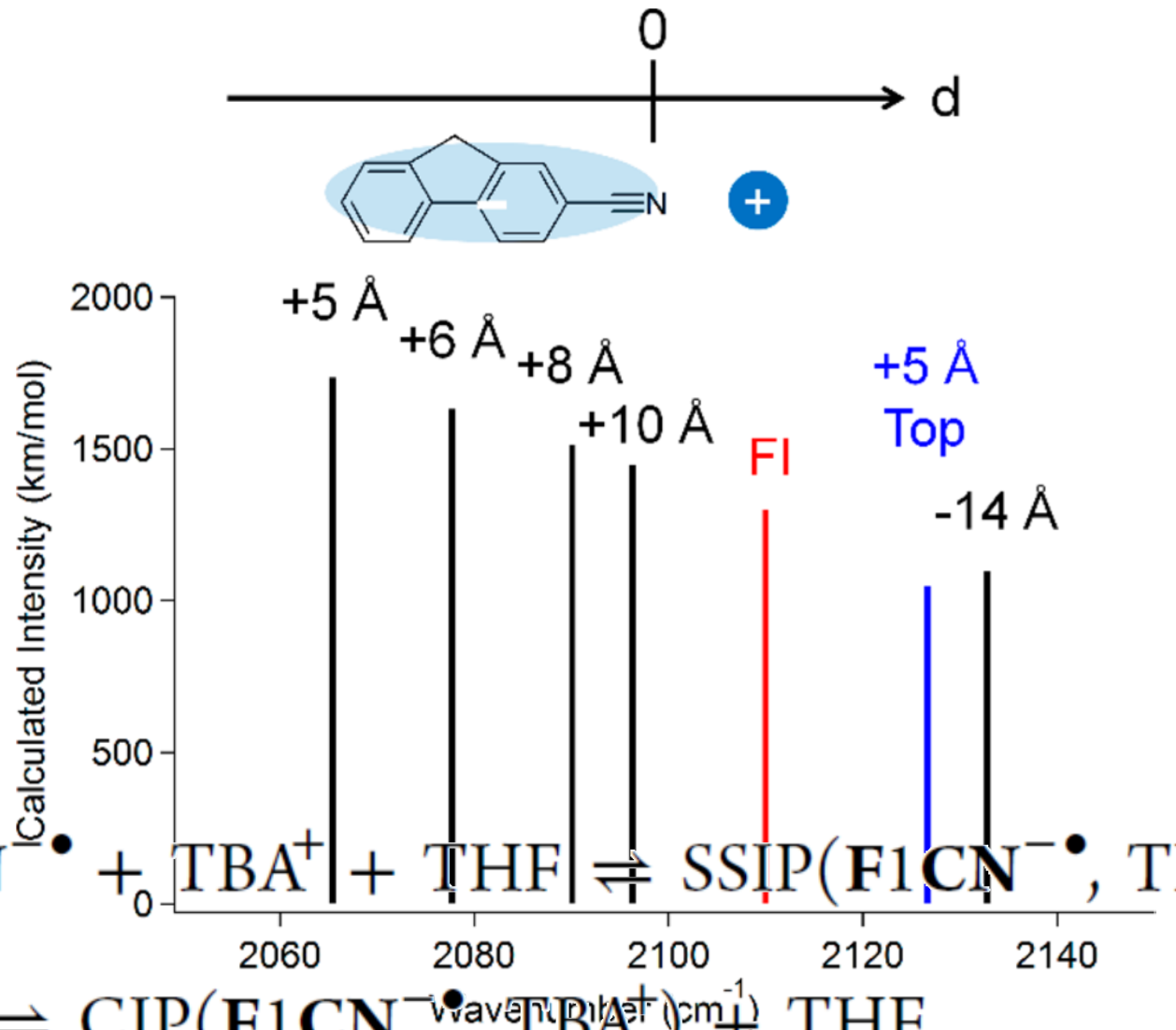
THF
$\varepsilon = 7.52$

Neutral
: F1CN in THF

FI (Free Ion)
: F1CN in THF + 50 ns after pulse radiolysis

Electrochemical
: FI + 100 mM $TBA^{+}BF_4^{-}$
CIP (Contact Ion Pair)
SSIP (Solvent Separated Ion Pair)

ab initio calculation : νCN stretching frequency



$$\mathbf{F1CN}^{-\bullet} + \mathrm{TBA}^{+} + \mathrm{THF} \rightleftharpoons \mathrm{SSIP}(\mathbf{F1CN}^{-\bullet}, \mathrm{THF}, \mathrm{TBA}^{+})$$

$$\mathrm{SSIP} \rightleftharpoons \mathrm{CIP}(\mathbf{F1CN}^{-\bullet}, \mathrm{TBA}^{+}) + \mathrm{THF}$$

