

Induction of asymmetric reactions in organic dust analogues by polarized quantum beam irradiation

Jun-ichi Takahashi
NTT Sci. & Core Tech. Lab.

偏極量子ビーム照射による模擬ダスト
有機物への不斉化学反応誘起

高橋淳一
日本電信電話 先端総研

Grain Formation Workshop 2012 (CPS, Kobe Univ.)

Chirality

(掌性・对掌性

=鏡像対称性の欠如)

Optical Anisotropy

(光学異方性)

Optical Activity

(光学活性)

神戸灘酒心館

Enantiomer (鏡像異性体・光学異性体)



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Asymmetric Synthesis

(不斉(非対称)合成)

Enantiomeric Excess

(鏡像体過剰率・光学異性体比の偏り)

Homochirality

(ホモカイラリティー)

Asymmetric Synthesis
(不斉(非対称)合成)



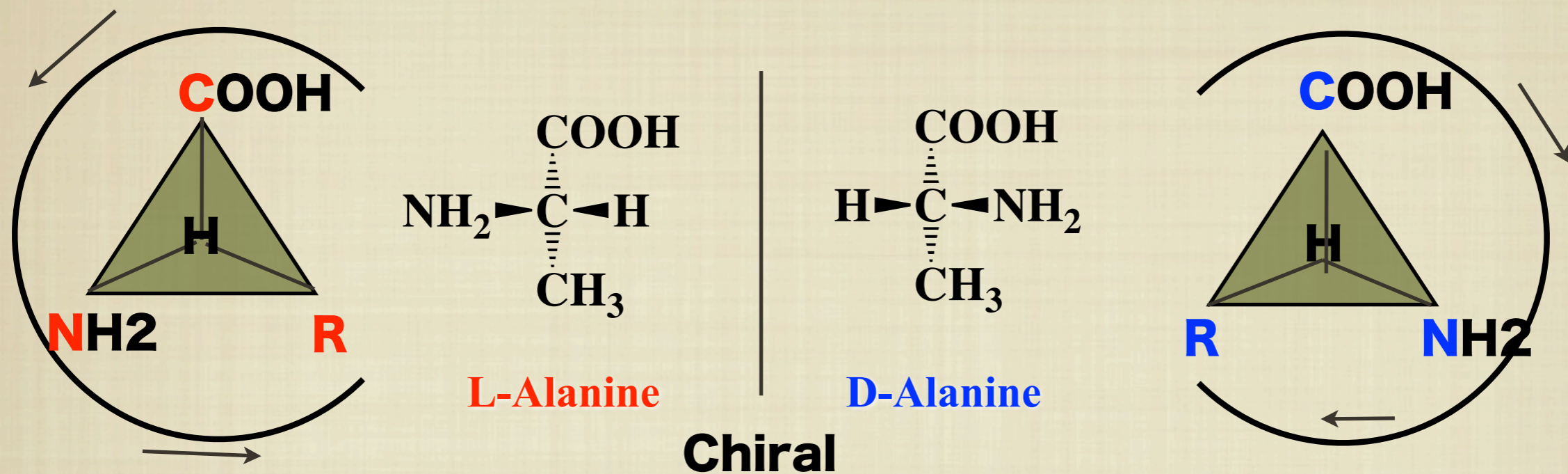
Enantiomeric Excess

(鏡像体過剰率・光学異性体比の偏り)

Homochirality

(ホモカイラリティー)

Biomolecular Homochirality in Amino Acids



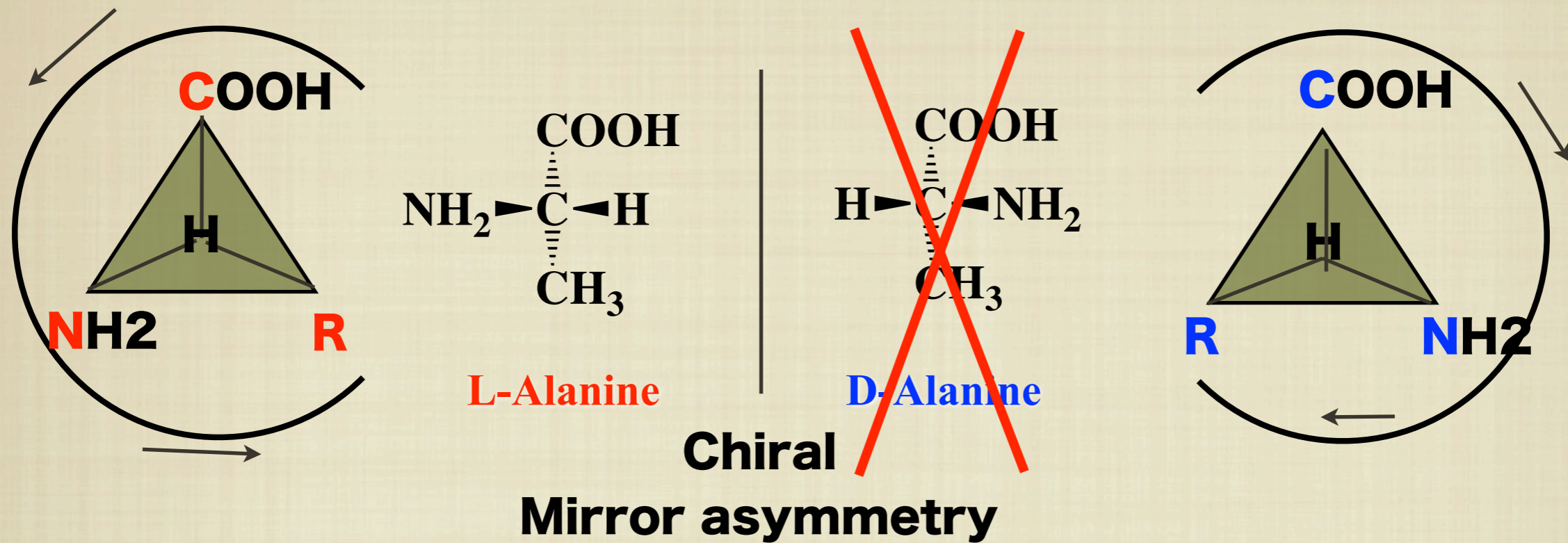
Mirror asymmetry

Abiotic synthesis of amino acids without bioorganic materials or catalysis generates **racemic body** (equivalent mixtures of L- and D-body enantiomer)

Enantiomers show **symmetry** in atomic or molecular level behavior.

Then, why **homochirality** (**asymmetry**) in terrestrial biomolecules
Furthermore, why dominant **L**-amino acids and **D**-sugars ?

Biomolecular Homochirality in Amino Acids



Abiotic synthesis of amino acids without bioorganic materials or catalysts generates **racemic body** (equivalent mixtures of L- and D-body enantiomer)

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Then, why **homochirality** (**asymmetry**) in terrestrial biomolecules
Furthermore, why dominant **L**-amino acids and **D**-sugars ?

The Origin of Terrestrial Biomolecular Homochirality and Symmetry Breaking in Nature

Purpose;

**Hypothesis verification of the relationship between
The Origin of Terrestrial Biomolecular Homochirality
and Symmetry Breaking in Nature**

Methods;

**Laboratory Experimental; High Energy Accelerators
Theoretical; First Principle Quantum Calculation**

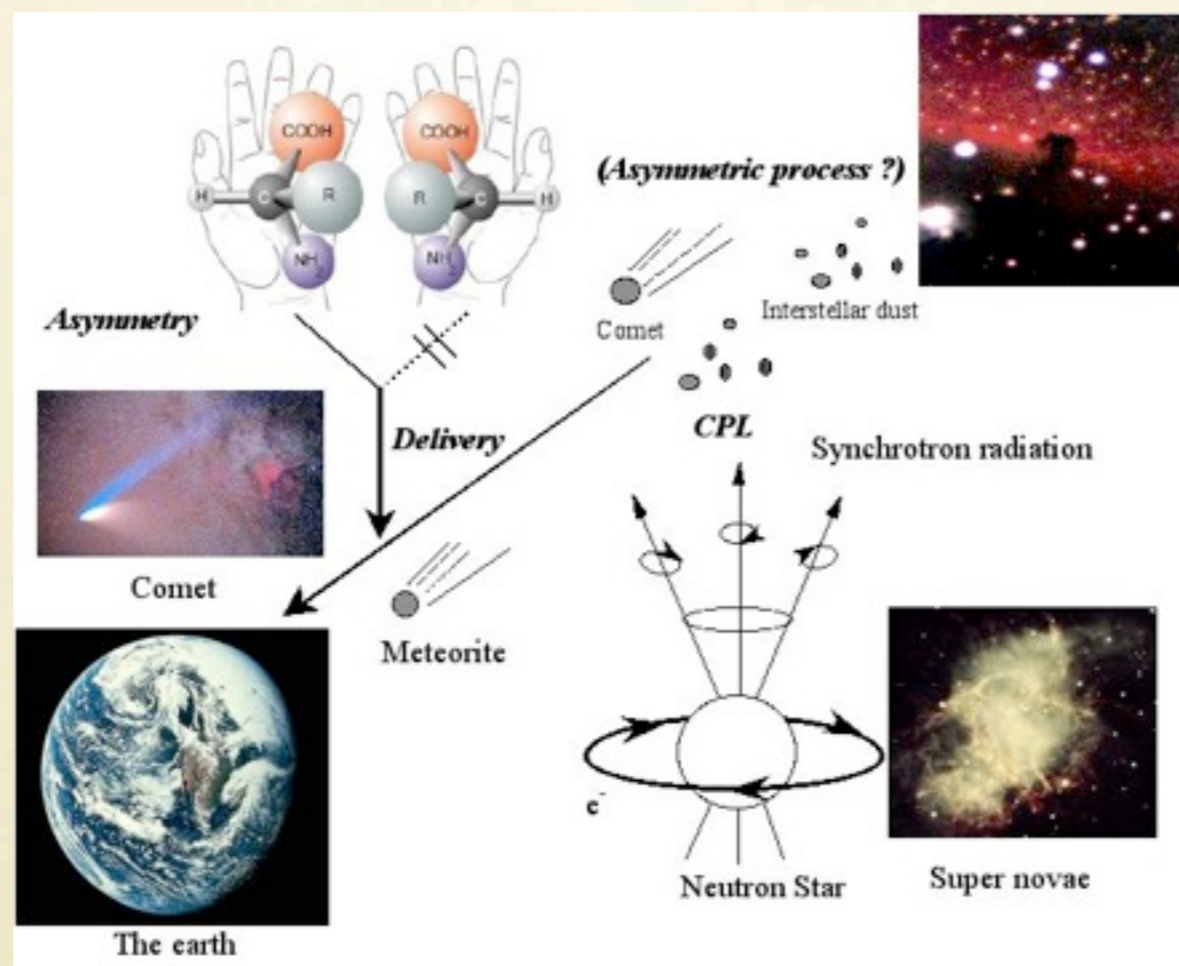
Cosmic Scenario

*chiral-preferential synthesis
or chiral-selective decomposition*

*asymmetric
chemical process on
interstellar media*

*delivery of
chiral seeds
to the earth*

*accumulation and
enhancement of
chiral purification*



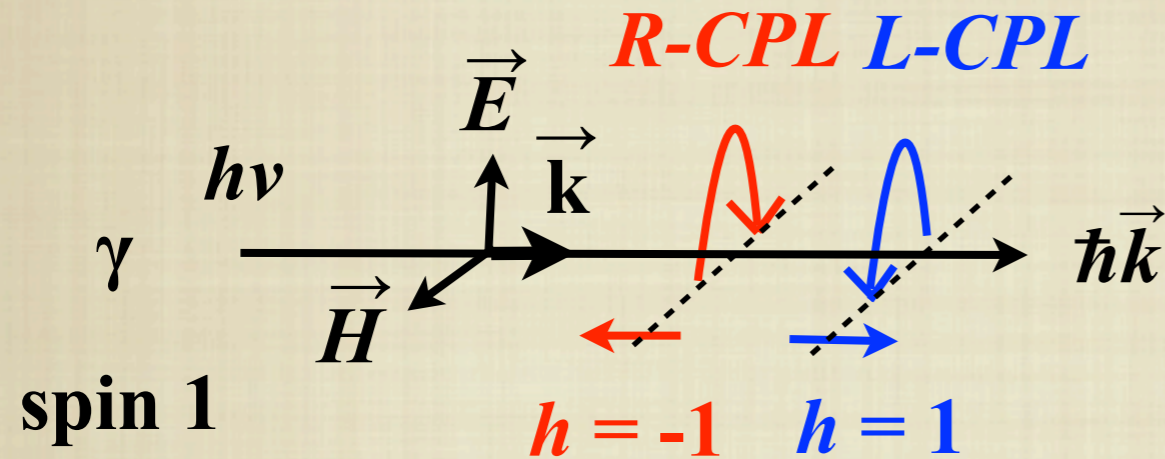
*chiral-impulse
radiation;
circularly
polarized light
(CPL)
or
spin polarized
radiation
(SPR)*

Cosmic Scenario

Chiral Impulse

- Polarized Quantum Beams -

Circularly polarized light

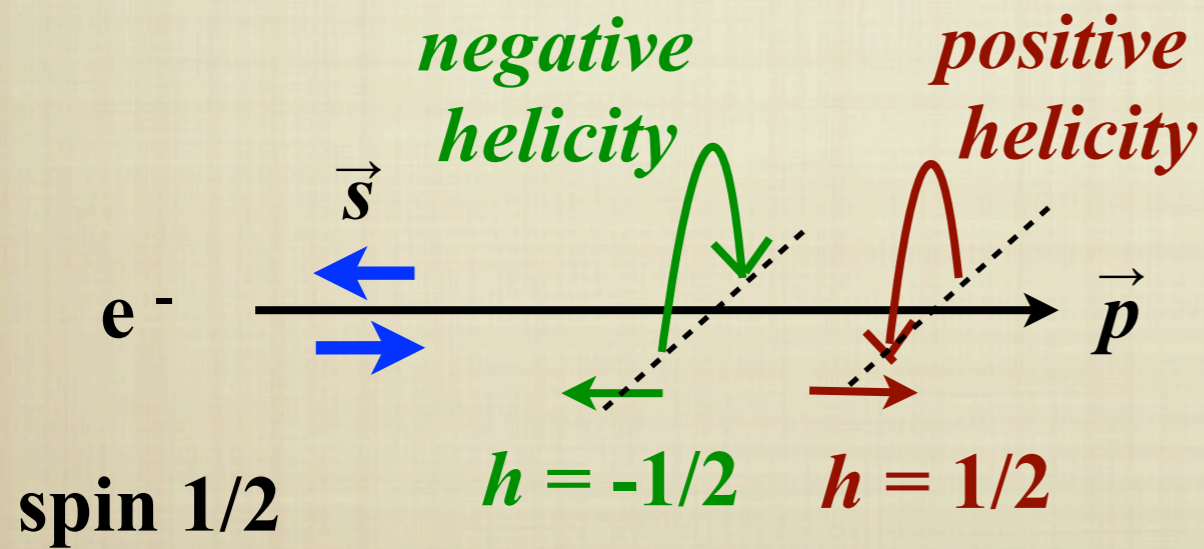


Helicity

$$h = \vec{s} \cdot \vec{p} / |\vec{p}|$$

right-handed (negative helicity)
left-handed (positive helicity)

Spin polarized radiation



positive helicity (right-handed)
negative helicity (left-handed)

Circularly polarized light in space (1)

(Generation)

Synchrotron radiation

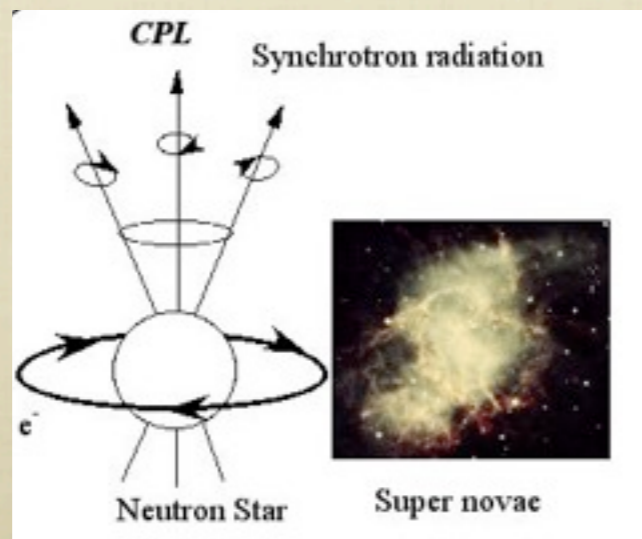
Asymmetric scattering

(Interaction with molecules)

Excitation of both electronic- and magnetic-dipole moments

Synchrotron radiation from orbital electrons captured by intense magnetic fields of **neutron stars or white dwarfs**

(observation not yet)



Scattered light from **a massive star forming region** in **high density interstellar molecular cloud**

T. Fukue et al. OLEB Vol.40 p.335 (2010)

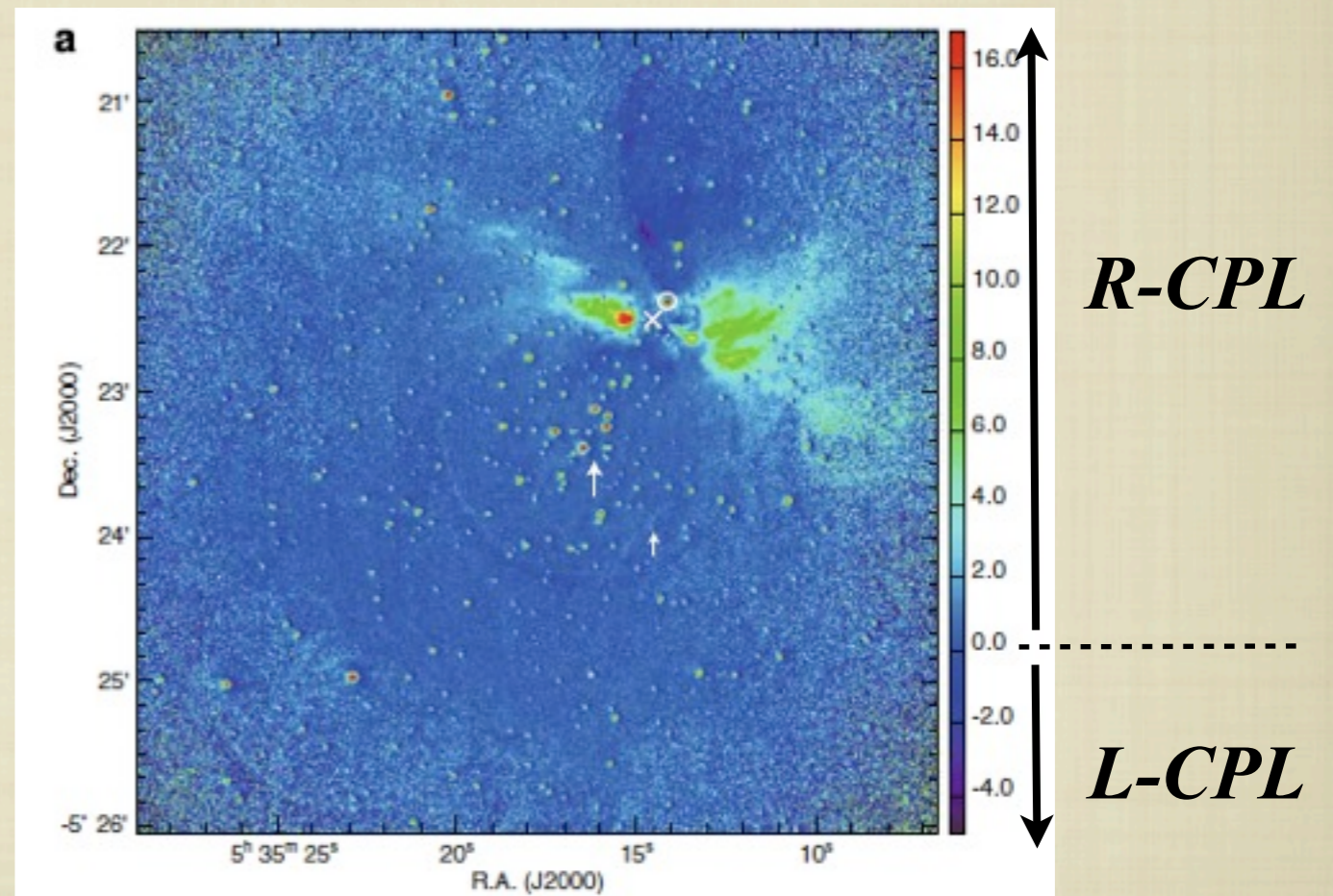


Image of degree of **circular polarization (%)** in the **Ks band (2.14 μm)** of the central region of the **Orion star forming region**.