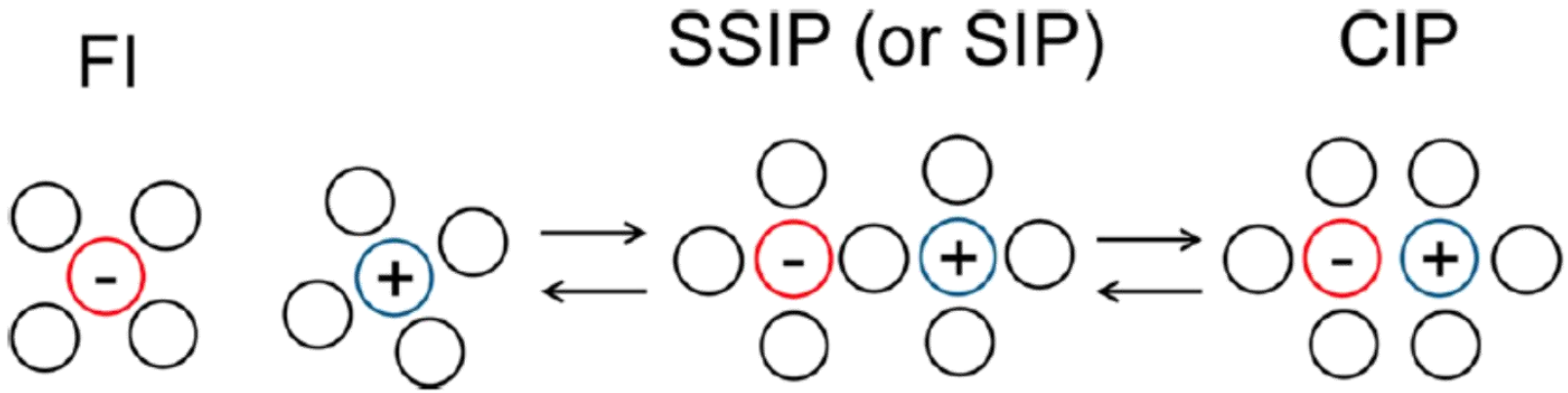
Model for CIP and SSIP

(1) Ion pairs consisting of CIP and SSIP

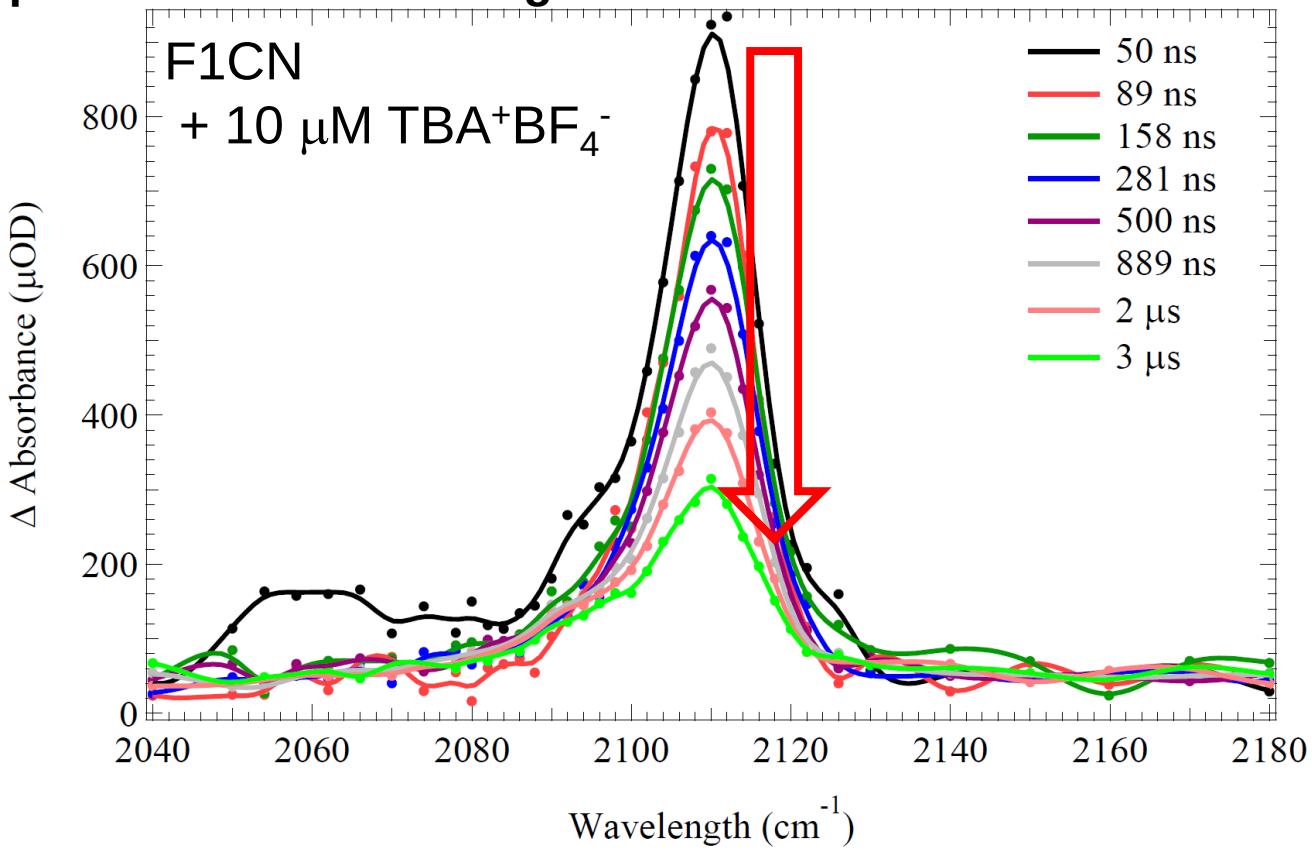
$$\mathbf{F1CN}^{-\bullet} + \mathrm{TBA}^{+} + \mathrm{THF} \rightleftharpoons \mathrm{SSIP}(\mathbf{F1CN}^{-\bullet}, \mathrm{THF}, \mathrm{TBA}^{+})$$

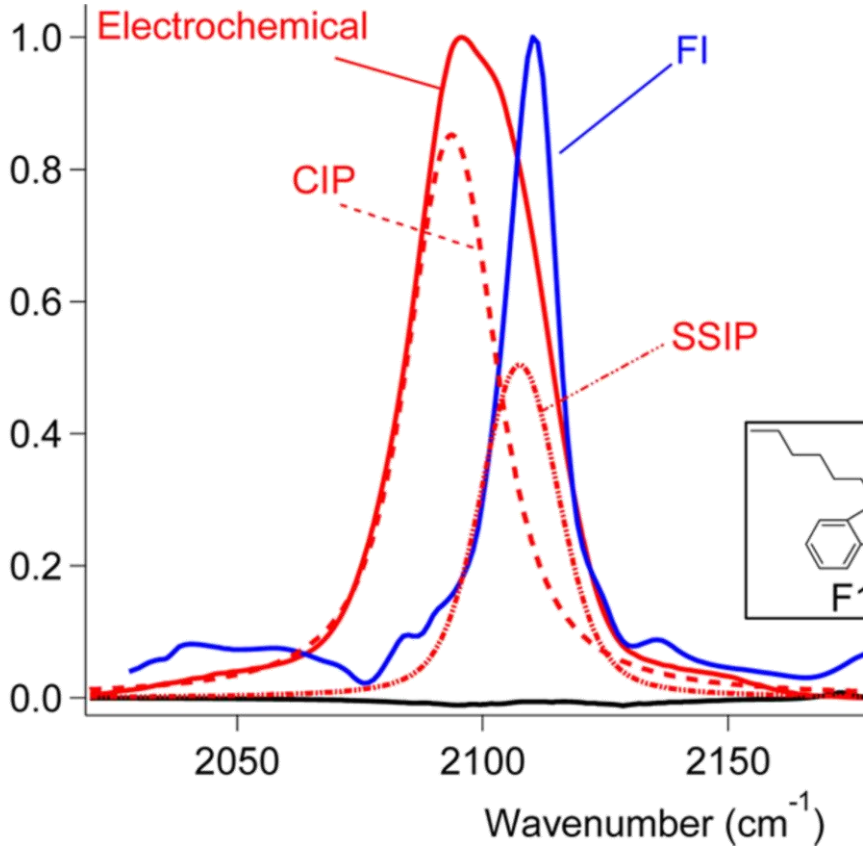
(2) Ratio between CIP and SSIP does not change with electrolyte concentration

$$\mathrm{SSIP} \rightleftharpoons \mathrm{CIP}(\mathbf{F1CN}^{-\bullet}, \mathrm{TBA}^{+}) + \mathrm{THF}$$



Time Dependence of Ion Pairing





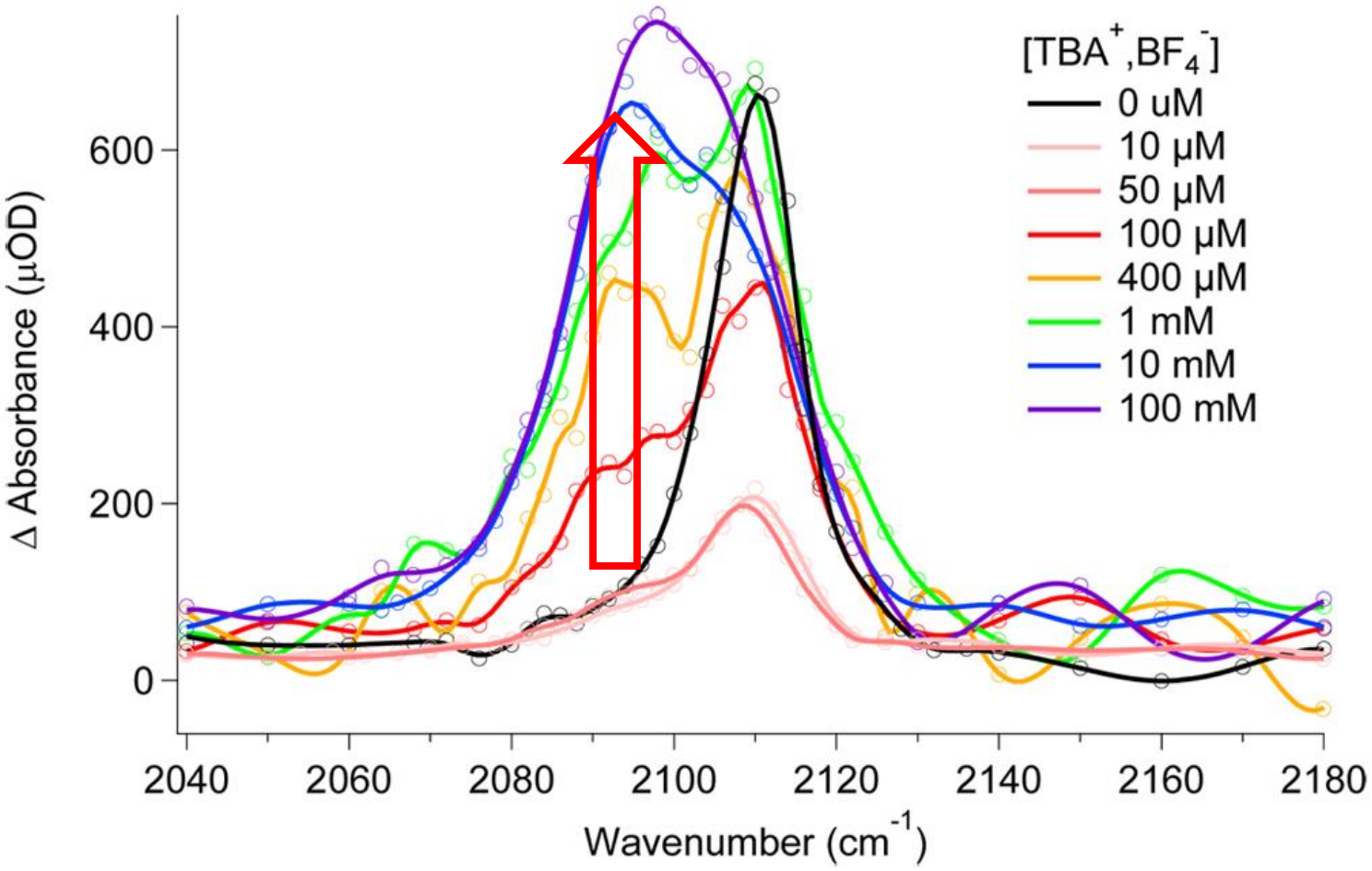
Disappearance of Free F1CN, the peak shape does not change after 2 μs (eq. between FI and CIP/SSIP)