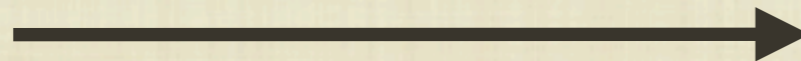
Polarized beam irradiation experiments

*simulated ISD
surface formation*

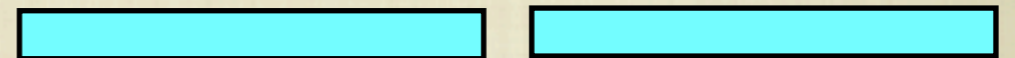
*chiral impulse
irradiation*

*optical anisotropy
measurement*

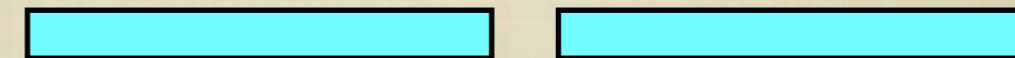
(a) preferential photolysis



(b) chiral polymerization



(c) chiral conformation change
or structural distortion

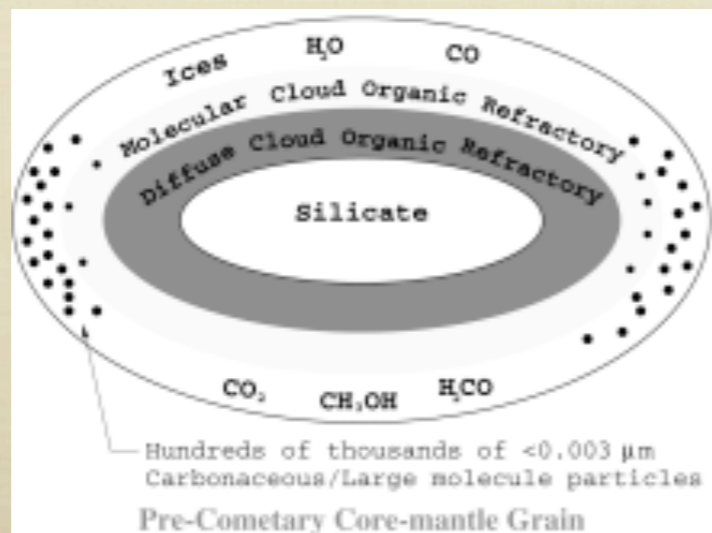


circular dichroism (CD) spectra
 σ (Left-CPL) - σ (Right-CPL)

Solid films of **racemic
organic compounds**
on glass substrate

polarized quantum
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**circularly polarized
light**

amino acids
Alanine
Isovaline
amino acid
precursors
Hydantoins



Polarized beam irradiation experiments

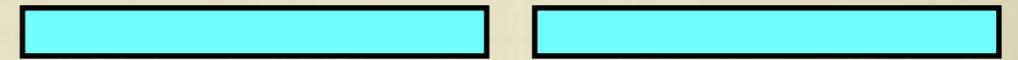
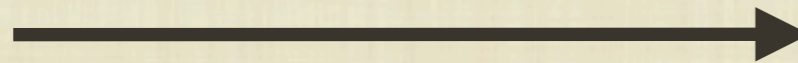
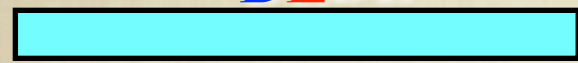
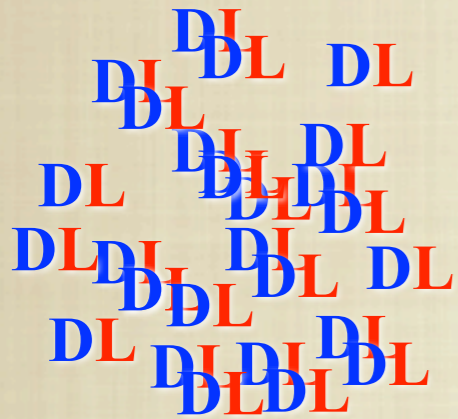
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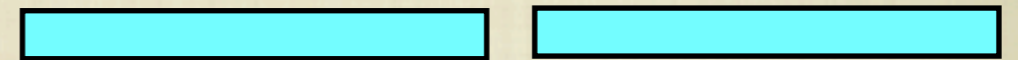
optical anisotropy

measurement

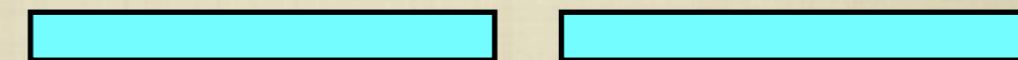
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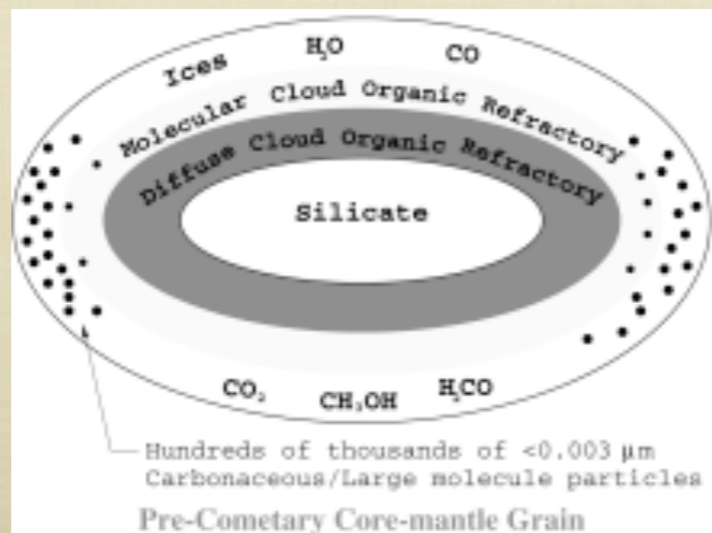
(c) chiral conformation change
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Solid films of **racemic
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**circularly polarized
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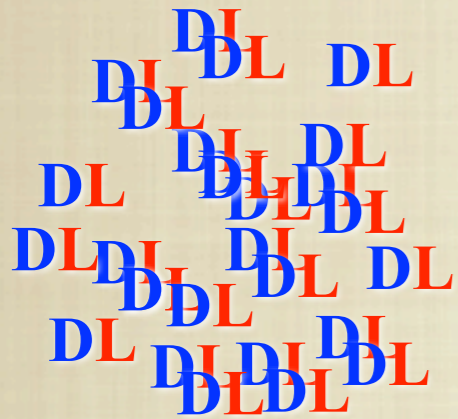
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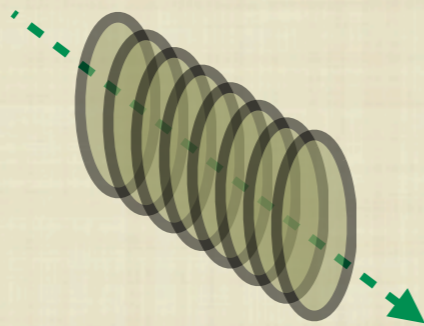
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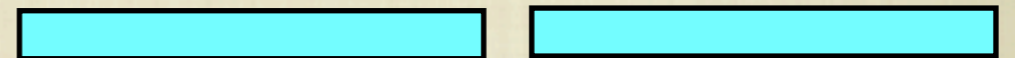
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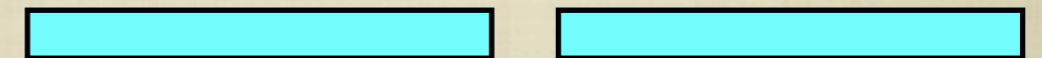
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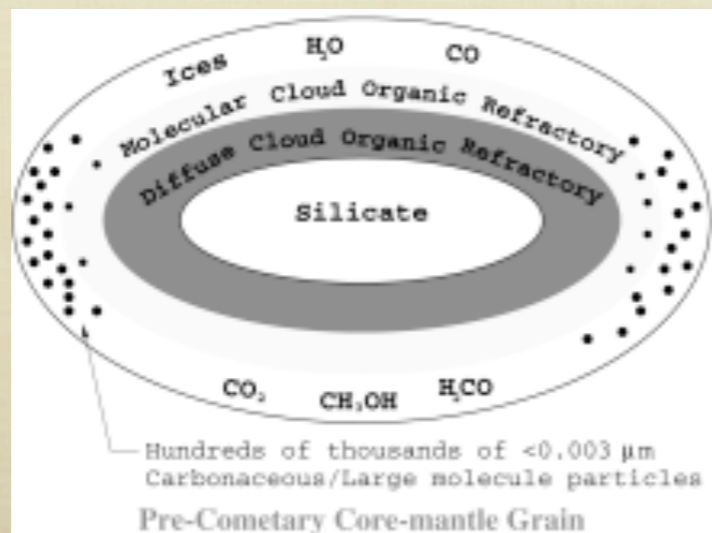
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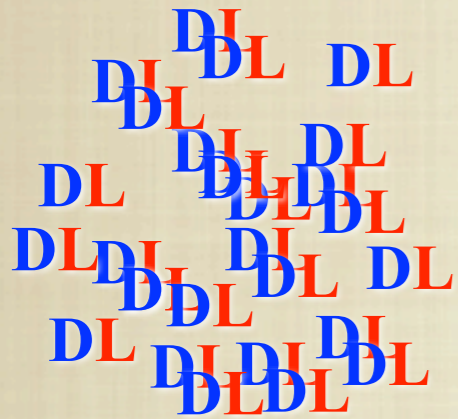
polarized quantum
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**circularly polarized
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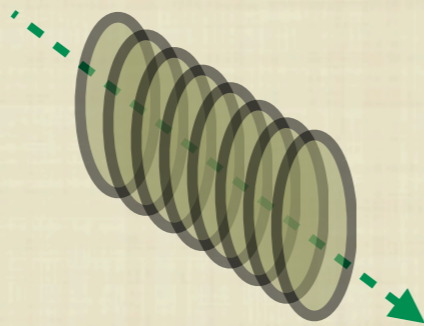
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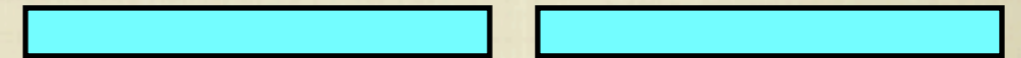
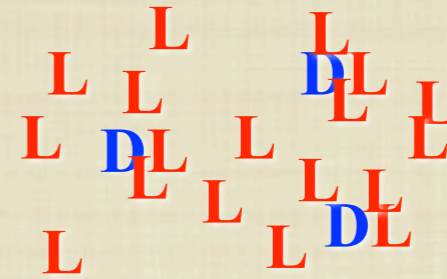


chiral impulse irradiation

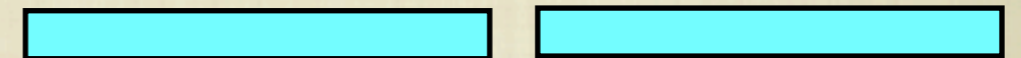


optical anisotropy measurement

(a) preferential photolysis



(b) chiral polymerization



(c) chiral conformation change or structural distortion

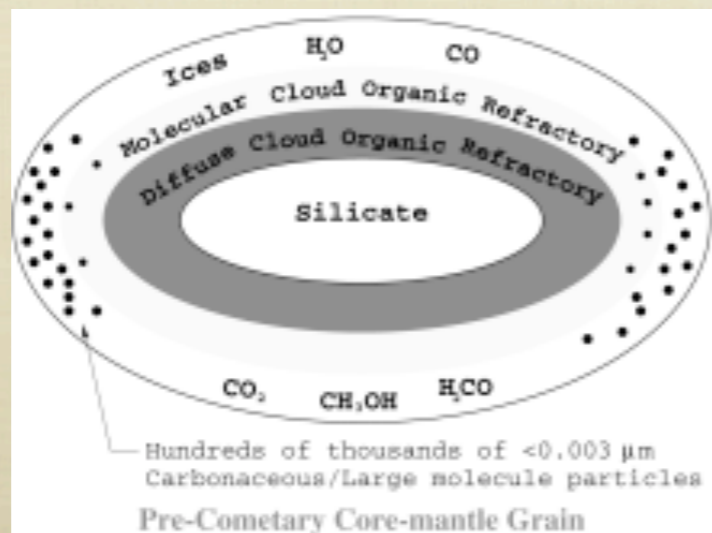


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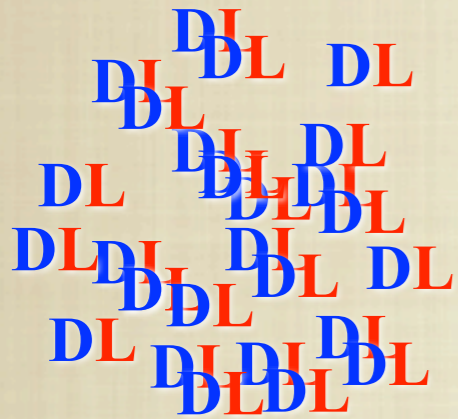
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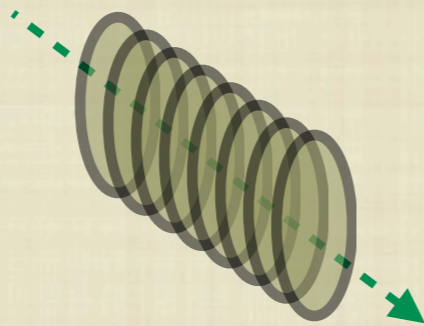


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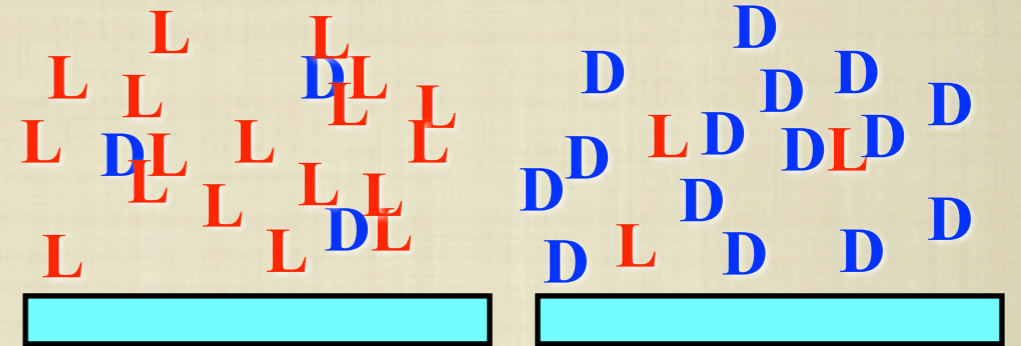


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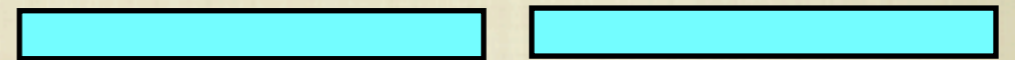


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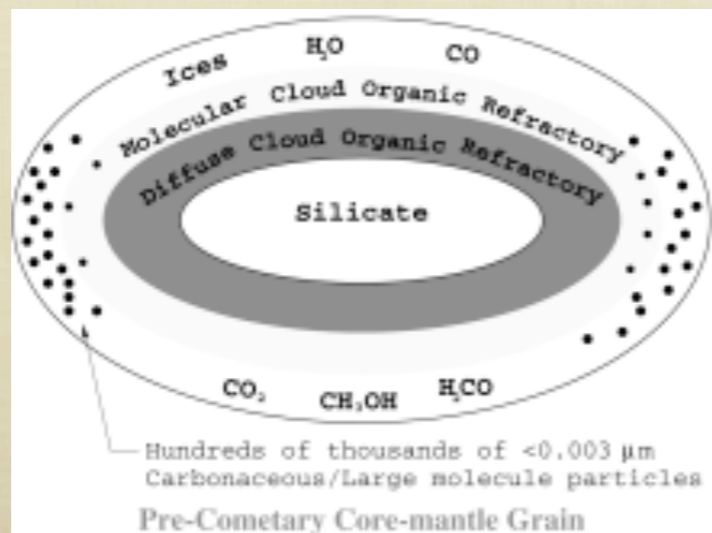


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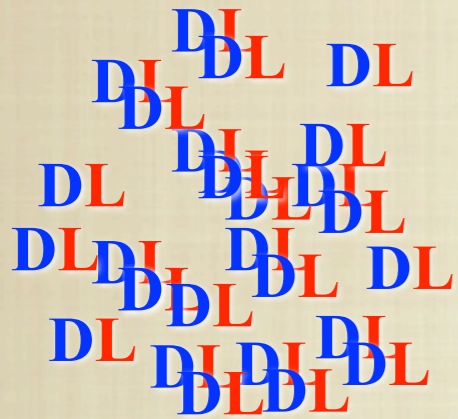
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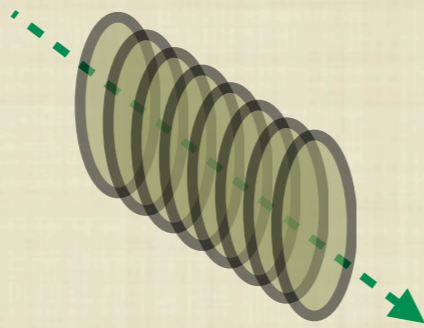


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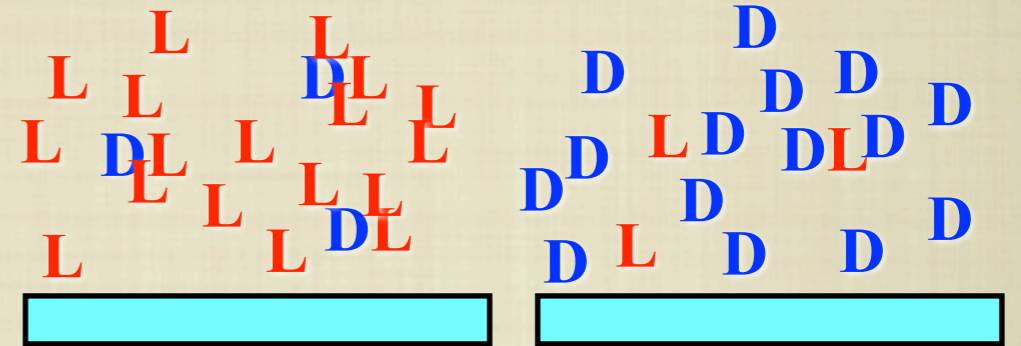


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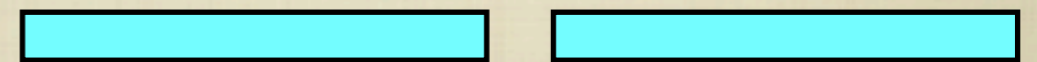
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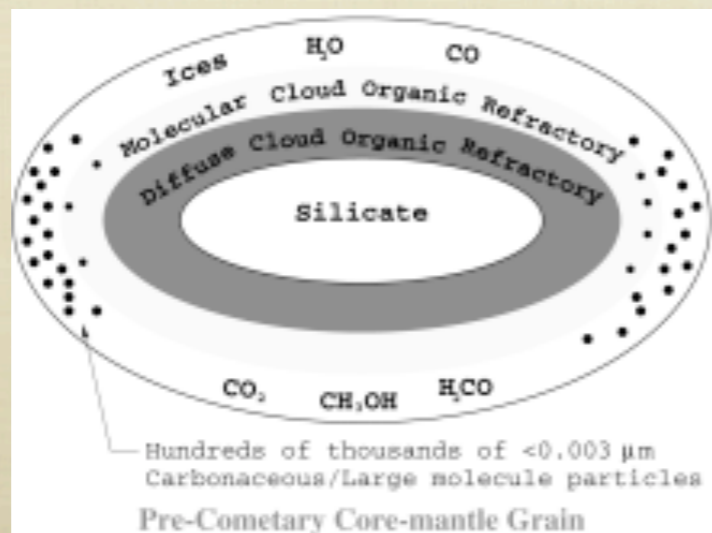


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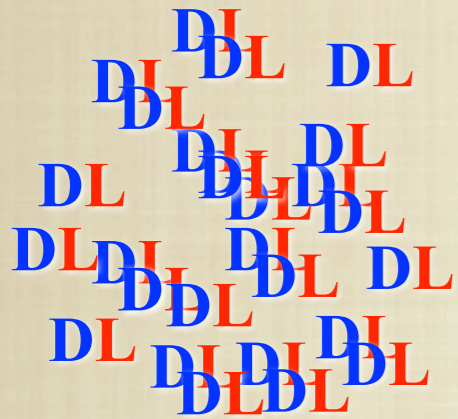
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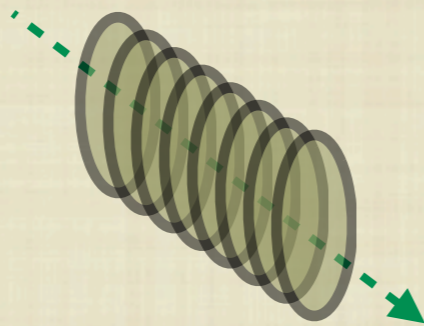


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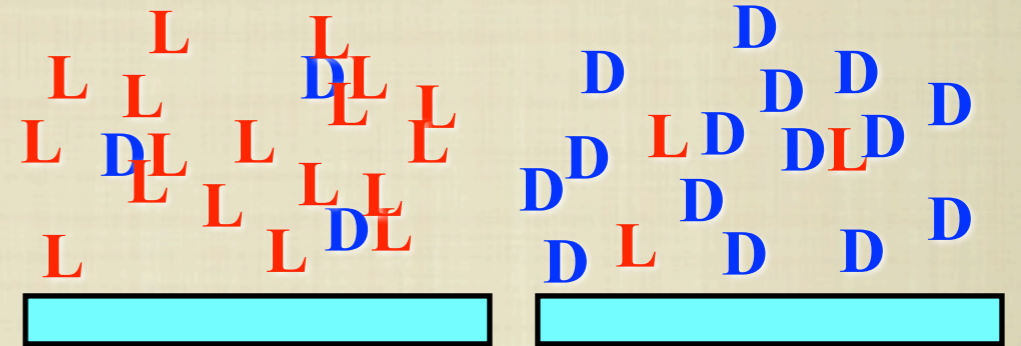


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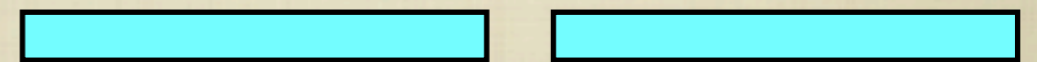
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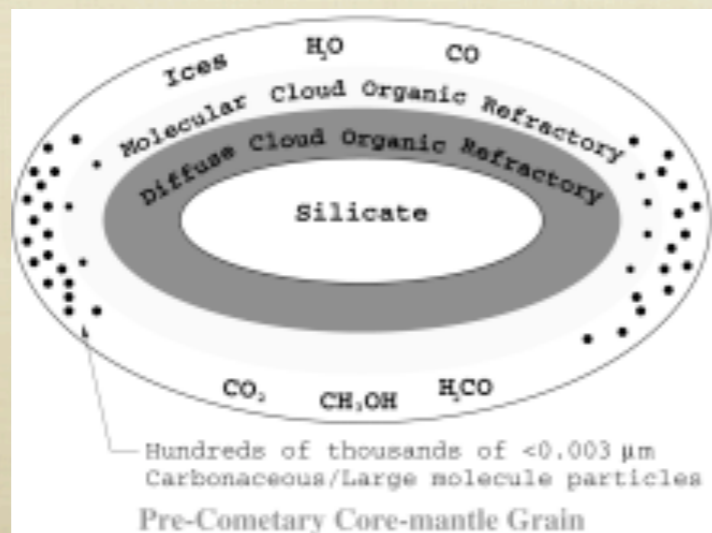


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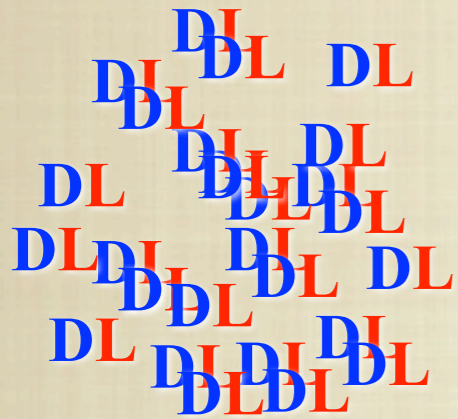
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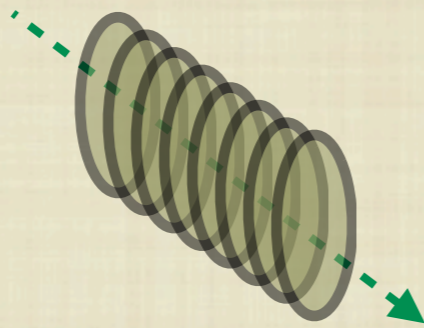


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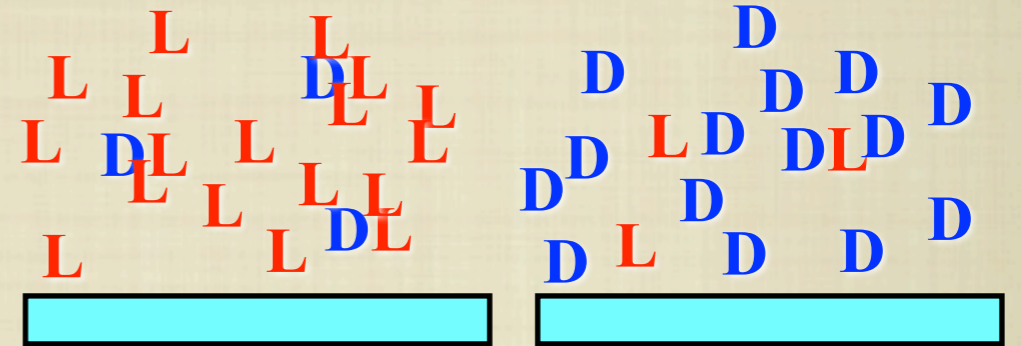