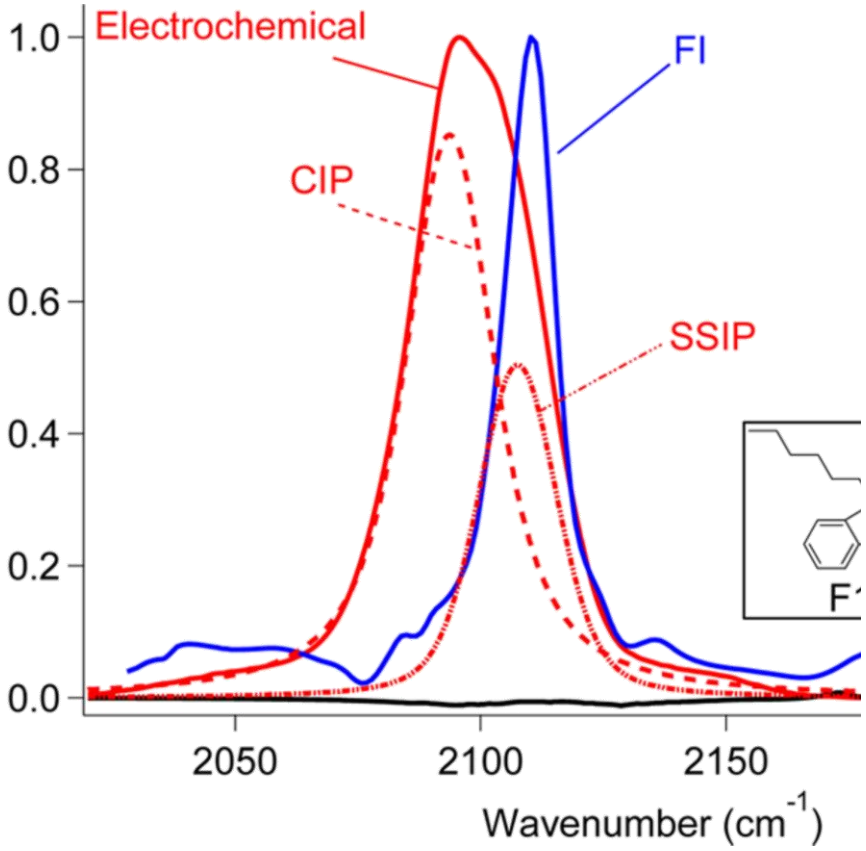
Rate constant of ion pairing : 2.1± 0.7 X 10^{11}/M/s

: much faster than diffusion-controlled reaction of neutral species (~ 10^{10}/M/s)

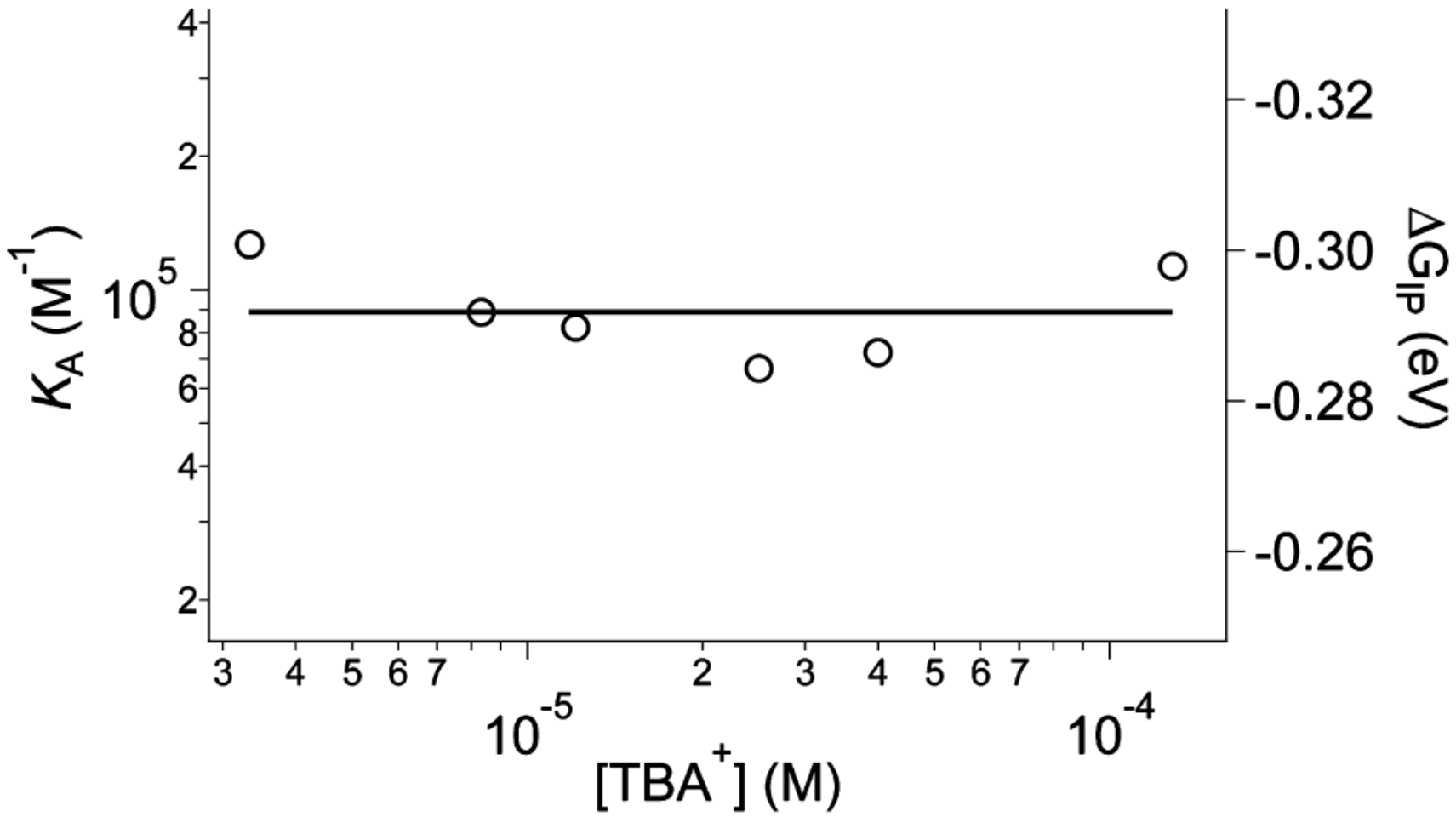
→ Coulomb interaction !!