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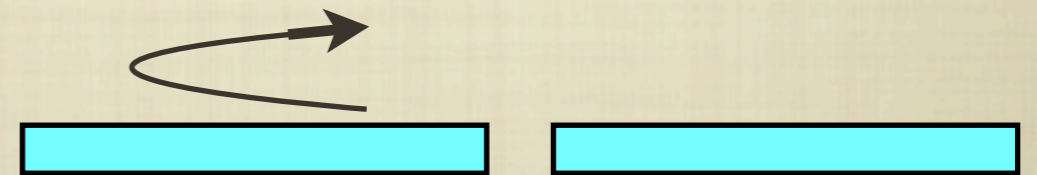
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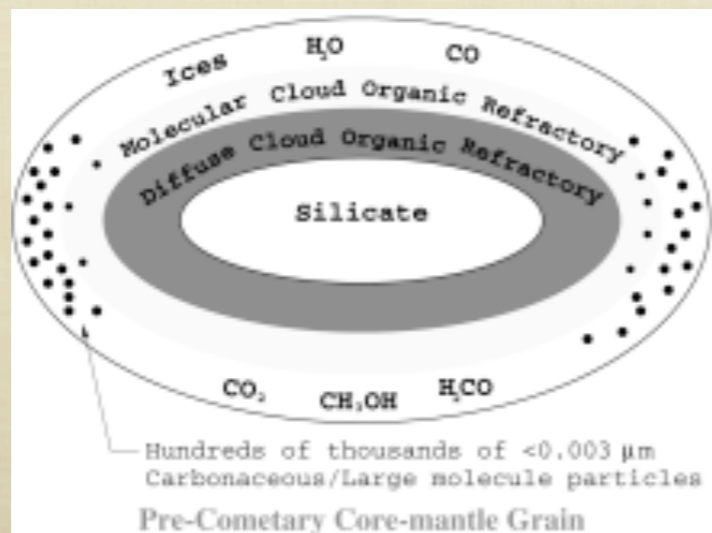


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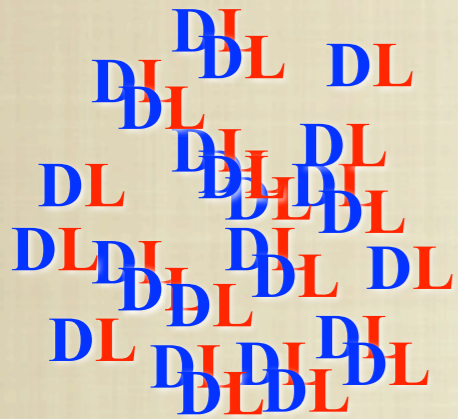
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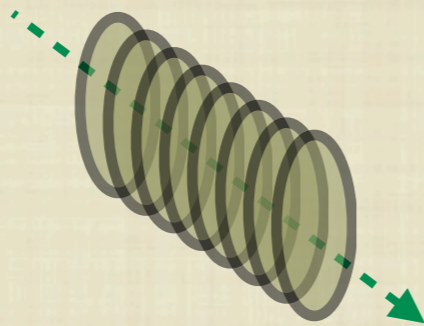


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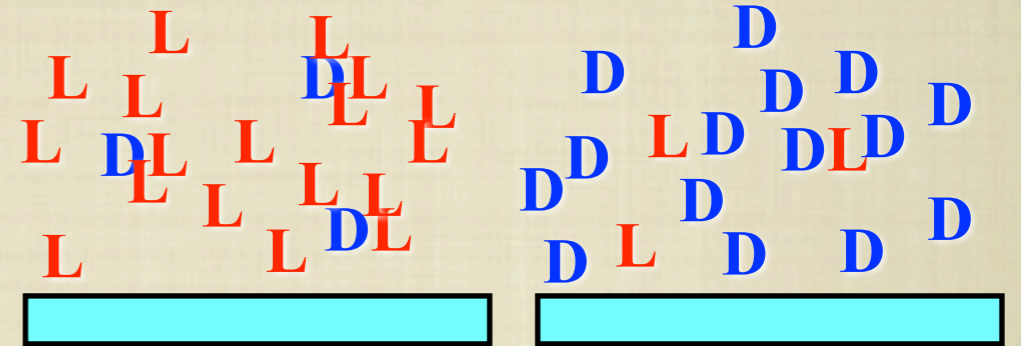
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polarized quantum beam irradiation
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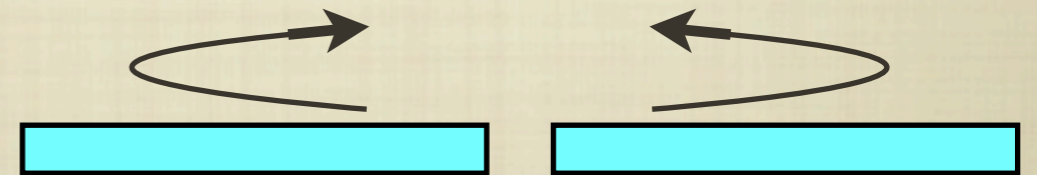
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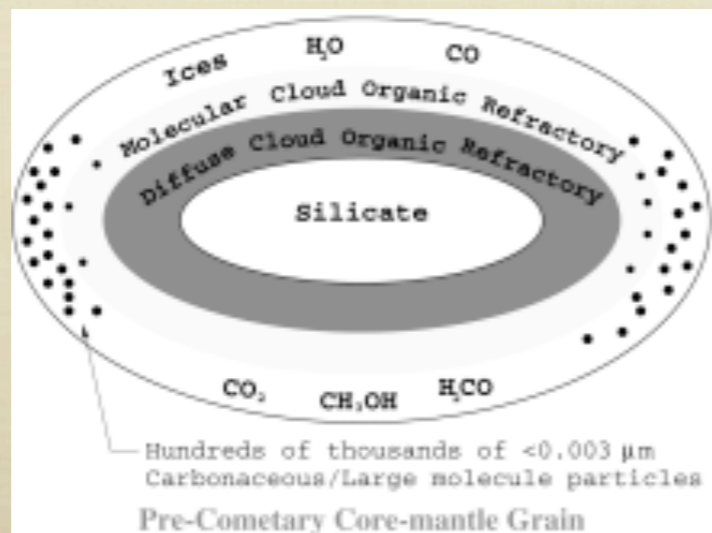
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Solid films of **racemic organic compounds** on glass substrate

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Circularly polarized photon irradiation

Light Source:

UVSOR-II (Oakazaki, Japan)

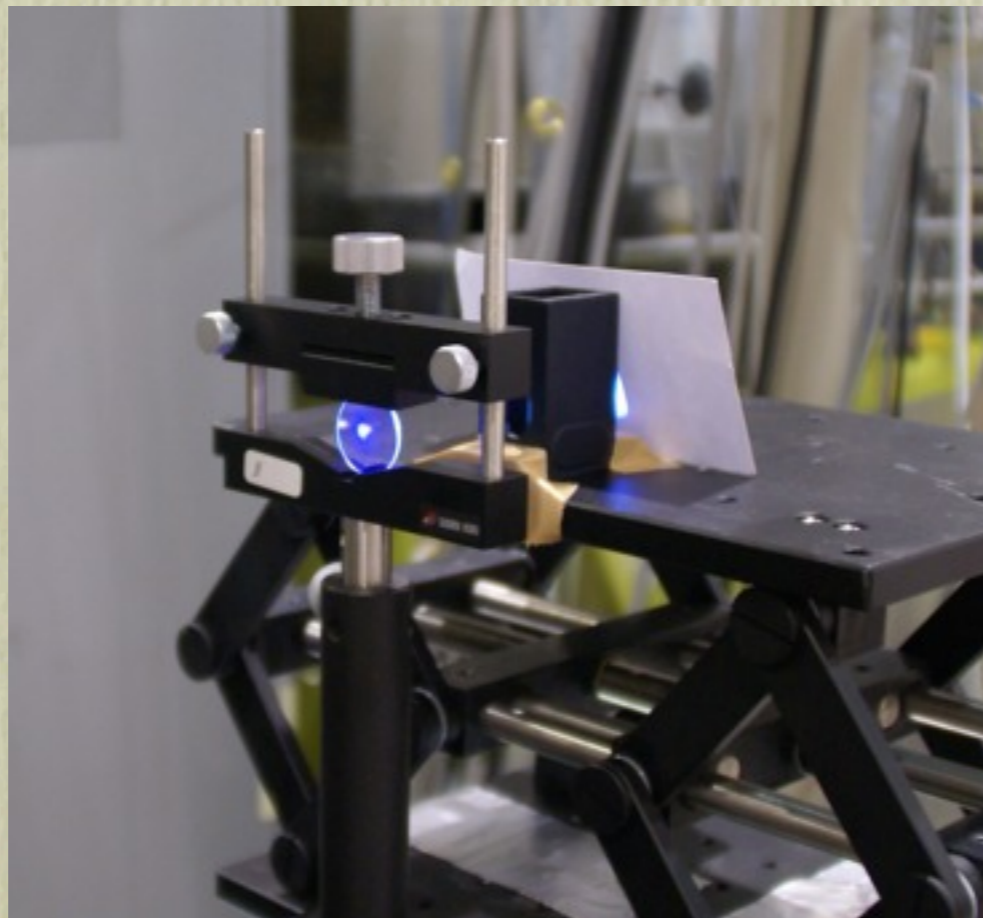
Free Electron Laser (FEL)

Circularly Polarized Light (CPL)

Polarization Purity > 98%

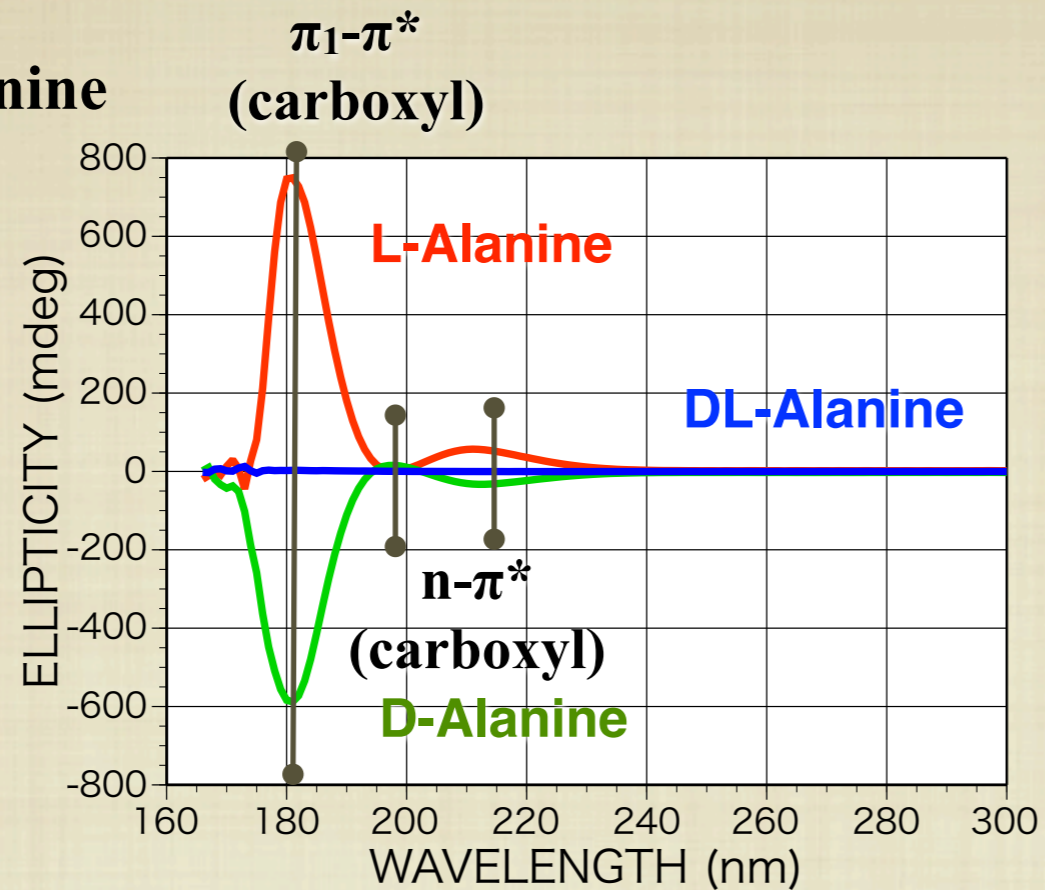
Wavelength $\lambda = 215 \sim 6 \text{ nm}$

Total Dose $\sim 10^{16} \text{ eV}$ (2~10 mWhour)



Circular Dichroism (CD)

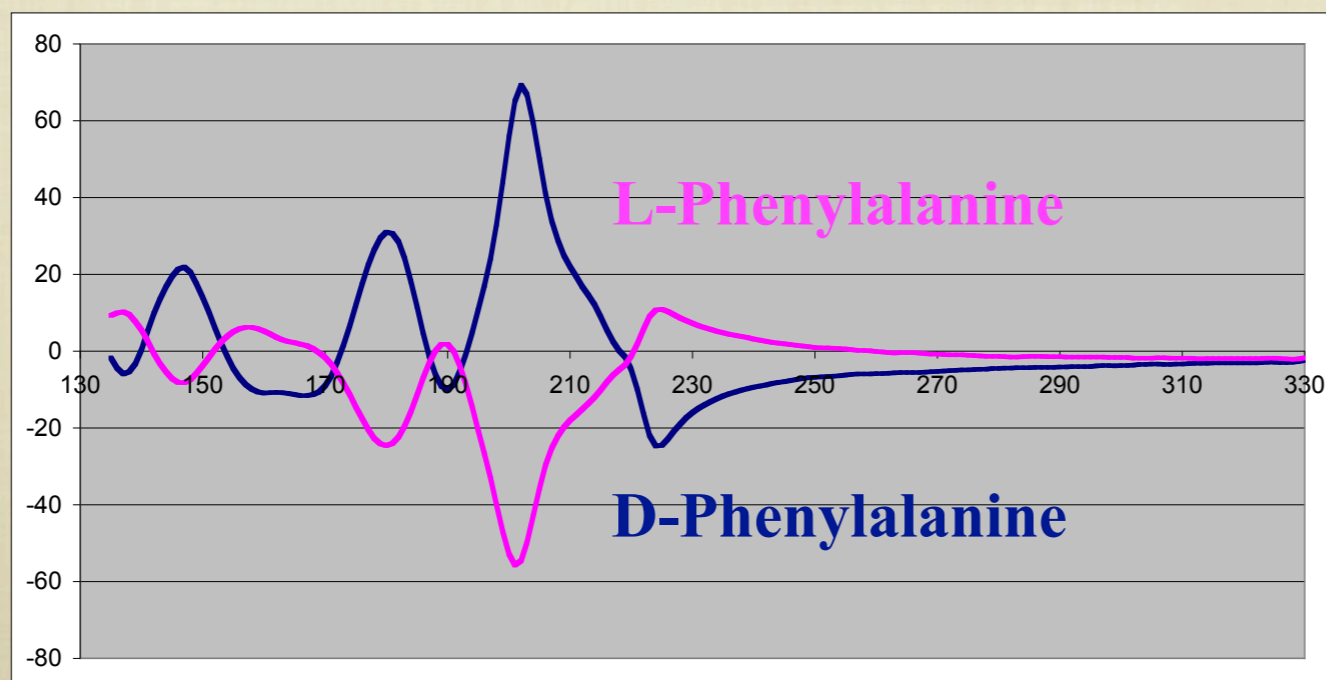
CD of Alanine



$\sigma_{LCPL} - \sigma_{RCPL}$

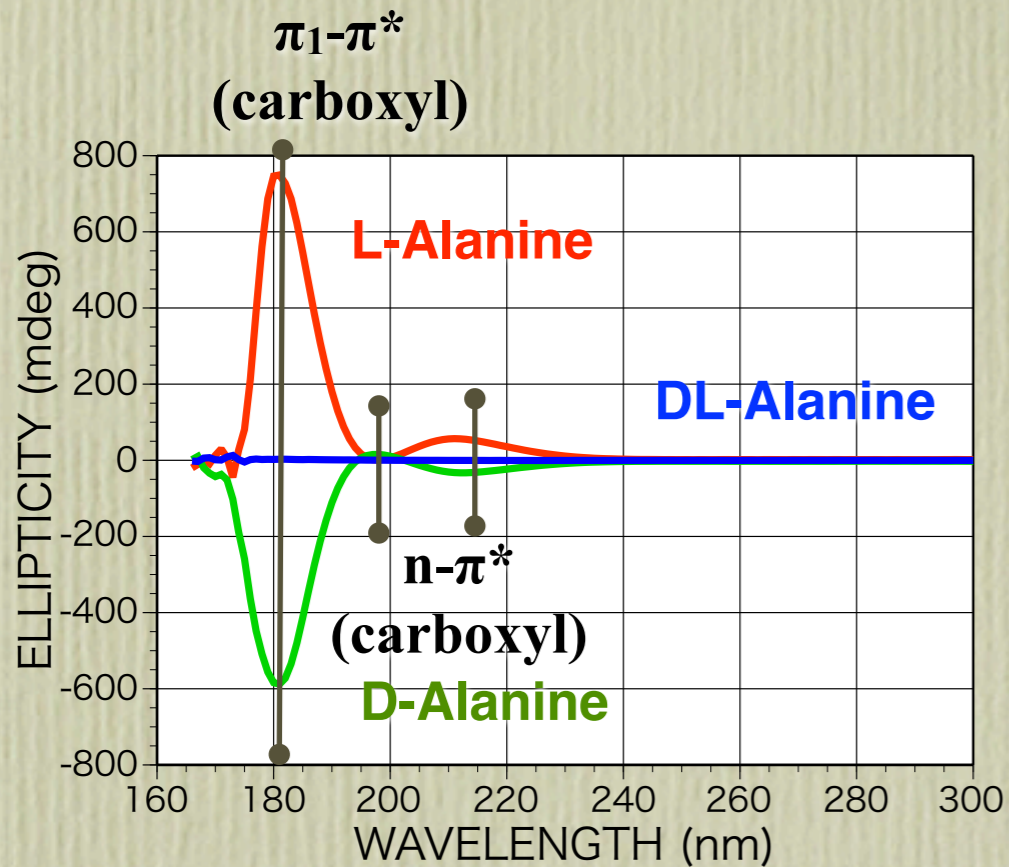


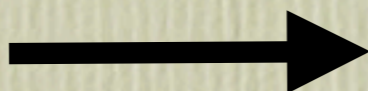
CD of Phenylalanine

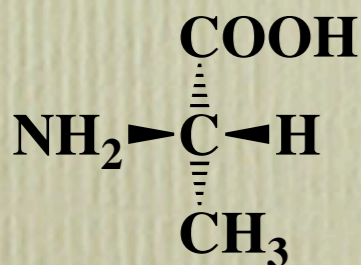


SR-CD beam line:
ASTRID (Denmark)

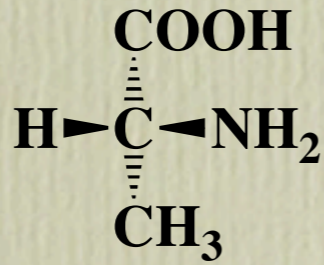
CPL irradiation (DL-Ala film)



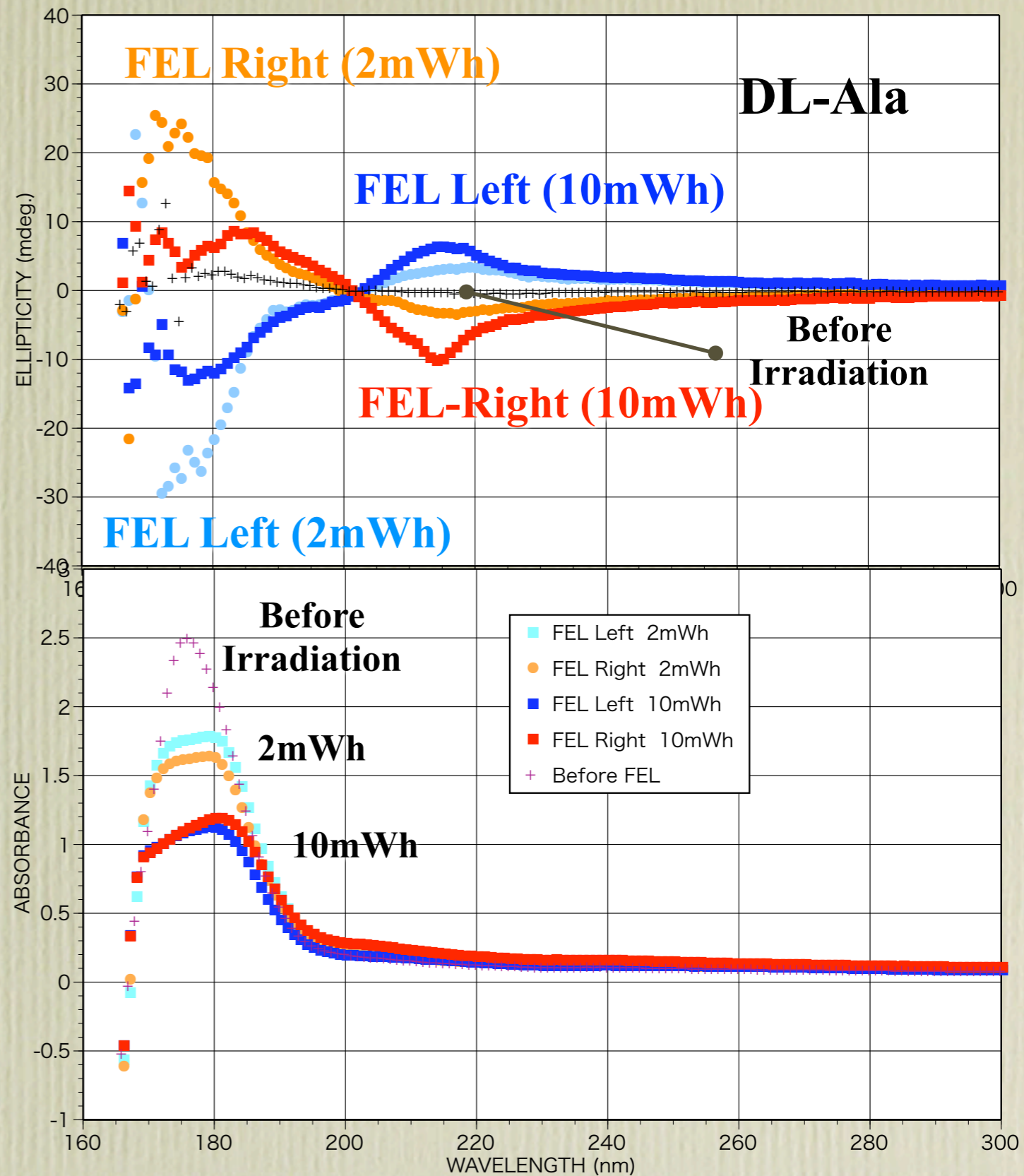

UVSOR-II FEL
 $\lambda = 215 \text{ nm}$



L-alanine



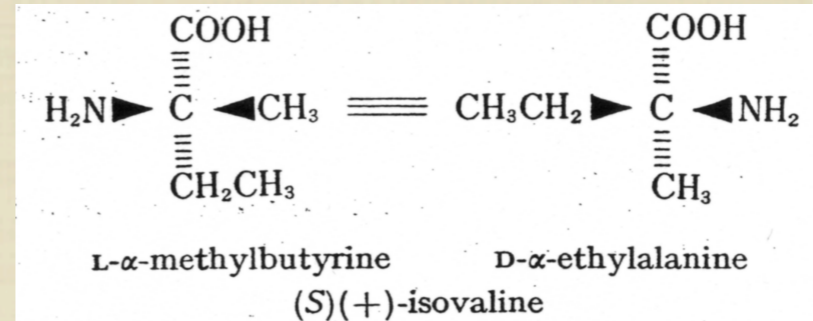
D-alanine



J. Takahashi, et al. Int. J. Mol. Sci. **10**, 3044 (2009).

Enantiomeric Excess in Meteorites

Isovaline (non-proteinic α -methyl amino acid)
 L-enantiomeric Excess in Murchison Meteorite
 S.Pizzarello, J.R.Cronin (2000)



chiral impulse

abiotically synthesized racemic amino acids

enantiomeric excess in amino acids

α -H amino acids
fast racemization

no enantiomeric excess remained

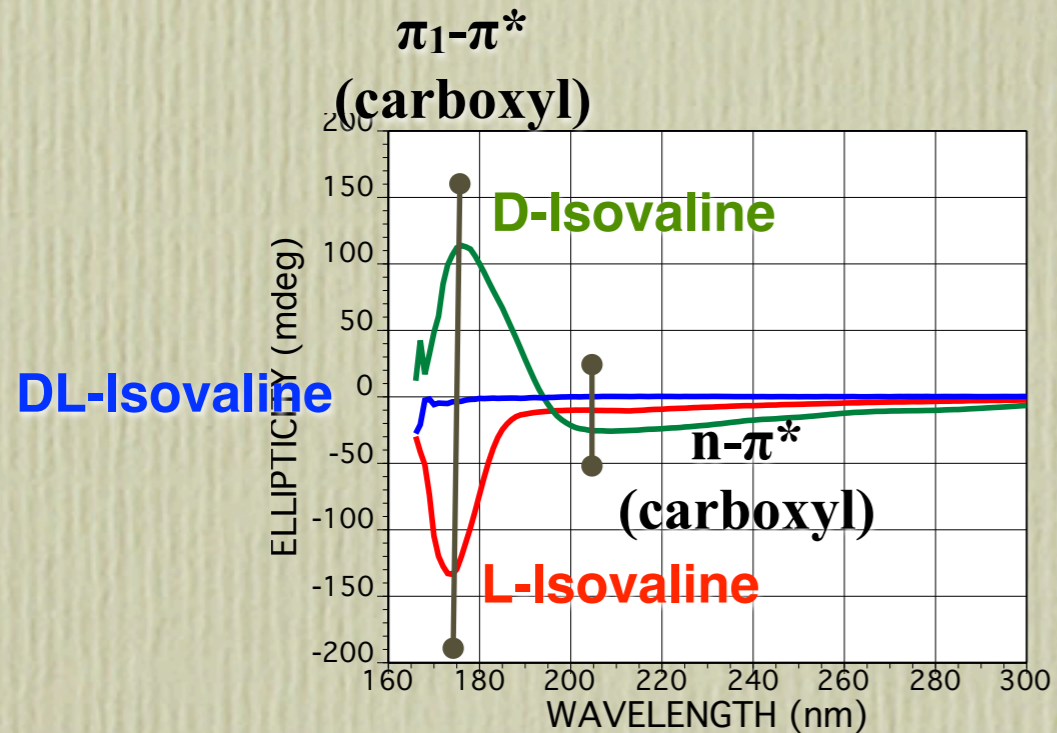
α -methyl amino acids
slow racemization

enantiomeric excess still remained

The observed enantiomeric excess in α -methyl amino acids suggests preferential synthesis or decomposition of enantiomers on interstellar materials were stimulated by **chiral impulse** !

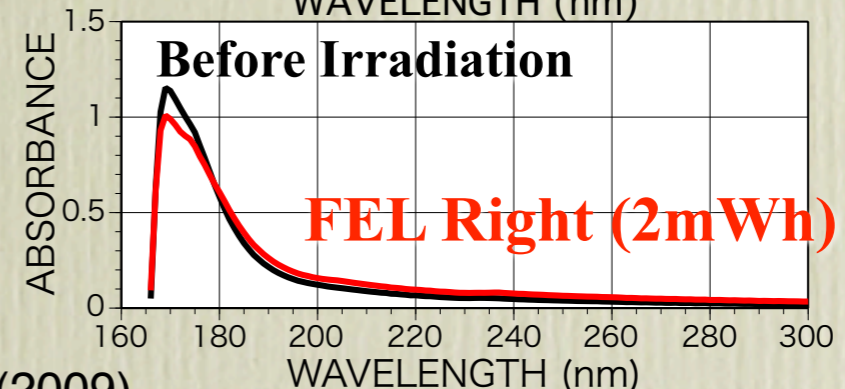
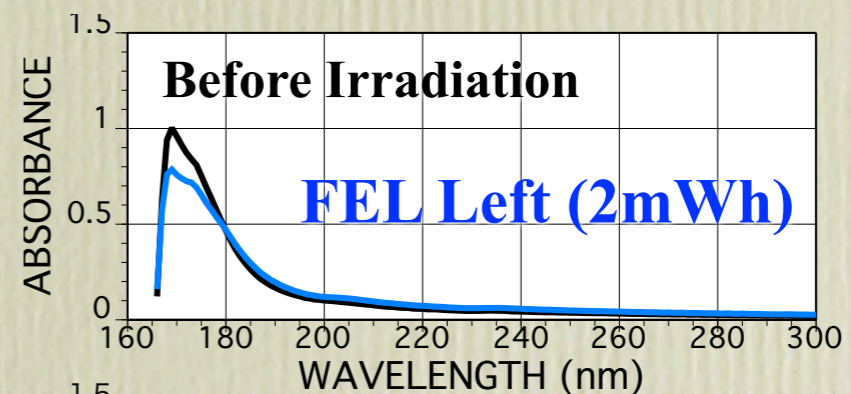
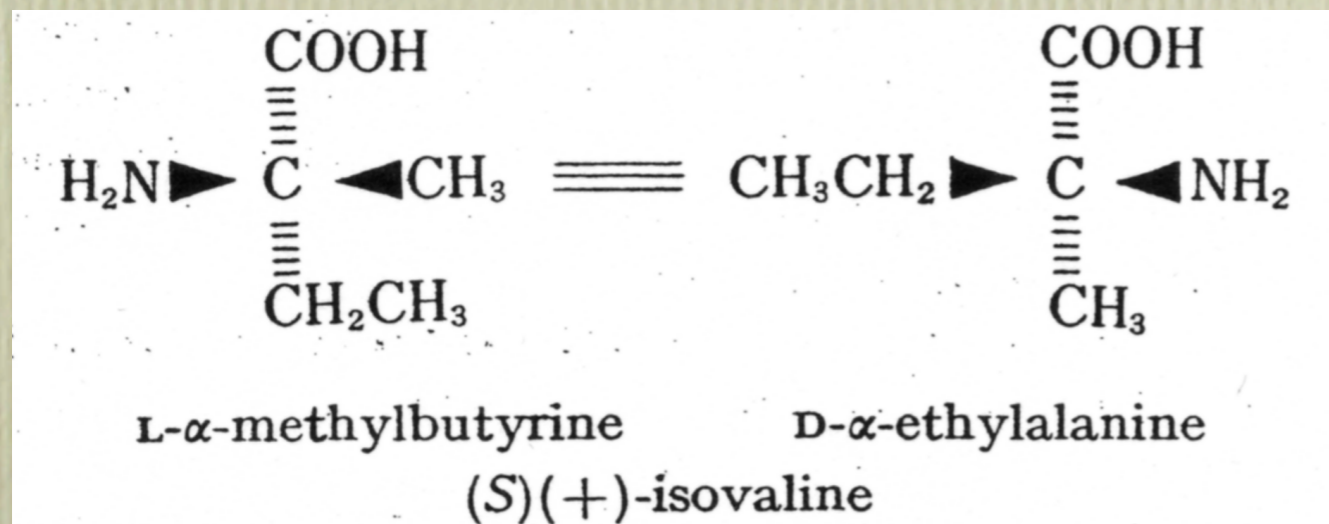
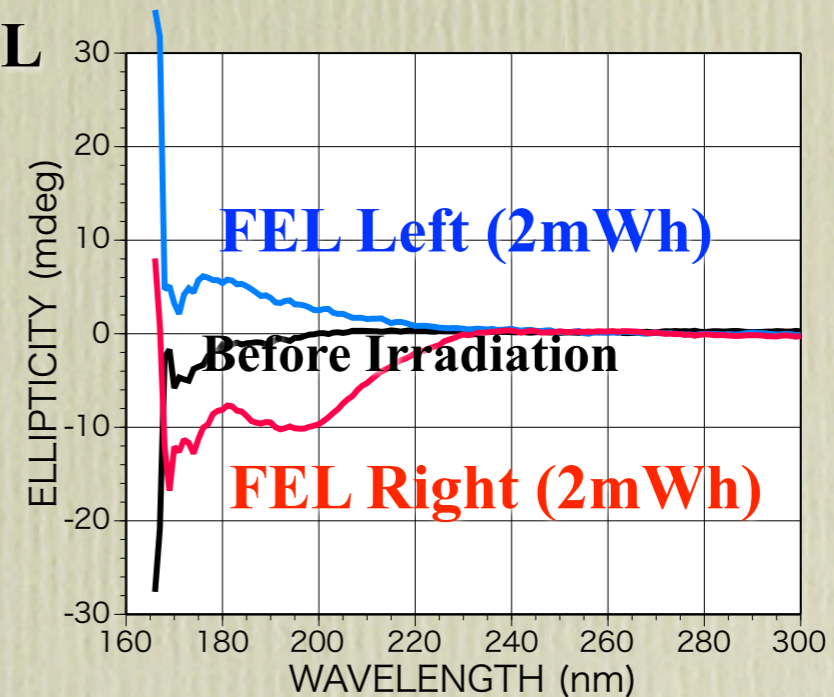
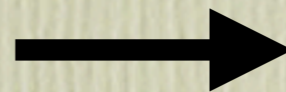
CPL irradiation (DL-Iva film)

Before Irradiation



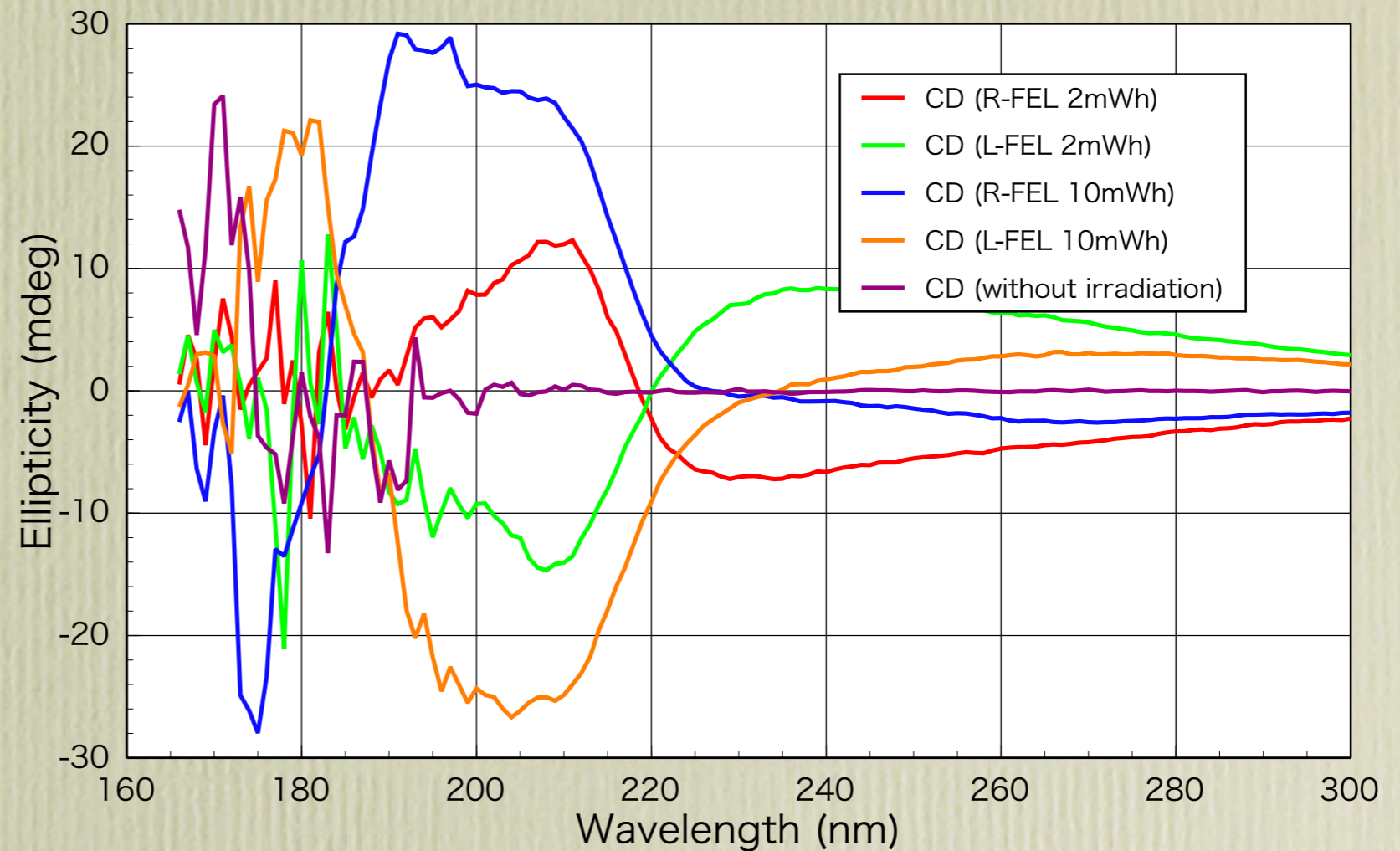
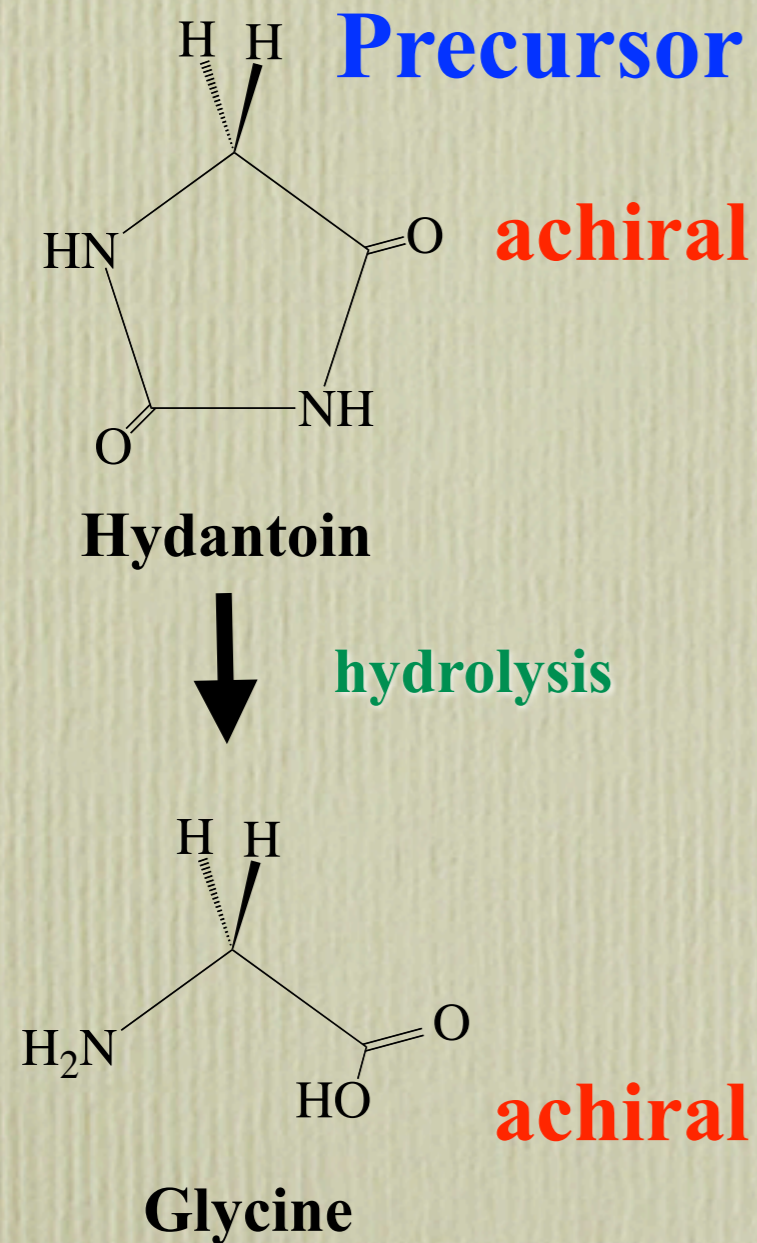
UVSOR-II FEL

$\lambda = 215 \text{ nm}$



J. Takahashi, et al. Int. J. Mol. Sci. **10**, 3044 (2009).

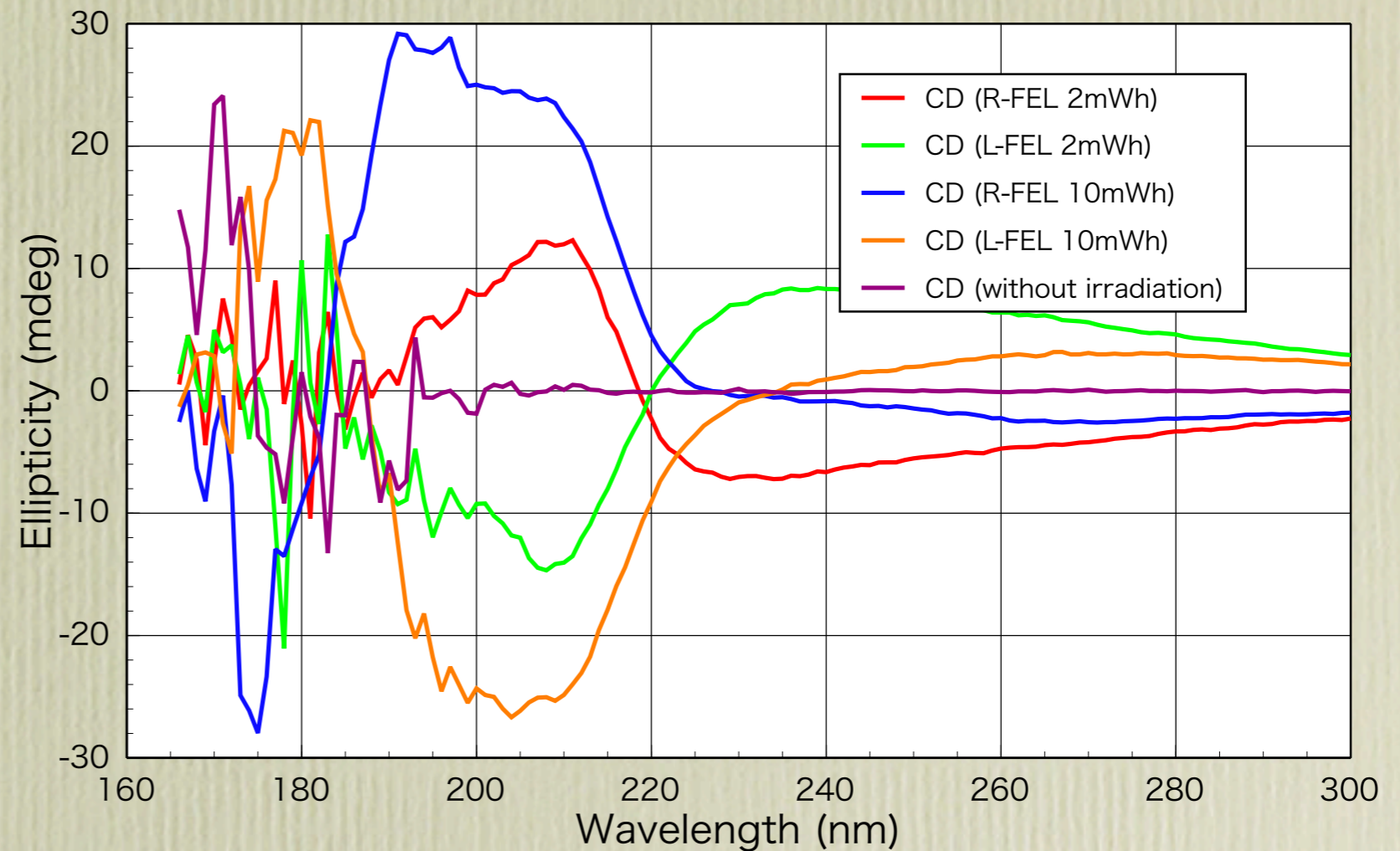
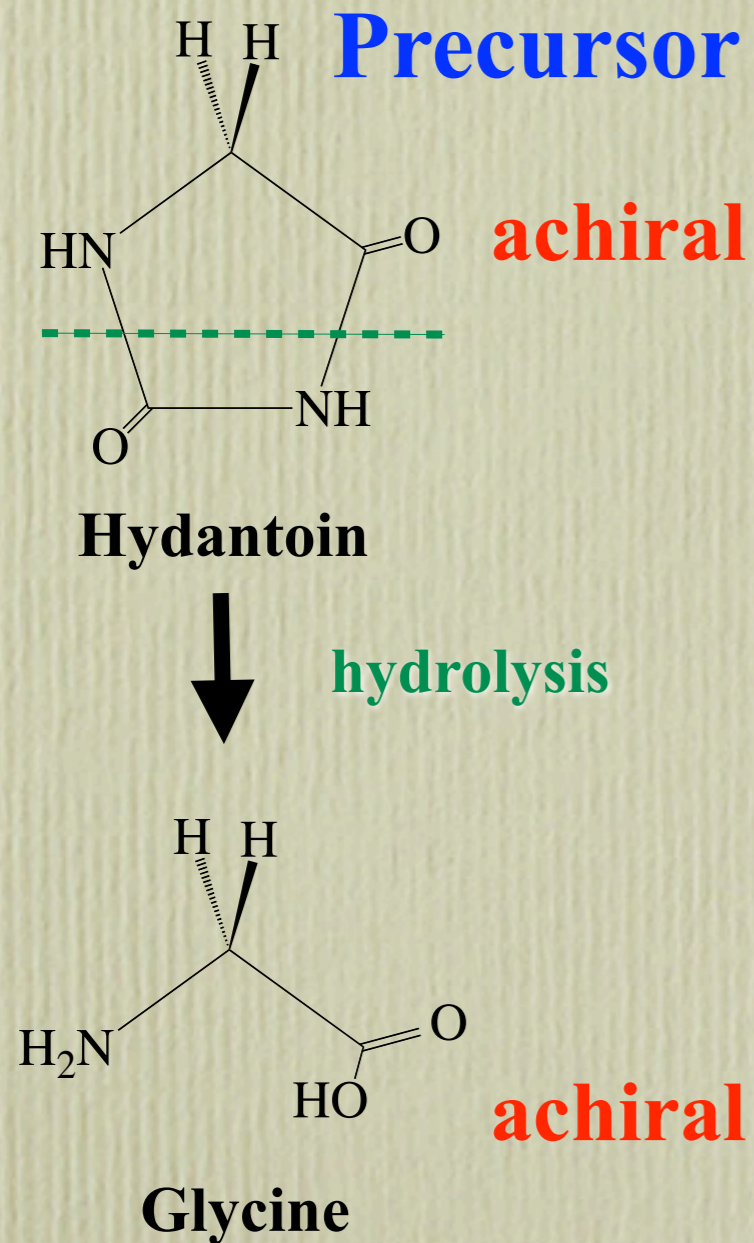
CPL irradiation (5-H-5-H-hydantoin film)