Electrolyte Concentration Dependence

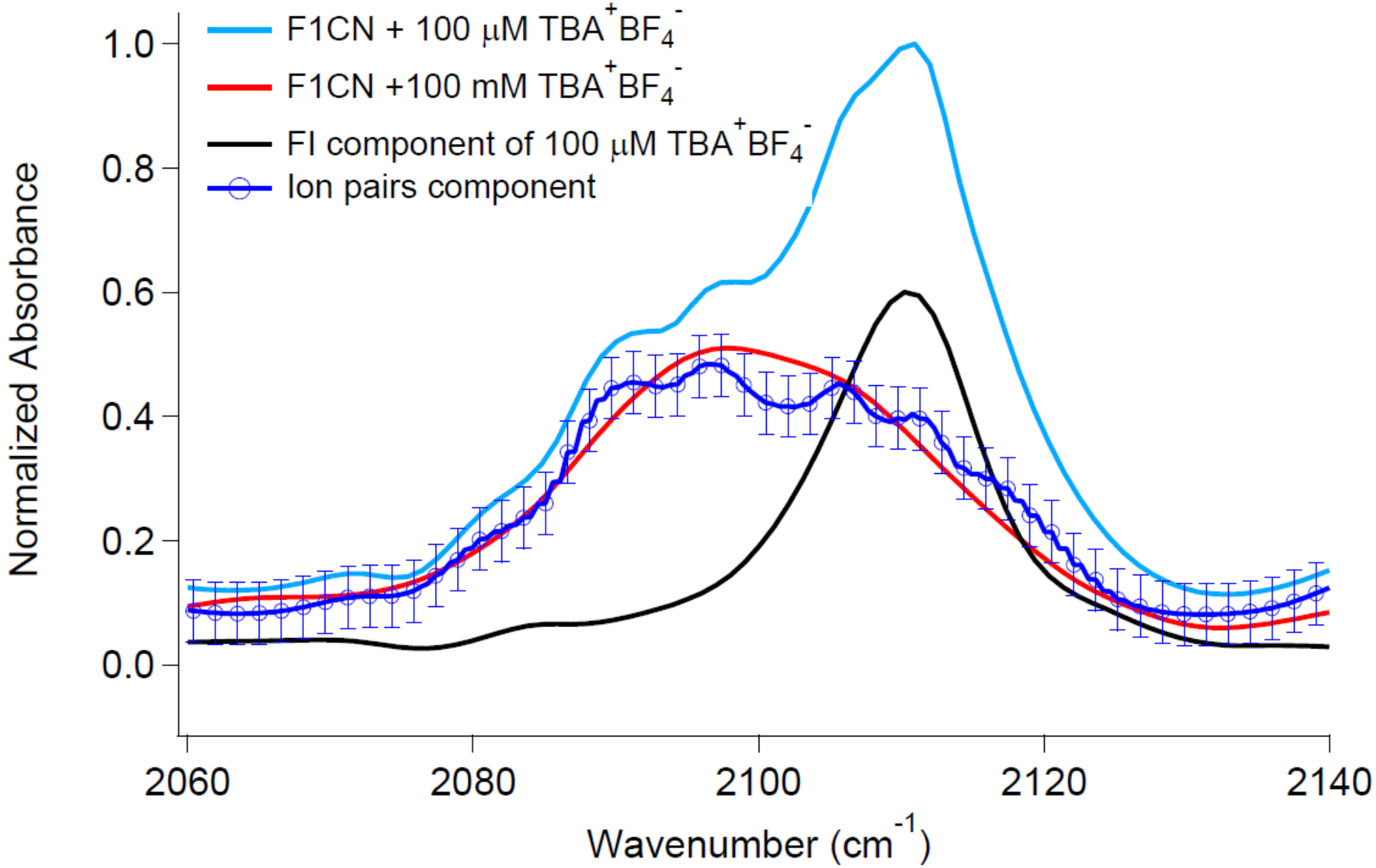




Electrolyte Concentration Dependence



Nature of Ion Pairing