↑ **FEL (215nm)**

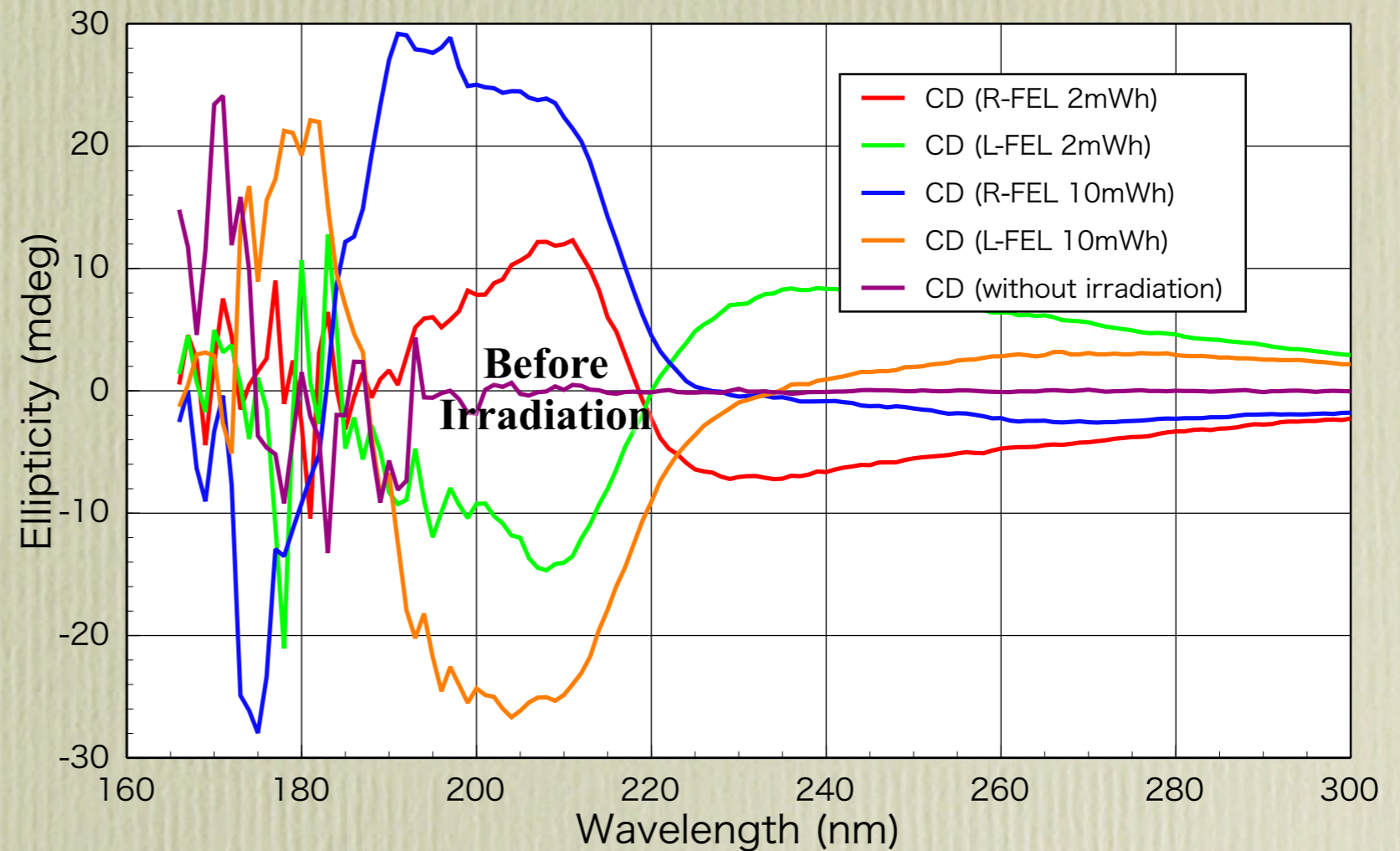
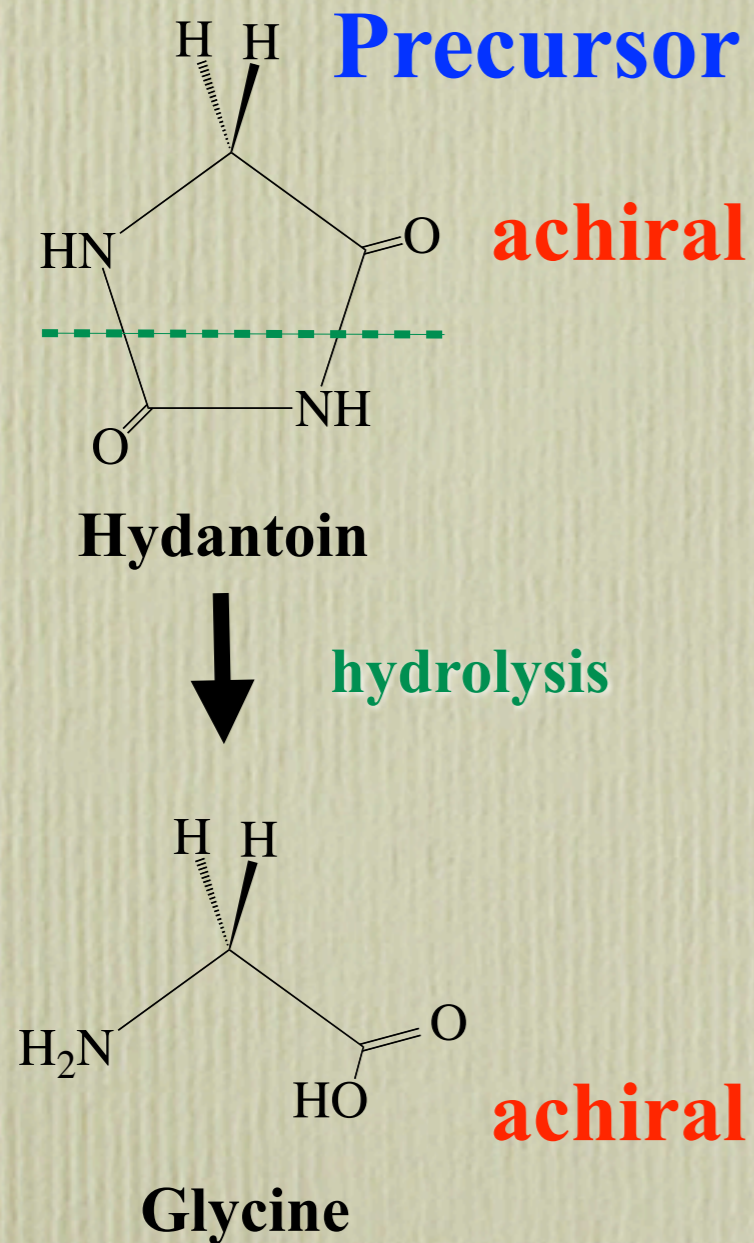
Optical anisotropy has been introduced into **achiral** amino acid precursor molecule by **circularly polarized light** !

CPL irradiation (5-H-5-H-hydantoin film)



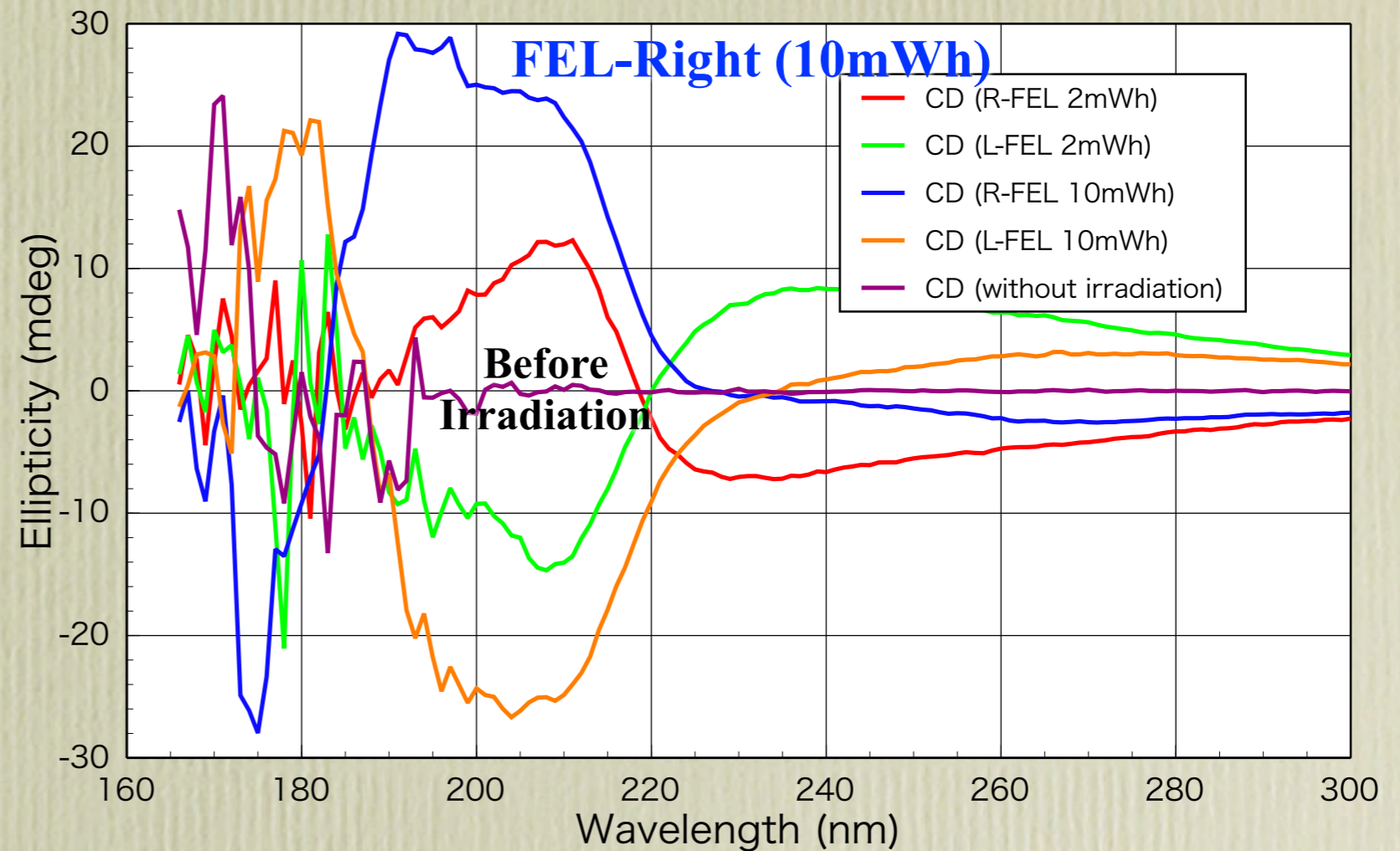
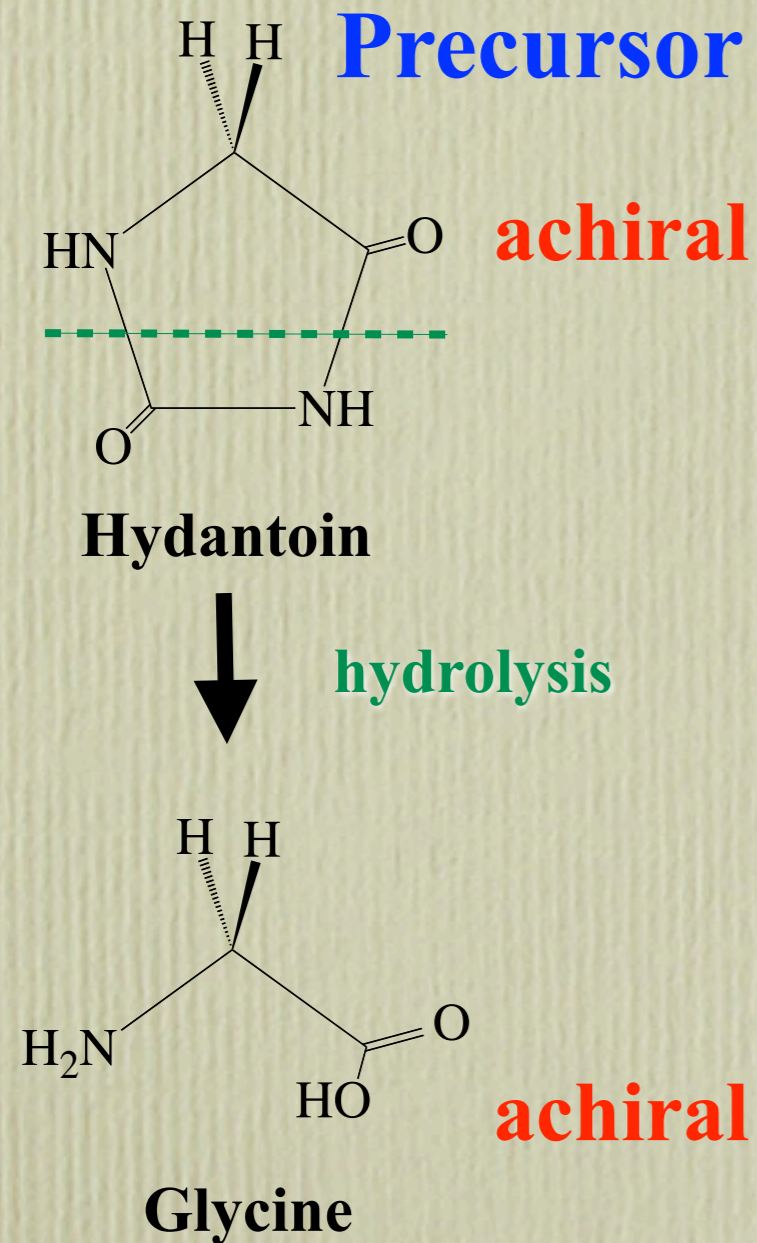
Optical anisotropy has been introduced into **achiral** amino acid precursor molecule by **circularly polarized light** !

CPL irradiation (5-H-5-H-hydantoin film)



Optical anisotropy has been introduced into **achiral** amino acid precursor molecule by **circularly polarized light** !

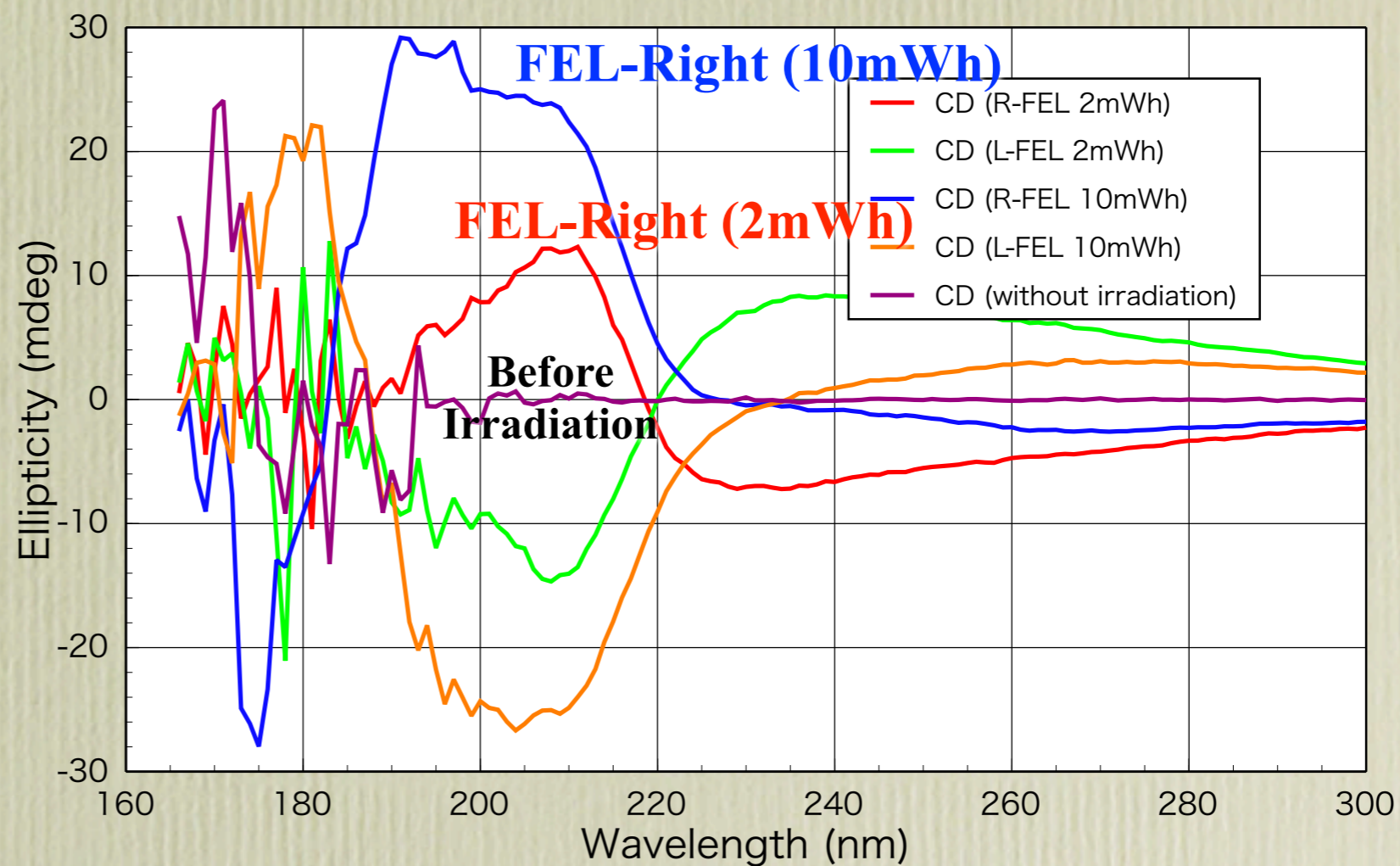
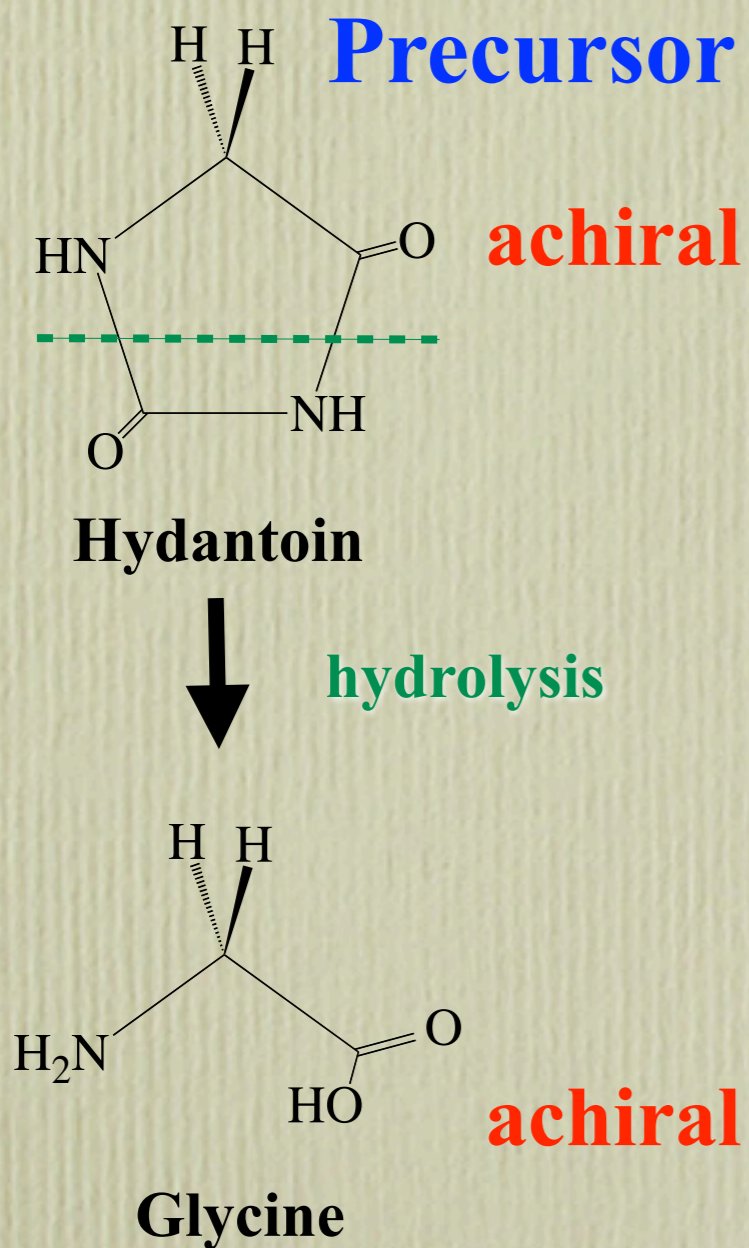
CPL irradiation (5-H-5-H-hydantoin film)



FEL (215nm)

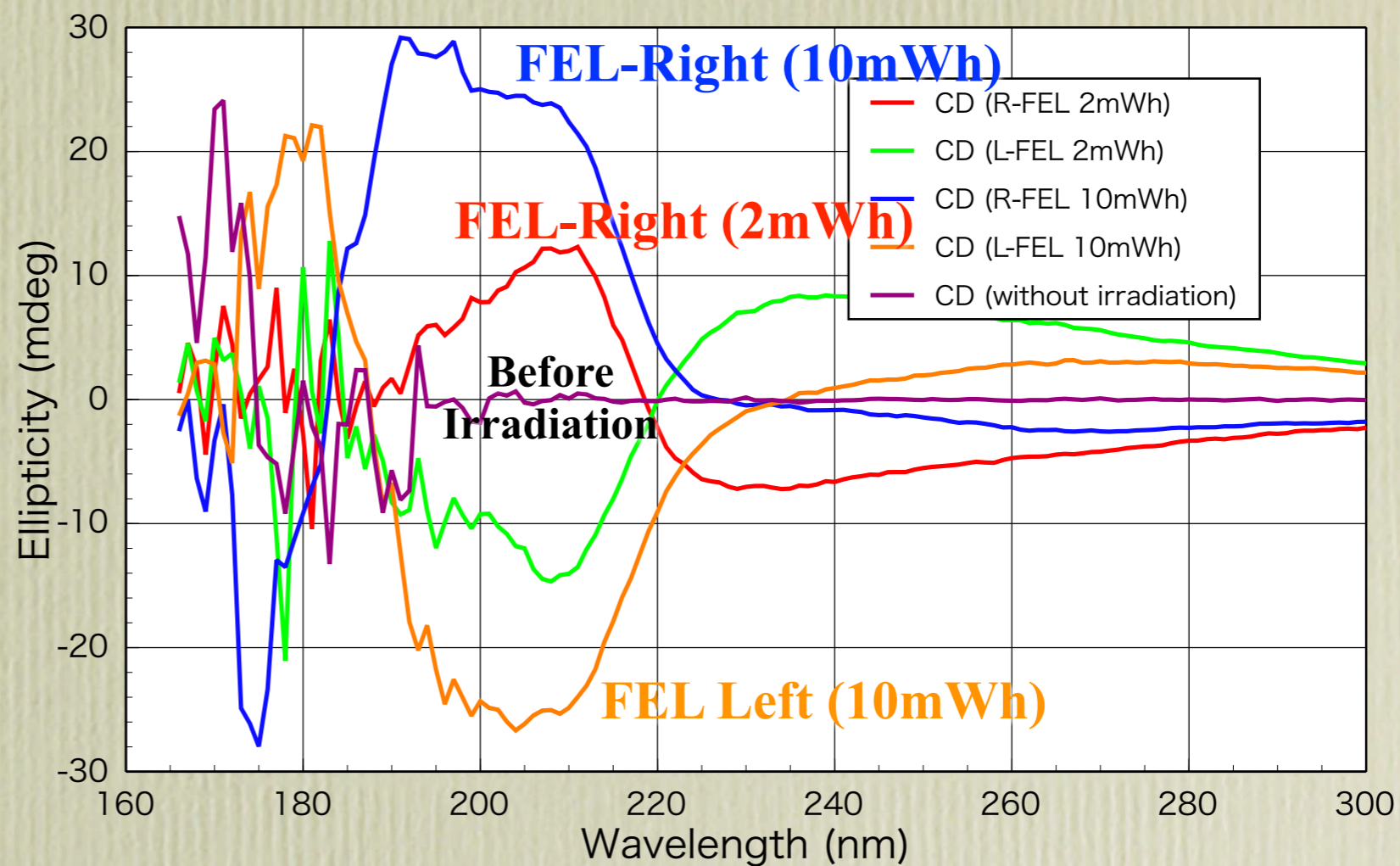
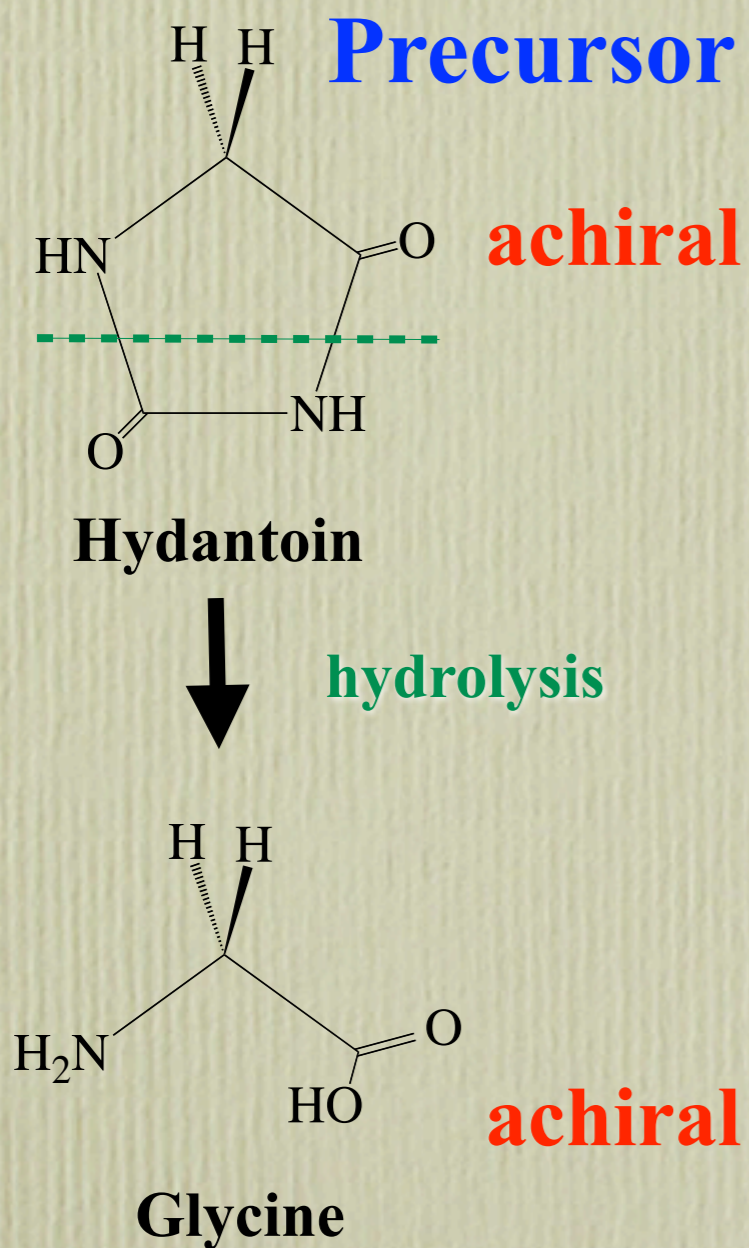
Optical anisotropy has been introduced into **achiral** amino acid precursor molecule by **circularly polarized light** !

CPL irradiation (5-H-5-H-hydantoin film)



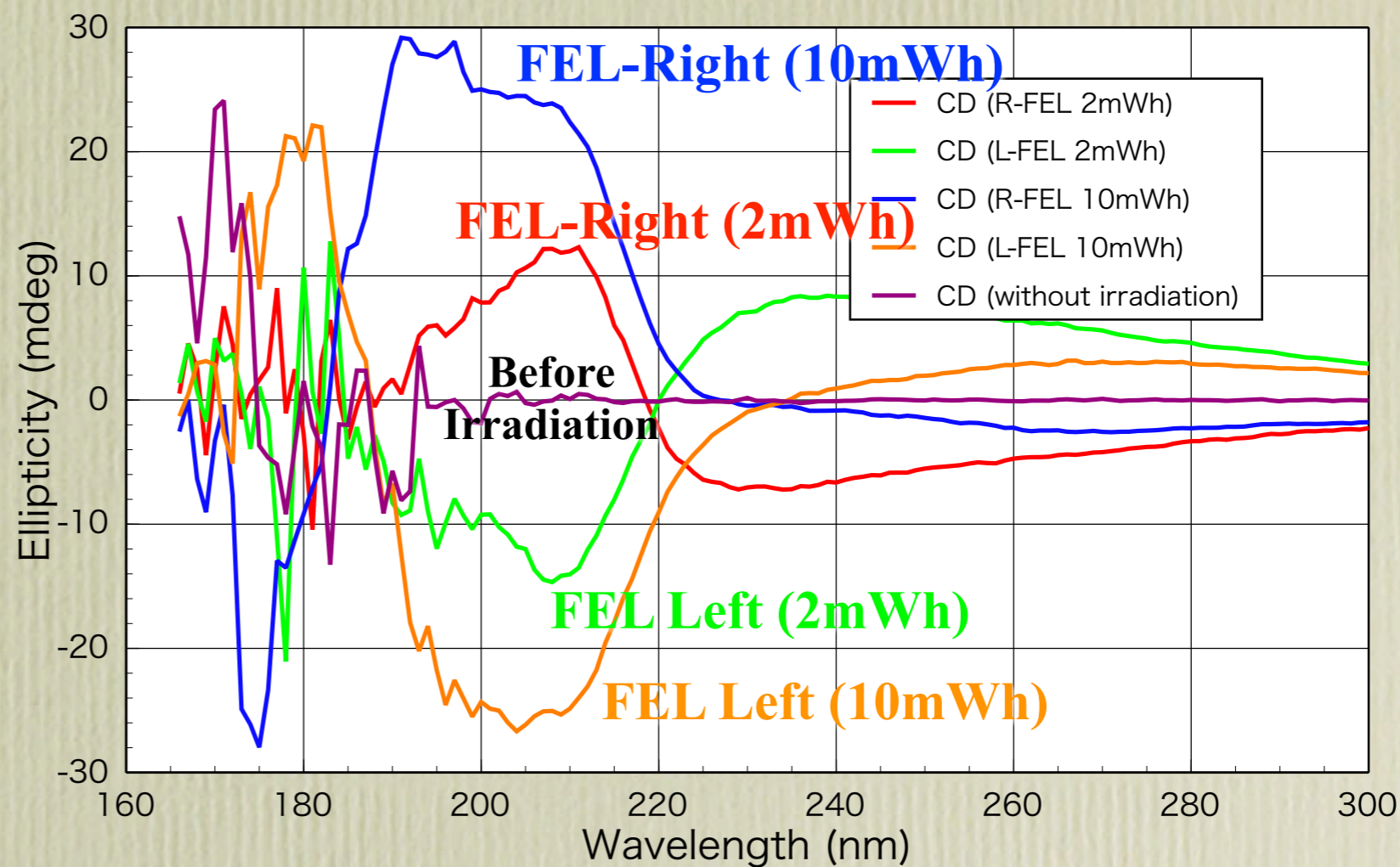
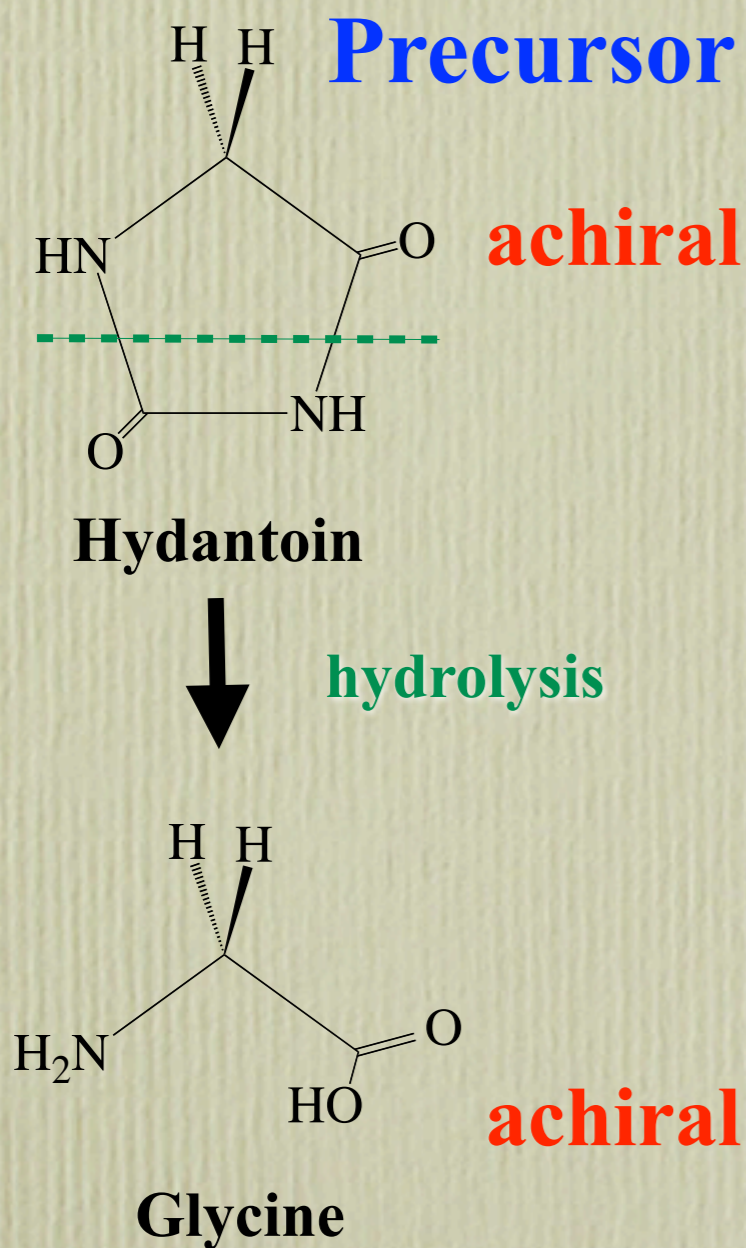
Optical anisotropy has been introduced into **achiral** amino acid precursor molecule by **circularly polarized light** !

CPL irradiation (5-H-5-H-hydantoin film)



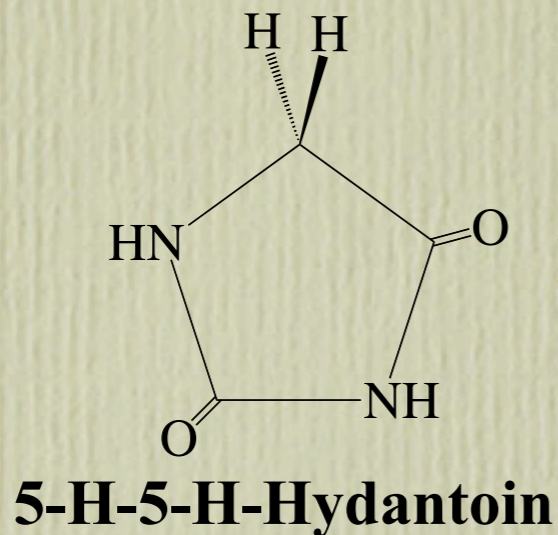
Optical anisotropy has been introduced into **achiral** amino acid precursor molecule by **circularly polarized light** !

CPL irradiation (5-H-5-H-hydantoin film)



Optical anisotropy has been introduced into **achiral** amino acid precursor molecule by **circularly polarized light** !

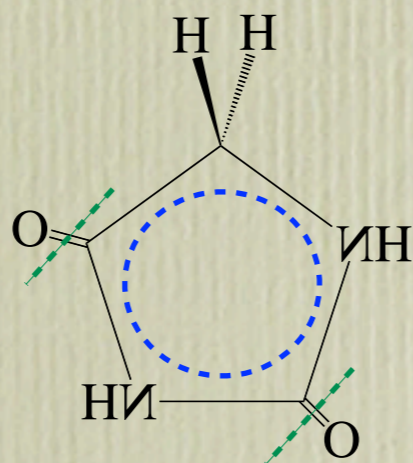
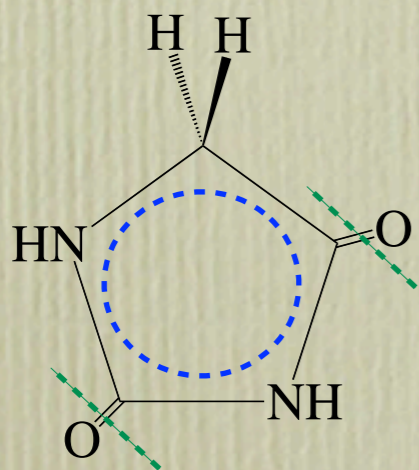
CPL irradiation (5-H-5-H hydantoin film)



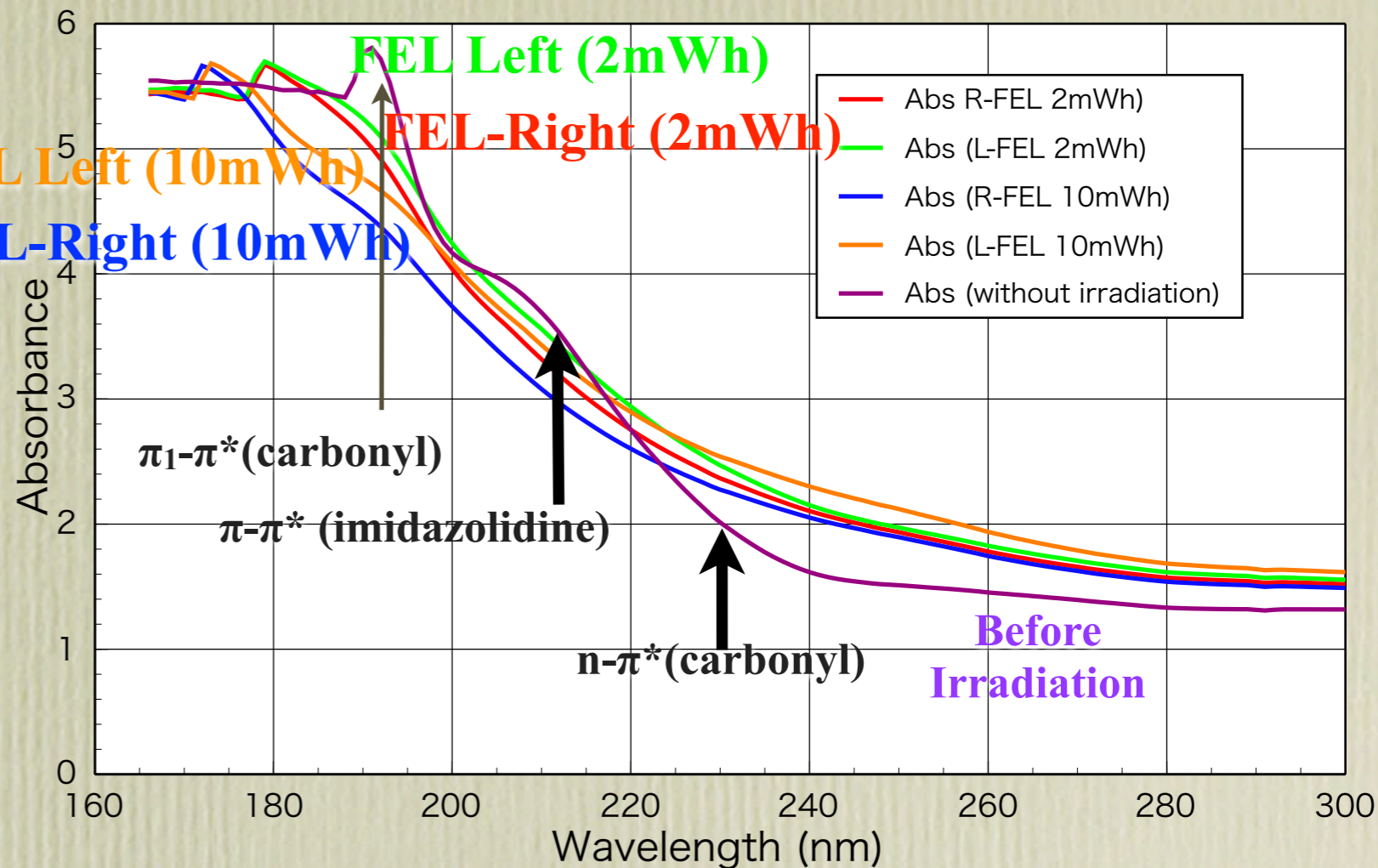
UV-CPL irradiation



interaction with π electrons in
5-membered-ring
bond cleavage by carbonyl $n-\pi^*$
excitation

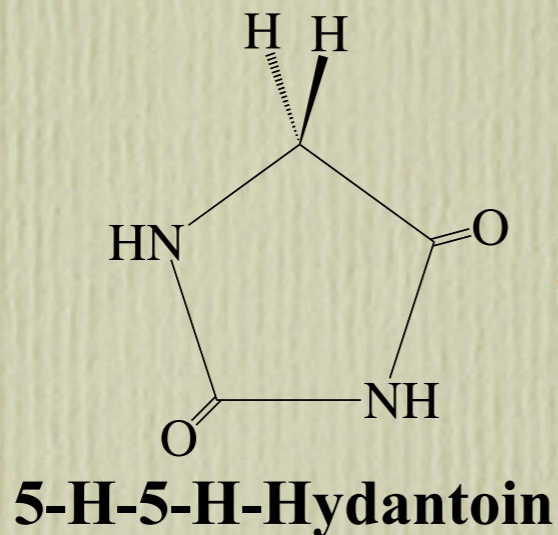


chiral conformation change or chiral structural distortion ?