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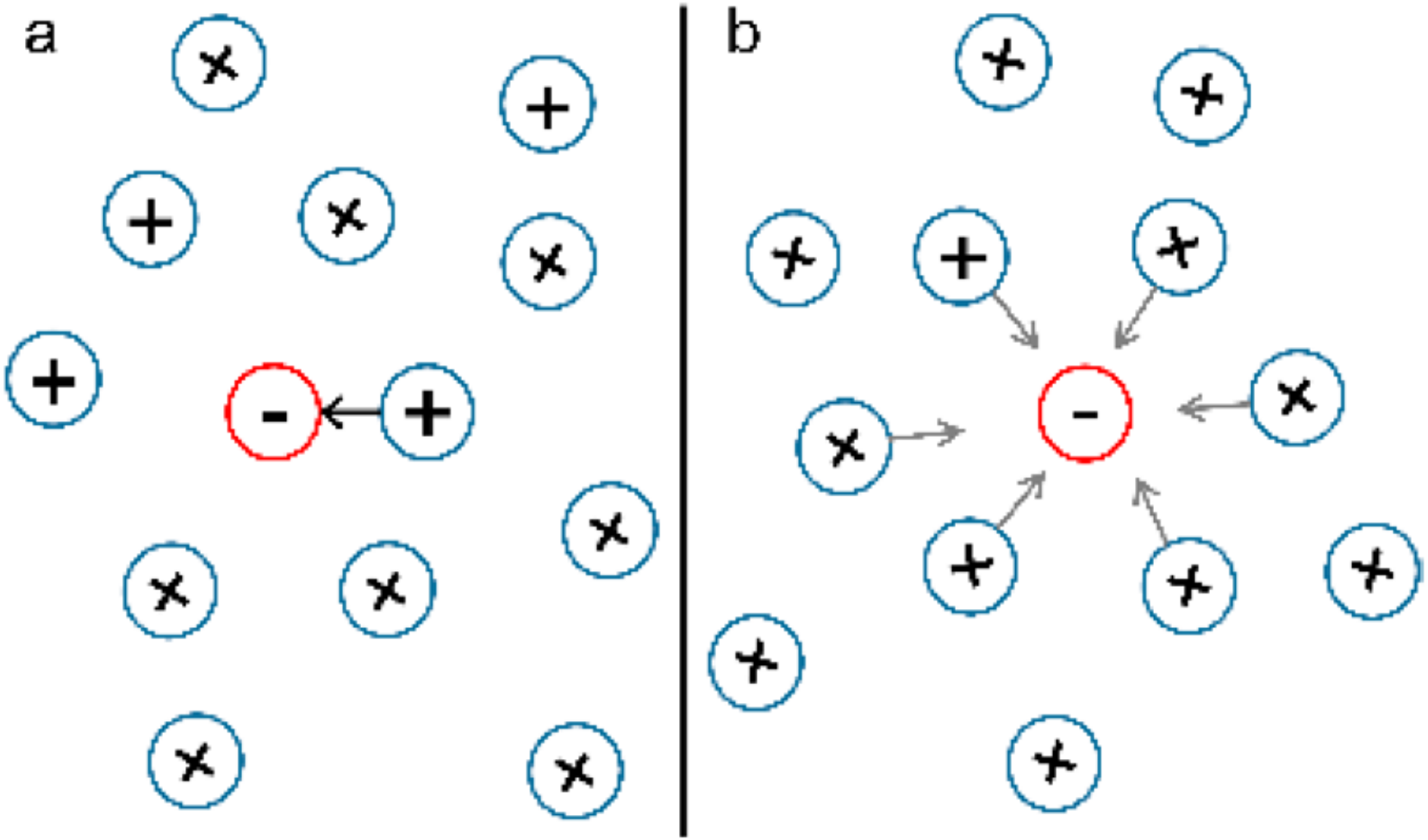
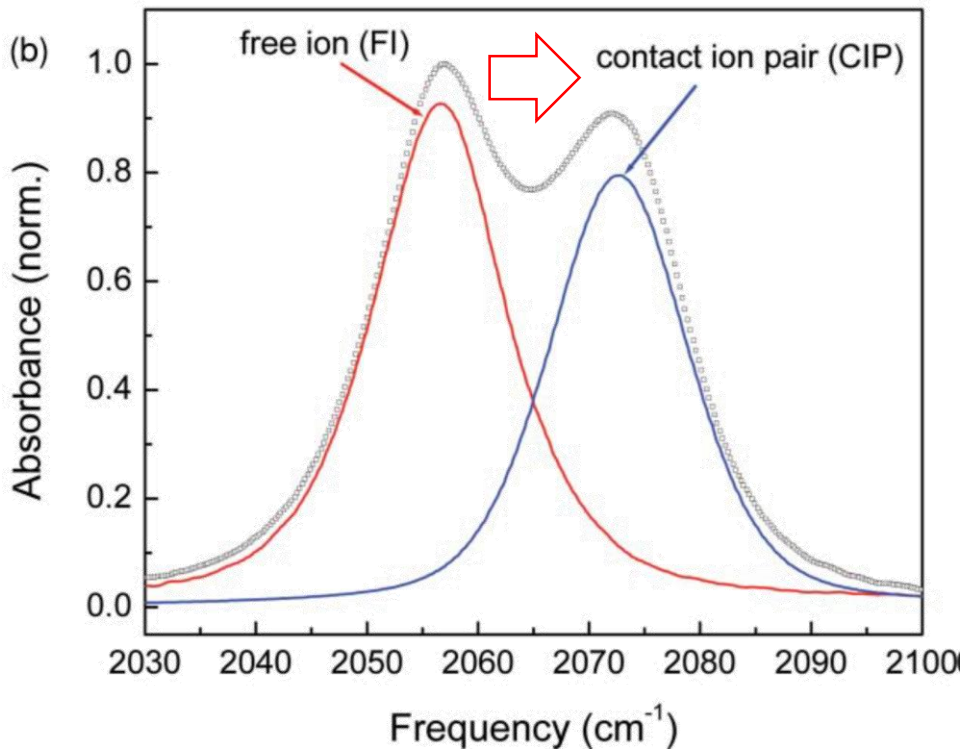
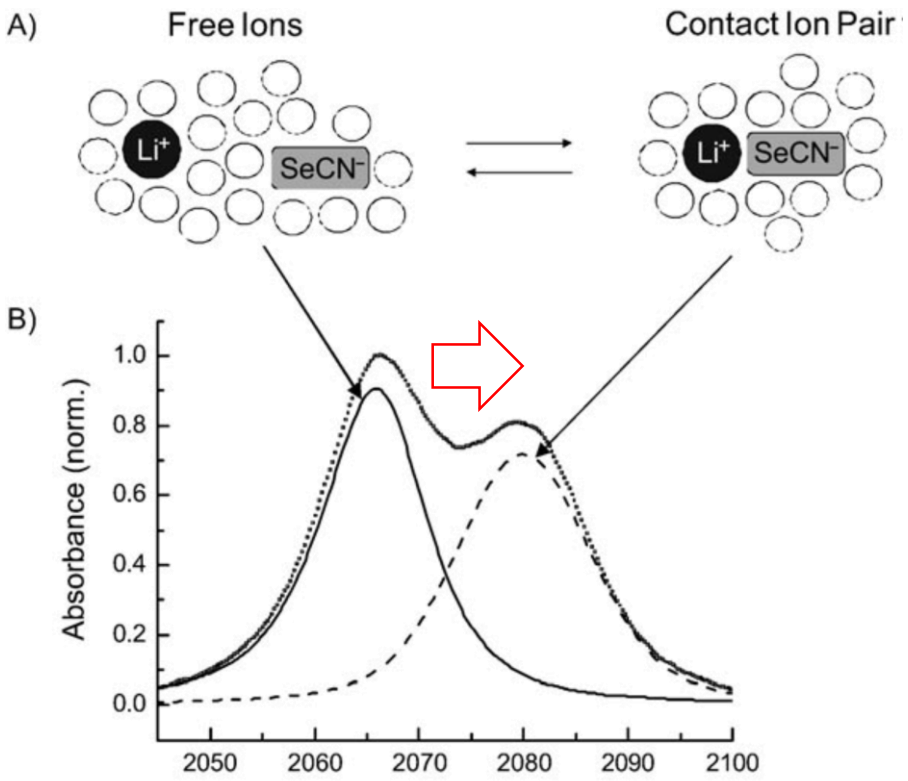