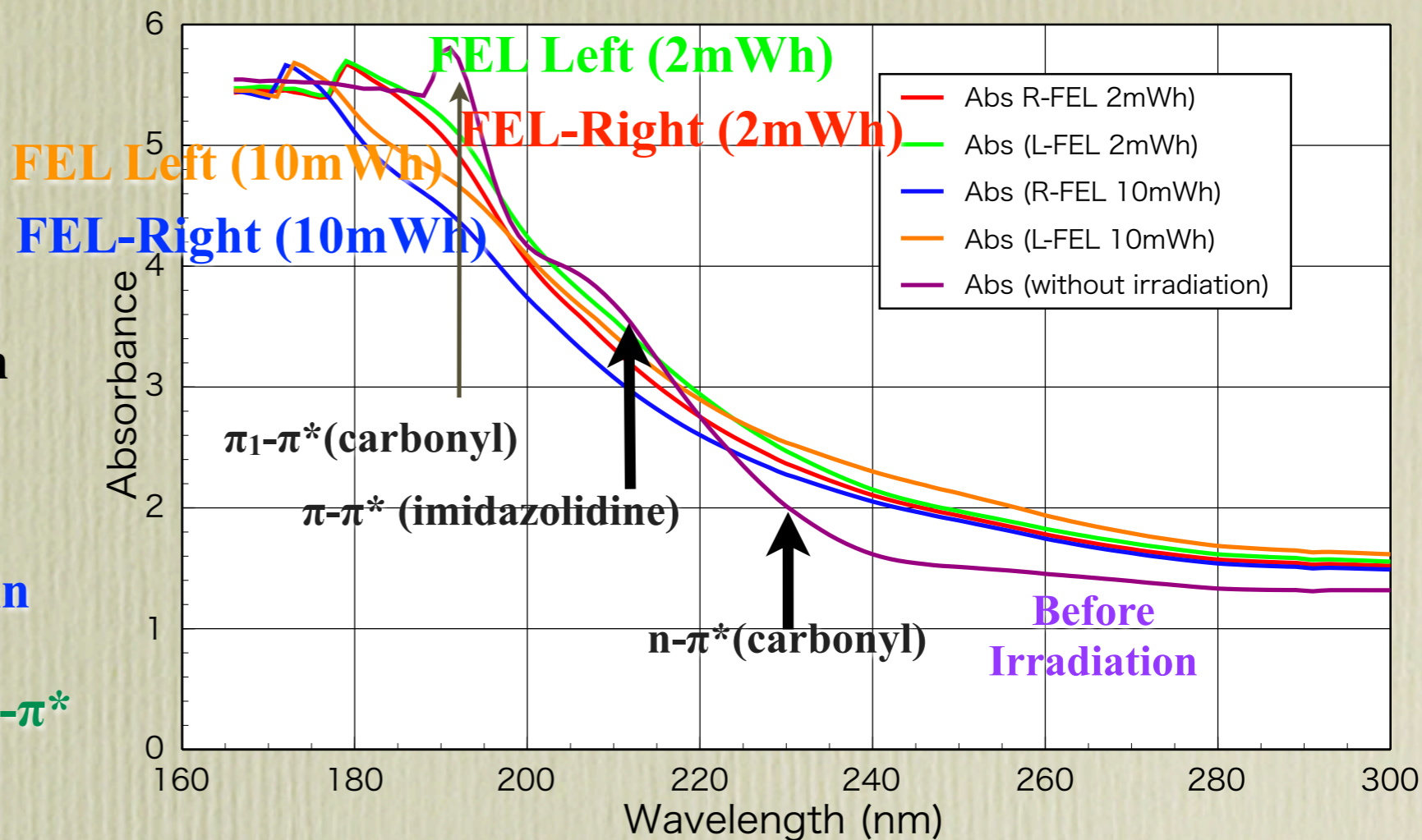
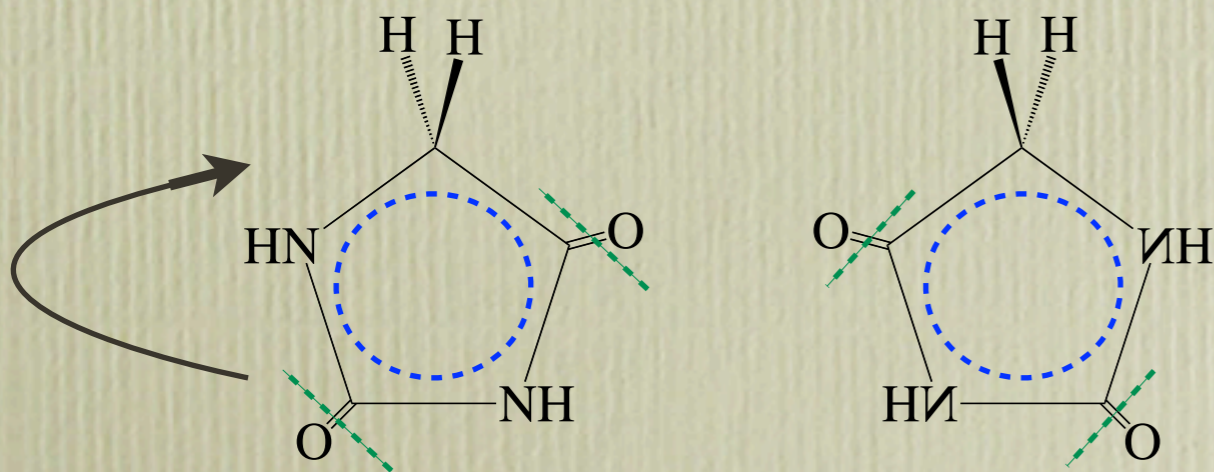
FEL (215nm)

CPL irradiation (5-H-5-H hydantoin film)



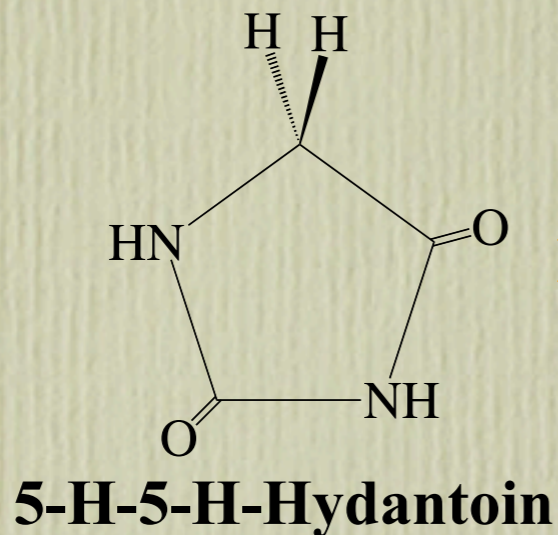
UV-CPL irradiation

interaction with π electrons in 5-membered-ring
bond cleavage by carbonyl $n-\pi^*$ excitation



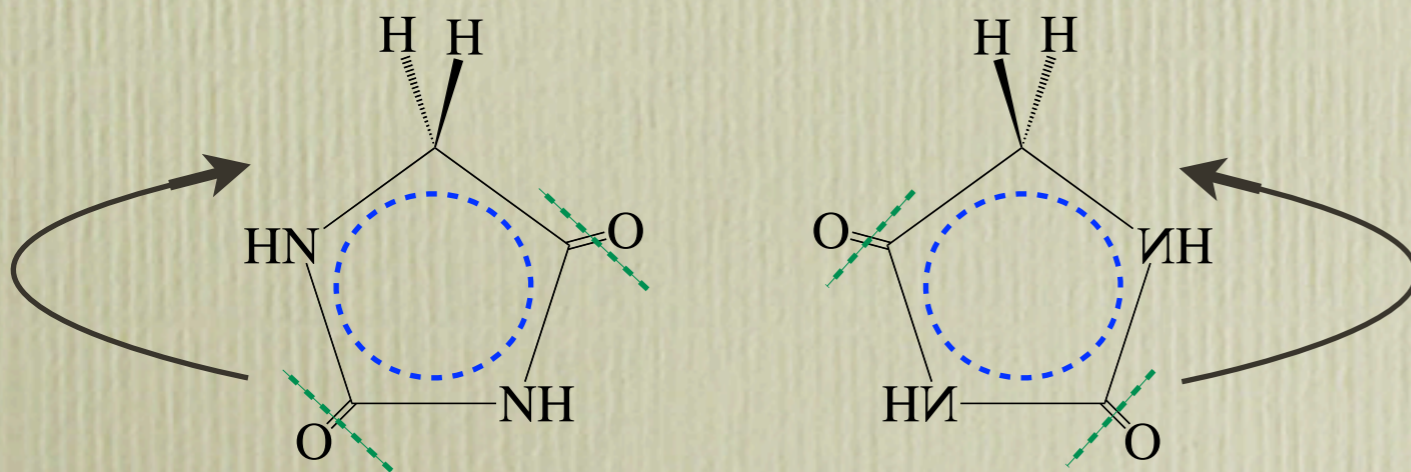
chiral conformation change or chiral structural distortion ?

CPL irradiation (5-H-5-H hydantoin film)

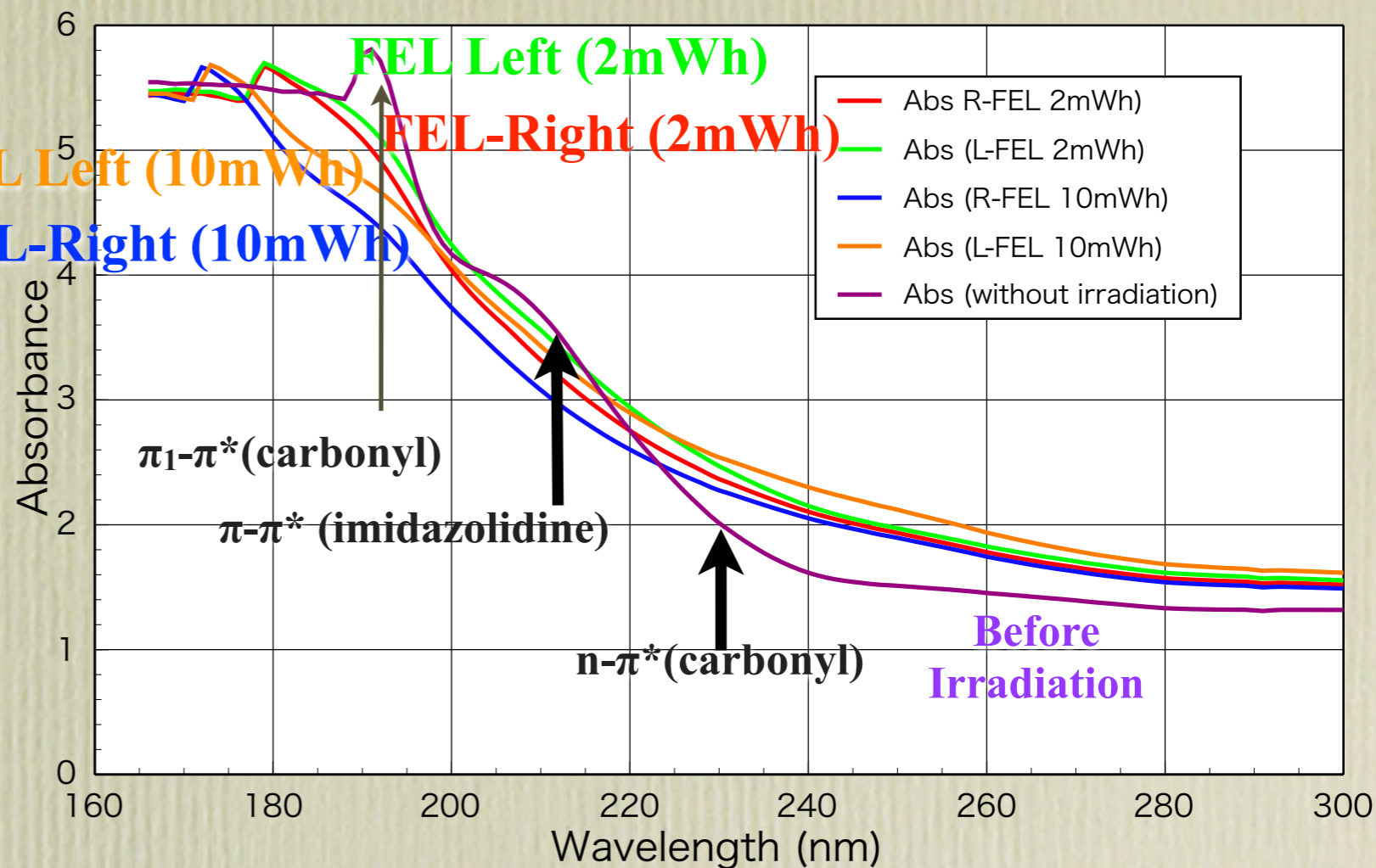


UV-CPL irradiation

interaction with π electrons in
5-membered-ring
bond cleavage by carbonyl $n-\pi^*$
excitation



chiral conformation change or chiral structural distortion ?



CD-related Molecular Orbital of hydantoin

hydantoin (stable)

hydantoin (distorted)

LUMO



LUMO



HOMO

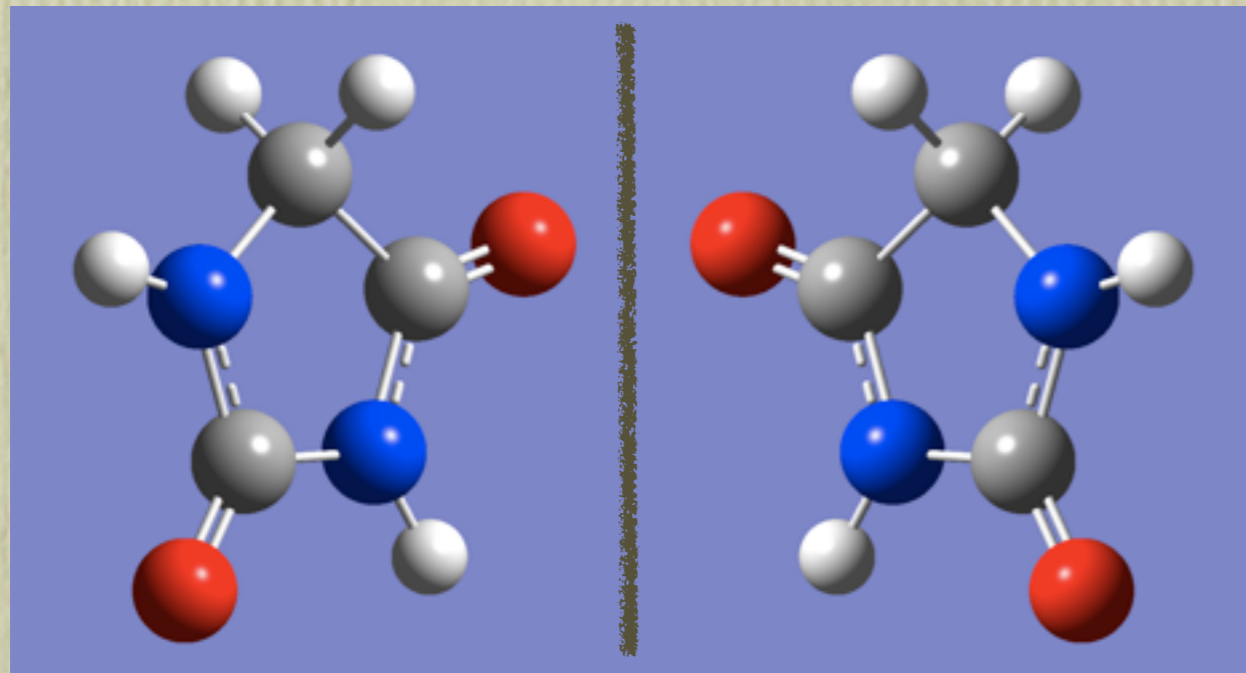


HOMO



Contribution of CO ($n-\pi^*$) which is sited near α -carbon

CPL irradiation distorted the 5-ring structure ?



hydantoin (**stable**)

achiral

CPL irradiation

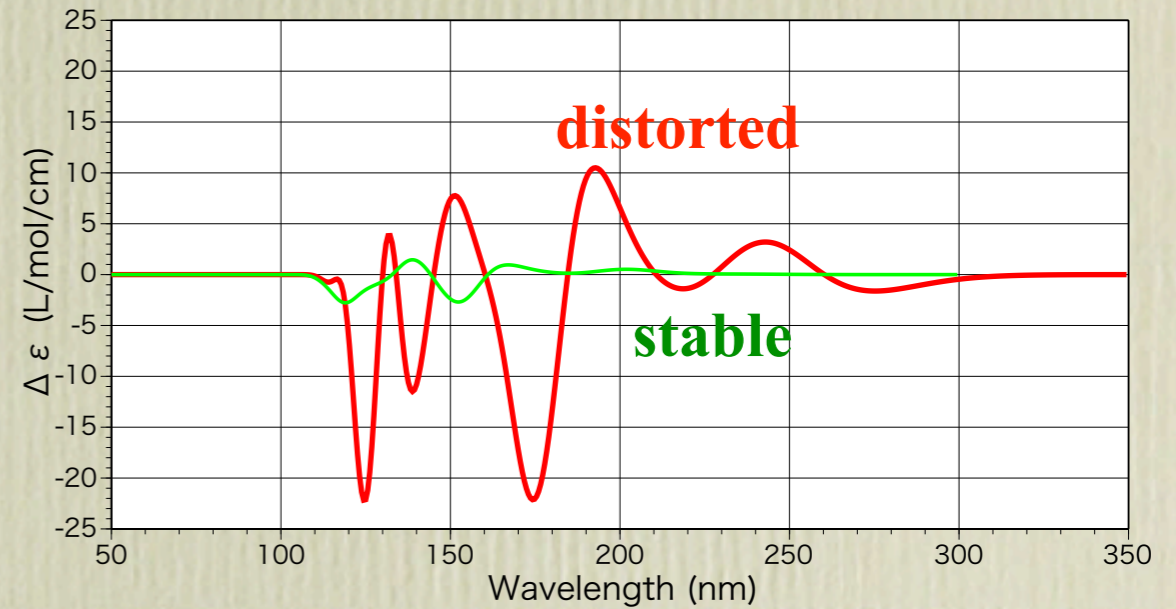


hydantoin (**distorted**)

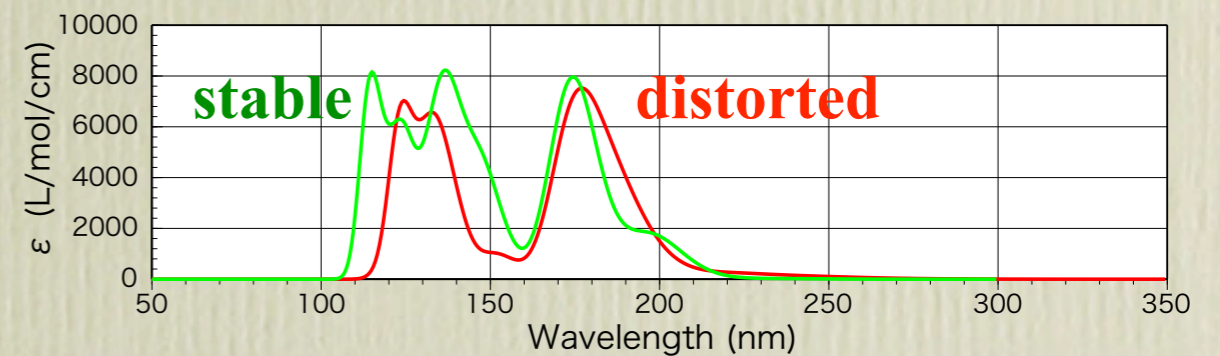
chiral

**ab initio calculation of
stable and distorted
hydantoin**

CD

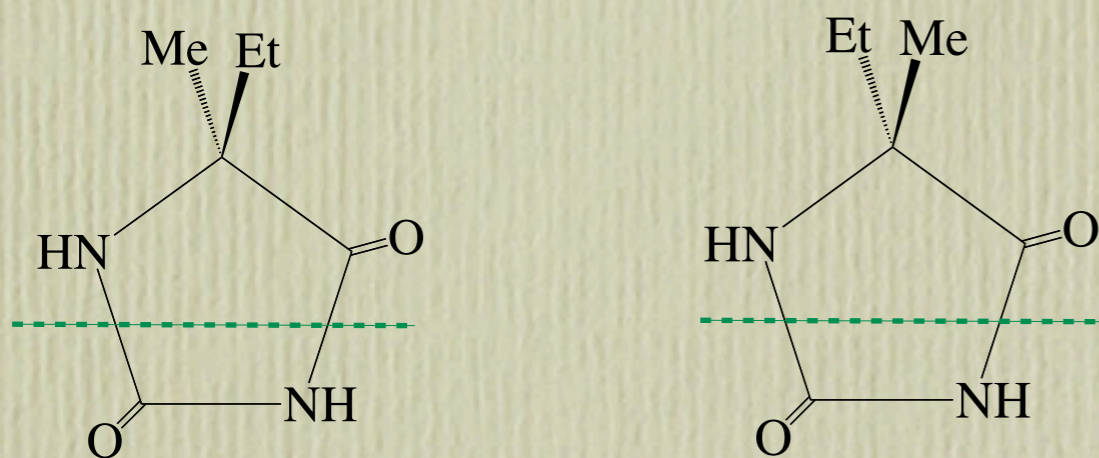


absorption



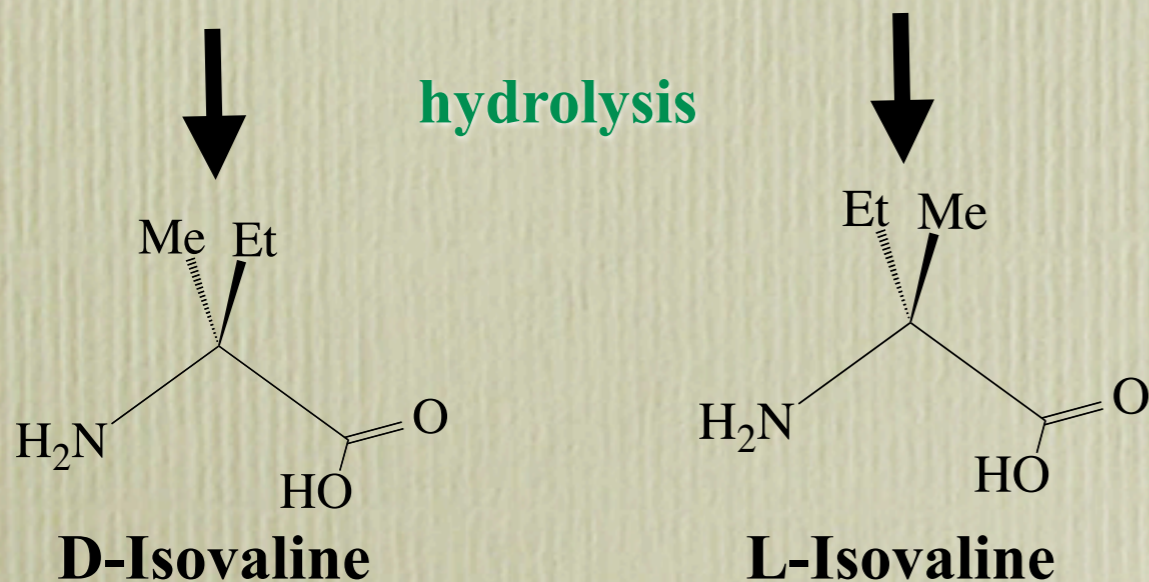
CPL irradiation (5-Et-5-Me-hydantoin solution)