Comparison to Other Ion Pairs (LiSCN / LiSeCN)



LiSCN + LiBr in DMF

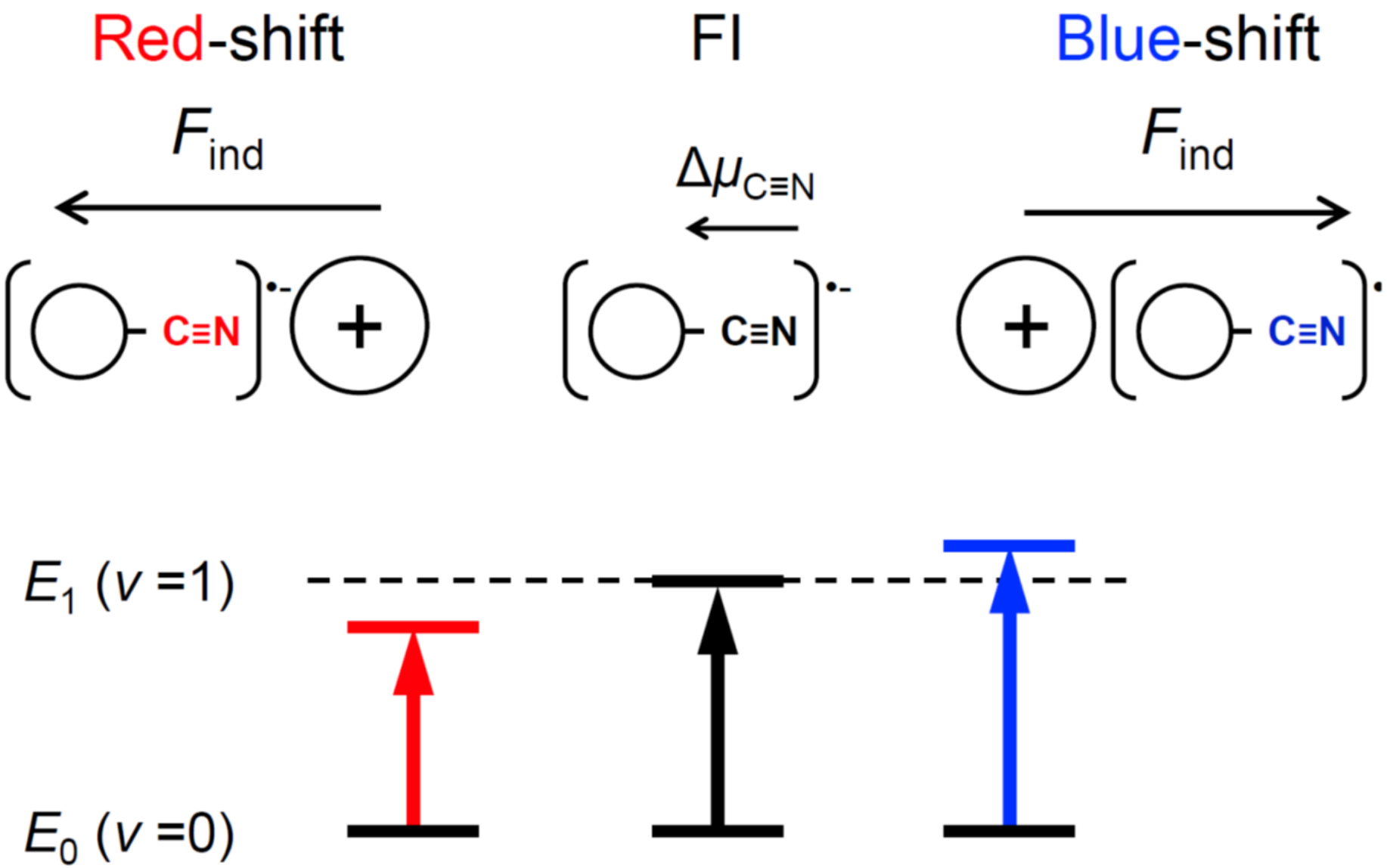


LiSCeN + LiBr in DMF

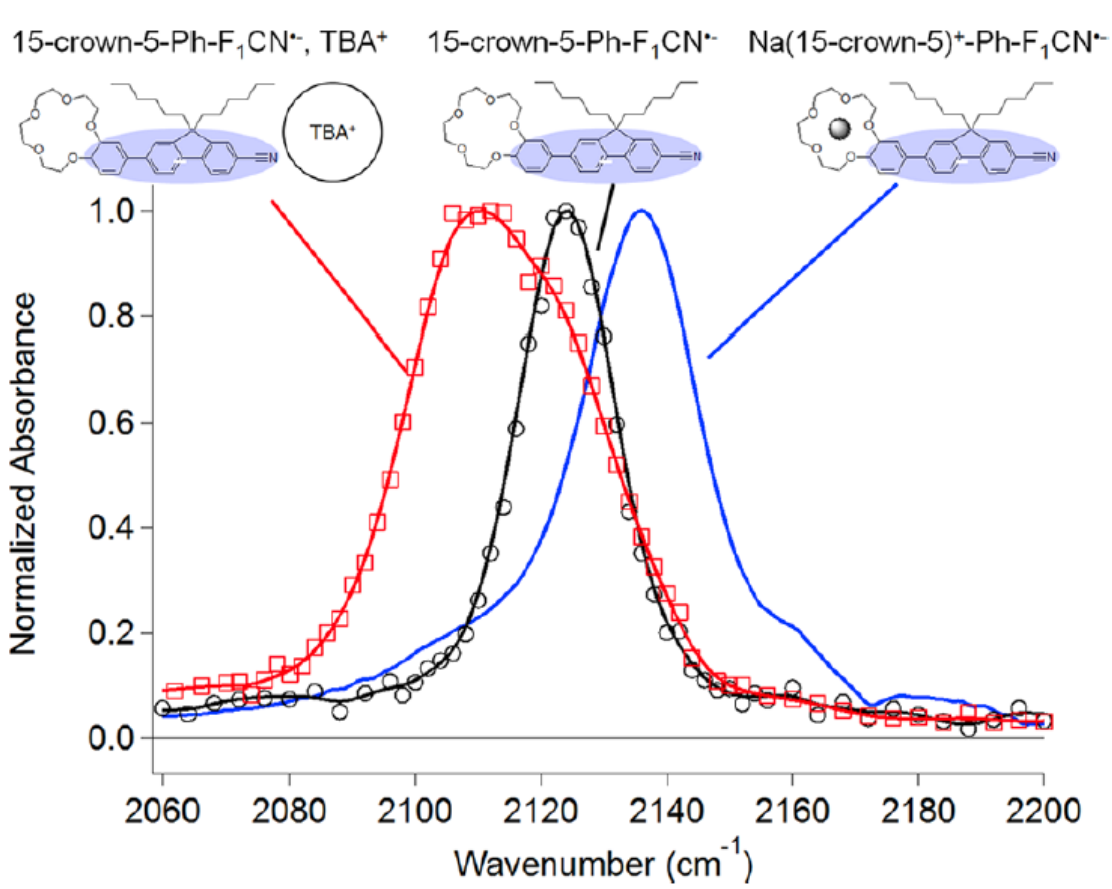
M. Cho and coworkers,
J. Chem. Phys (2010) 134 064506

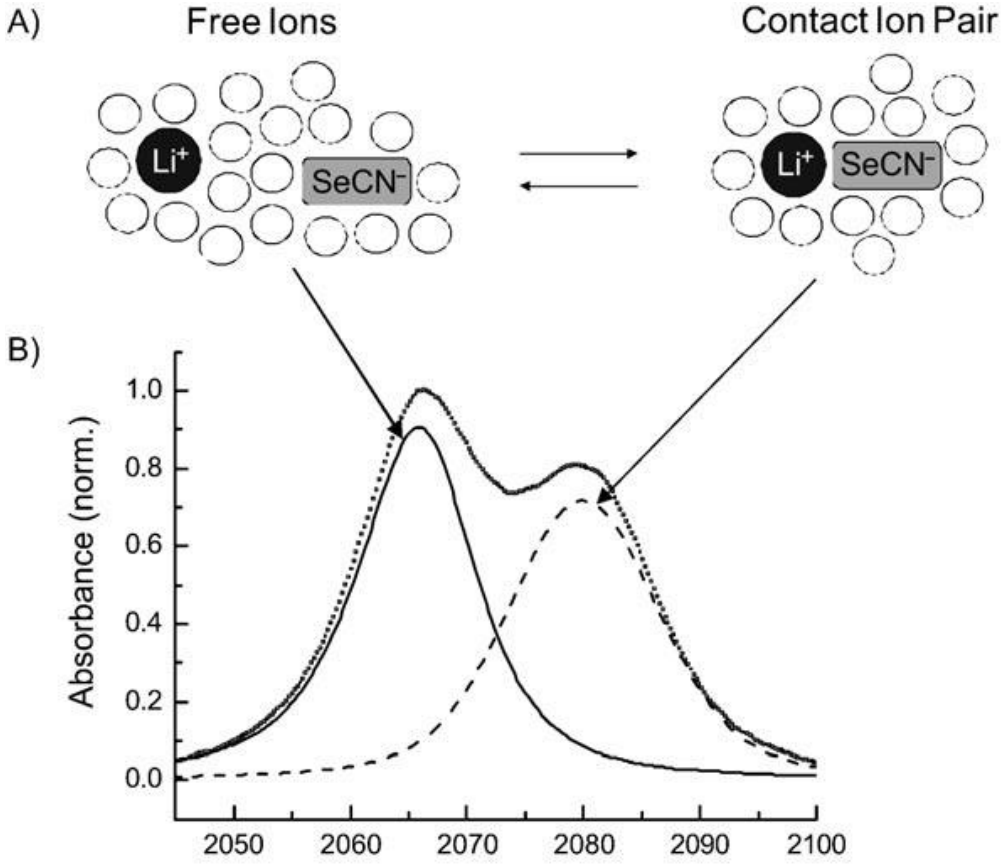
M. Cho and coworkers,
ChemPhysChem (2010) 11 3632

Vibrational Stark Effect



Vibrational Stark Effect : Redshift or Blueshift?





Summary

(1) Electric field changes vibrational frequencies

(2) Ion pairing was detected by using frequencies shift

(3) Field direction changes the signs of frequency change