Precursor of Isovaline



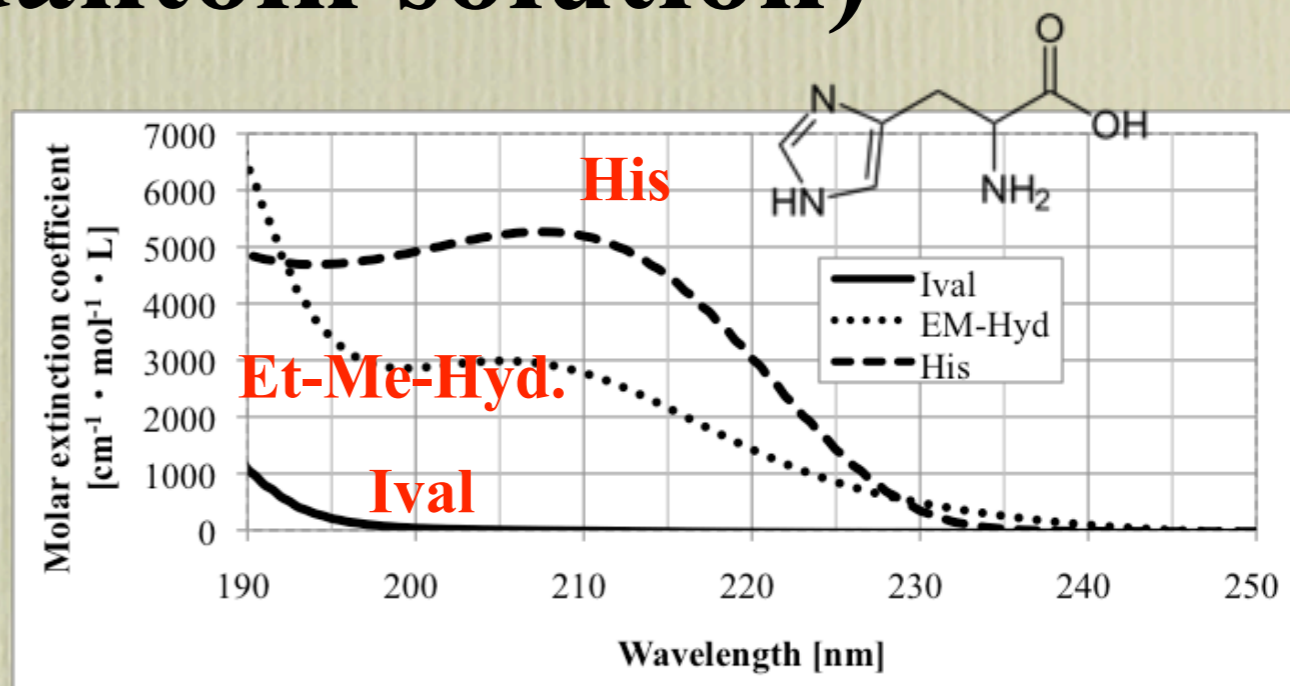
D-5-Et-5-Me-hydantoin **L-5-Et-5-Me-hydantoin**

hydrolysis



D-Isovaline

L-Isovaline



Absorption of free Ival and EM-Hyd

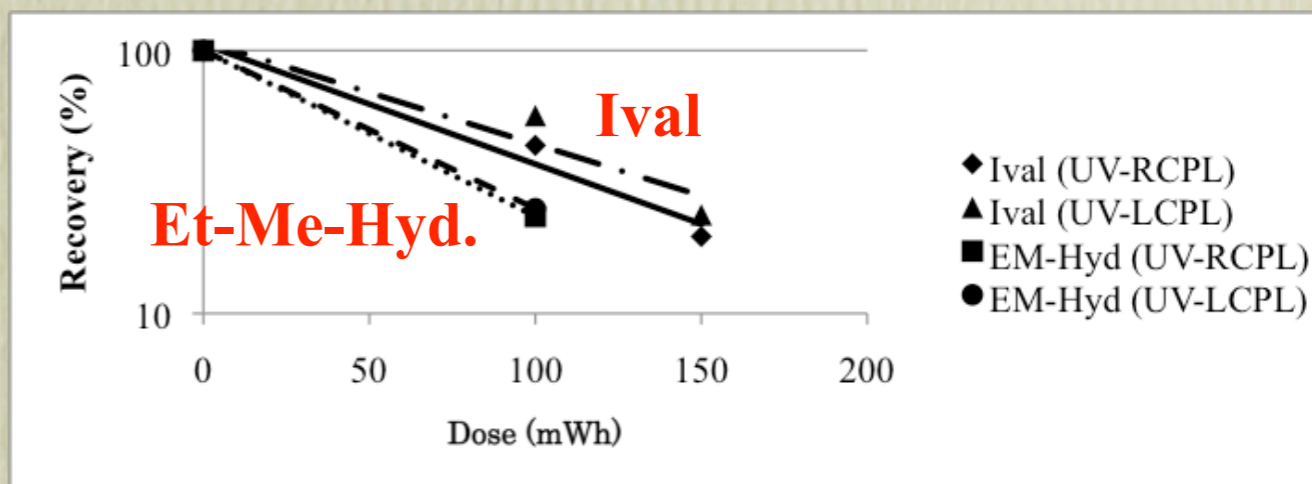
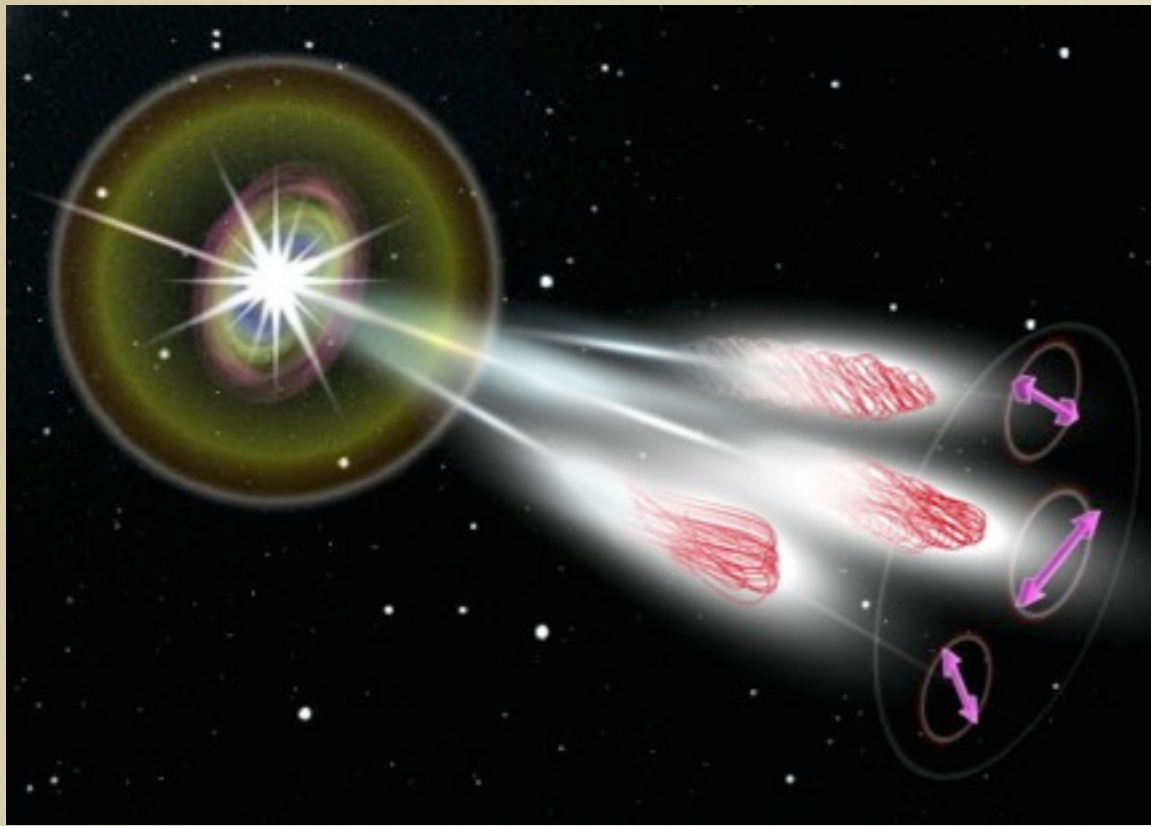


Photo-stability of free Ival and EM-Hyd against UV-CPL irradiation

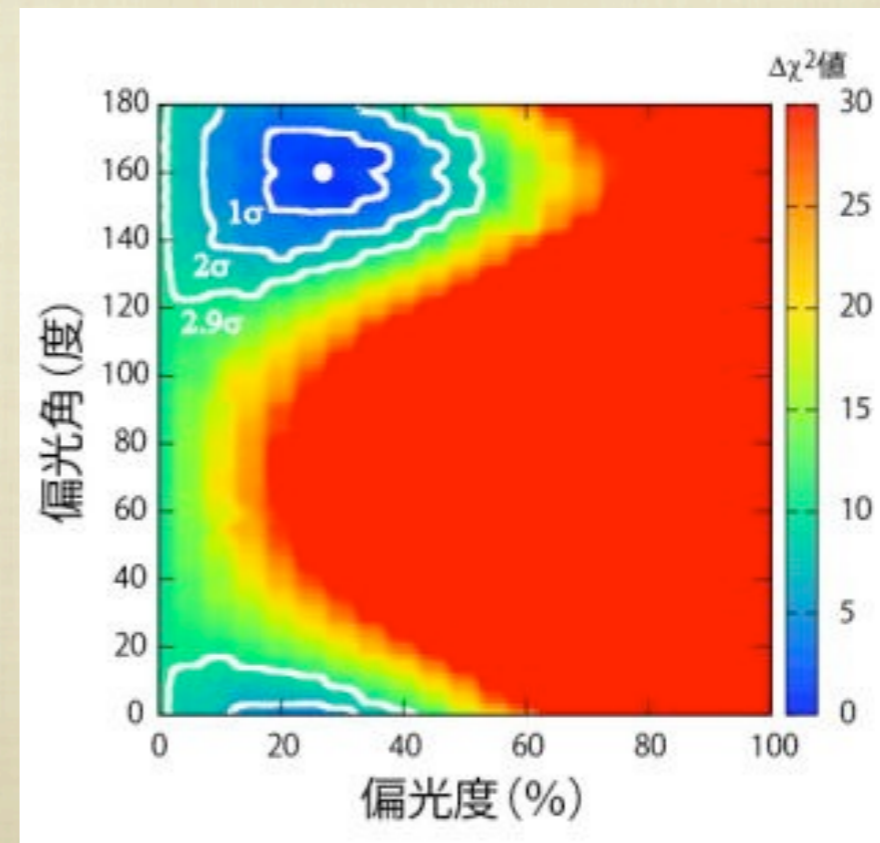
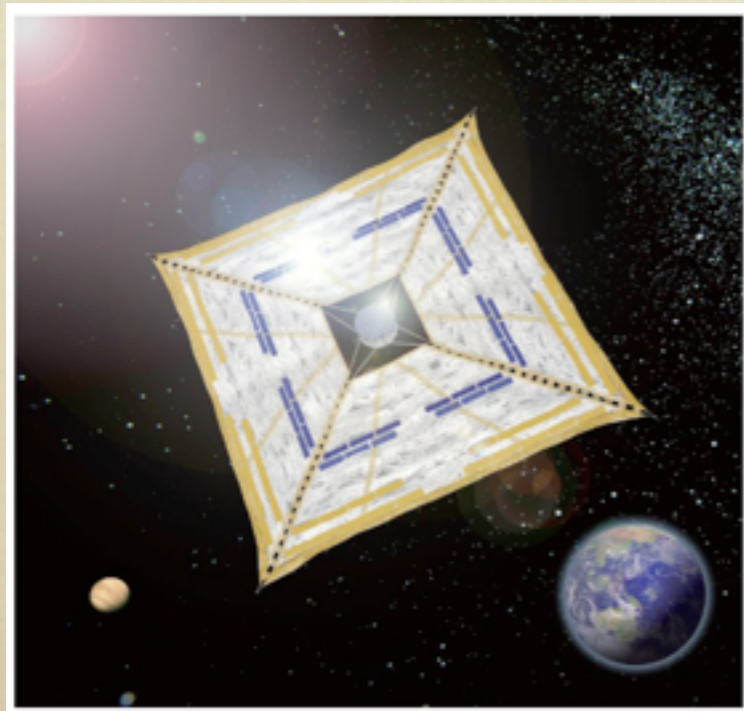
Circularly Polarized Light in Space (2)



Observation of Linear Polarization in Gamma-ray Burst

Detection of Gamma-ray Burst Polarization with GAP on board IKAROS

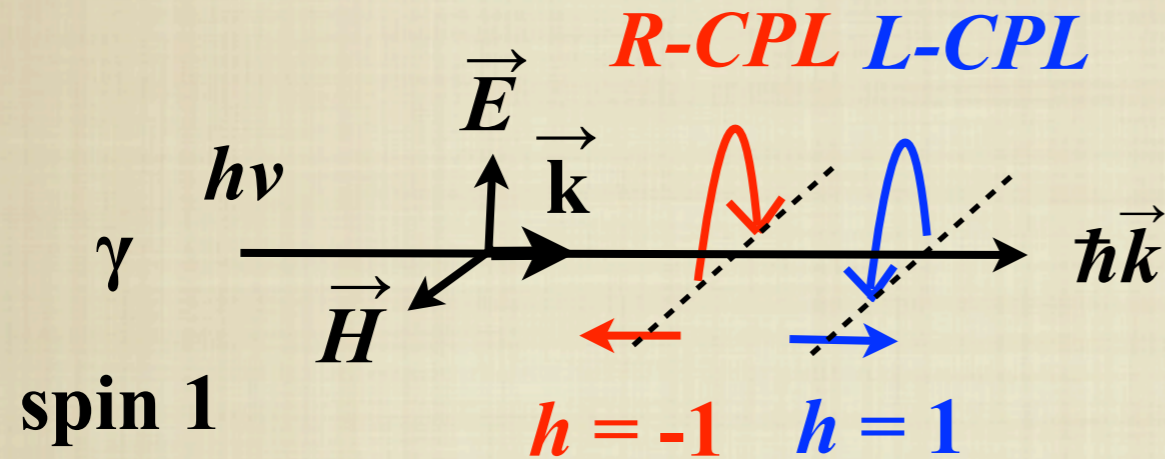
T.Murakami et al. Butsuri Vol.67 p.758 (2012)



Chiral Impulse

- Polarized Quantum Beams -

Circularly polarized light

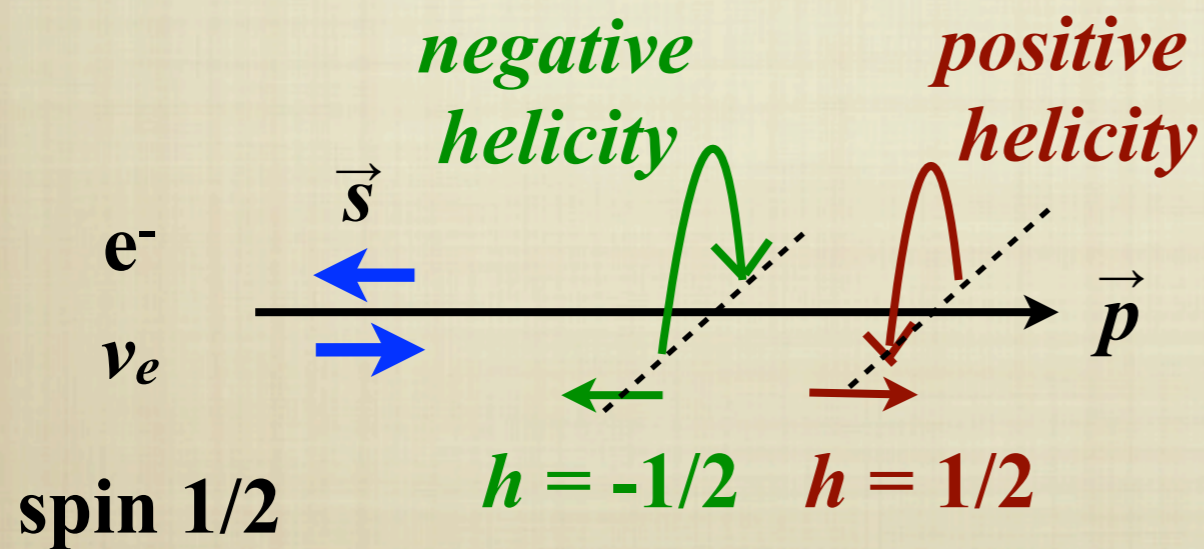


Helicity

$$h = \vec{s} \cdot \vec{p} / |\vec{p}|$$

right-handed (negative helicity)
left-handed (positive helicity)

Spin polarized radiation **in nature**

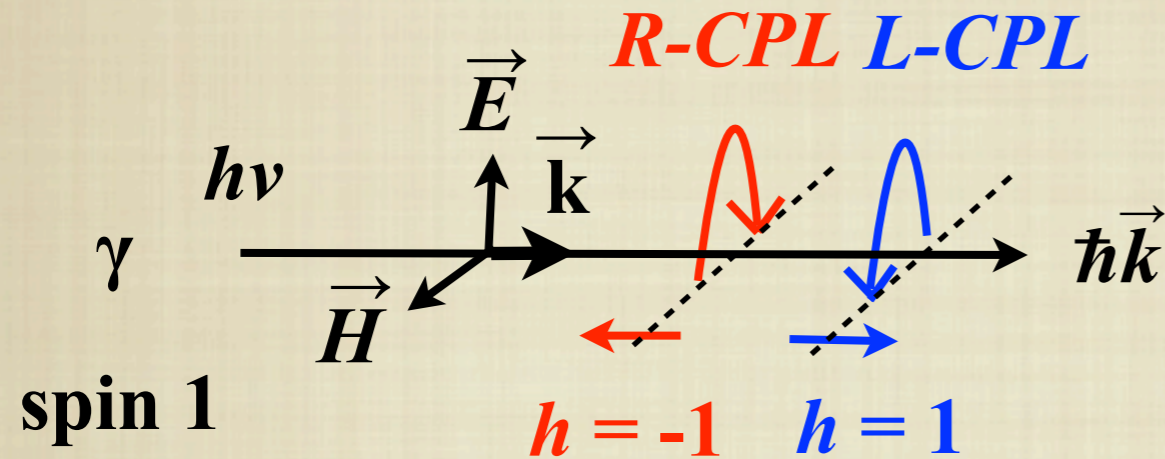


positive helicity (right-handed)
negative helicity (left-handed)

Chiral Impulse

- Polarized Quantum Beams -

Circularly polarized light

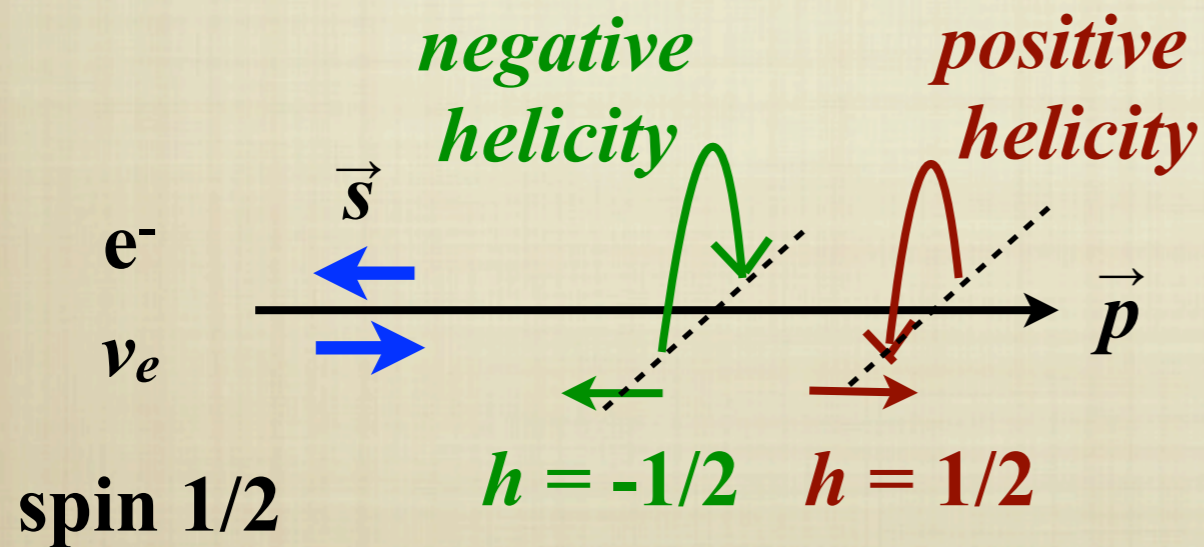


Helicity

$$h = \vec{s} \cdot \vec{p} / |\mathbf{p}|$$

right-handed (negative helicity)
left-handed (positive helicity)

Spin polarized radiation **in nature**



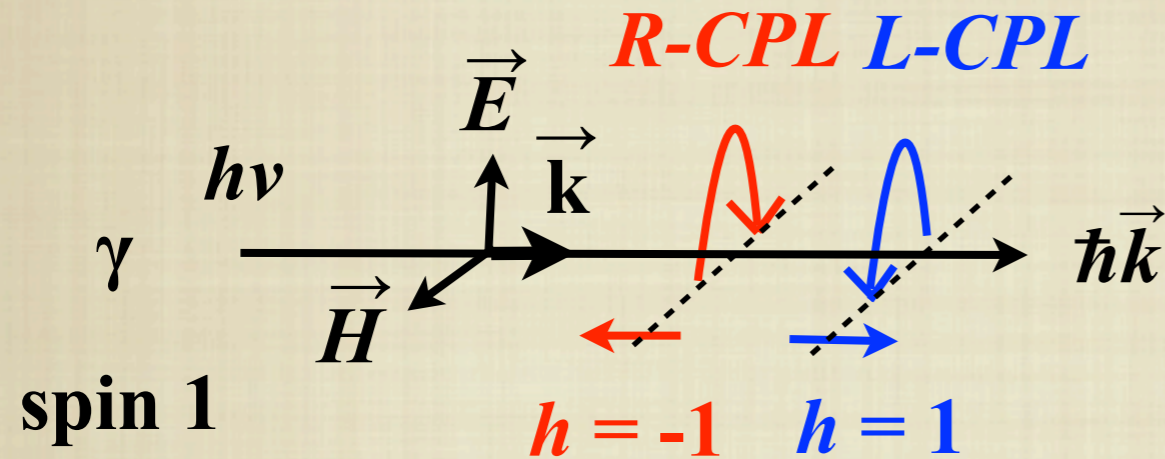
e^- ; β^- -ray electron
 ν_e ; electron neutrino
 (only **negative** helicity,
left-handed)

positive helicity (right-handed)
negative helicity (left-handed)

Chiral Impulse

- Polarized Quantum Beams -

Circularly polarized light

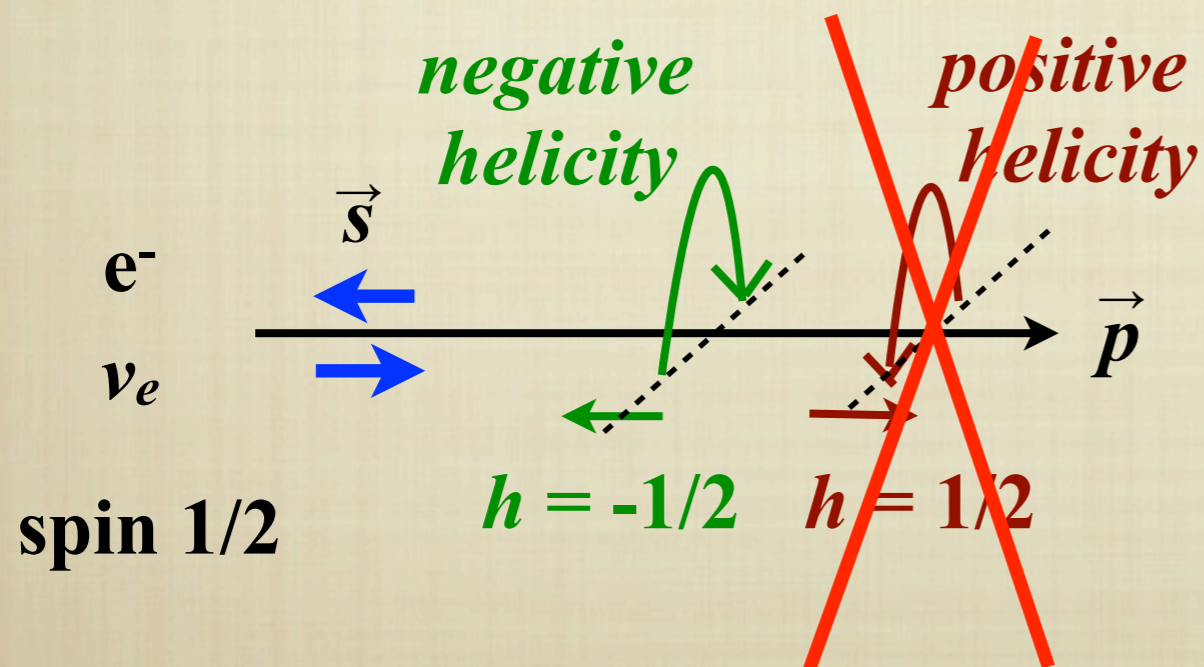


Helicity

$$h = \vec{s} \cdot \vec{p} / |\vec{p}|$$

right-handed (negative helicity)
left-handed (positive helicity)

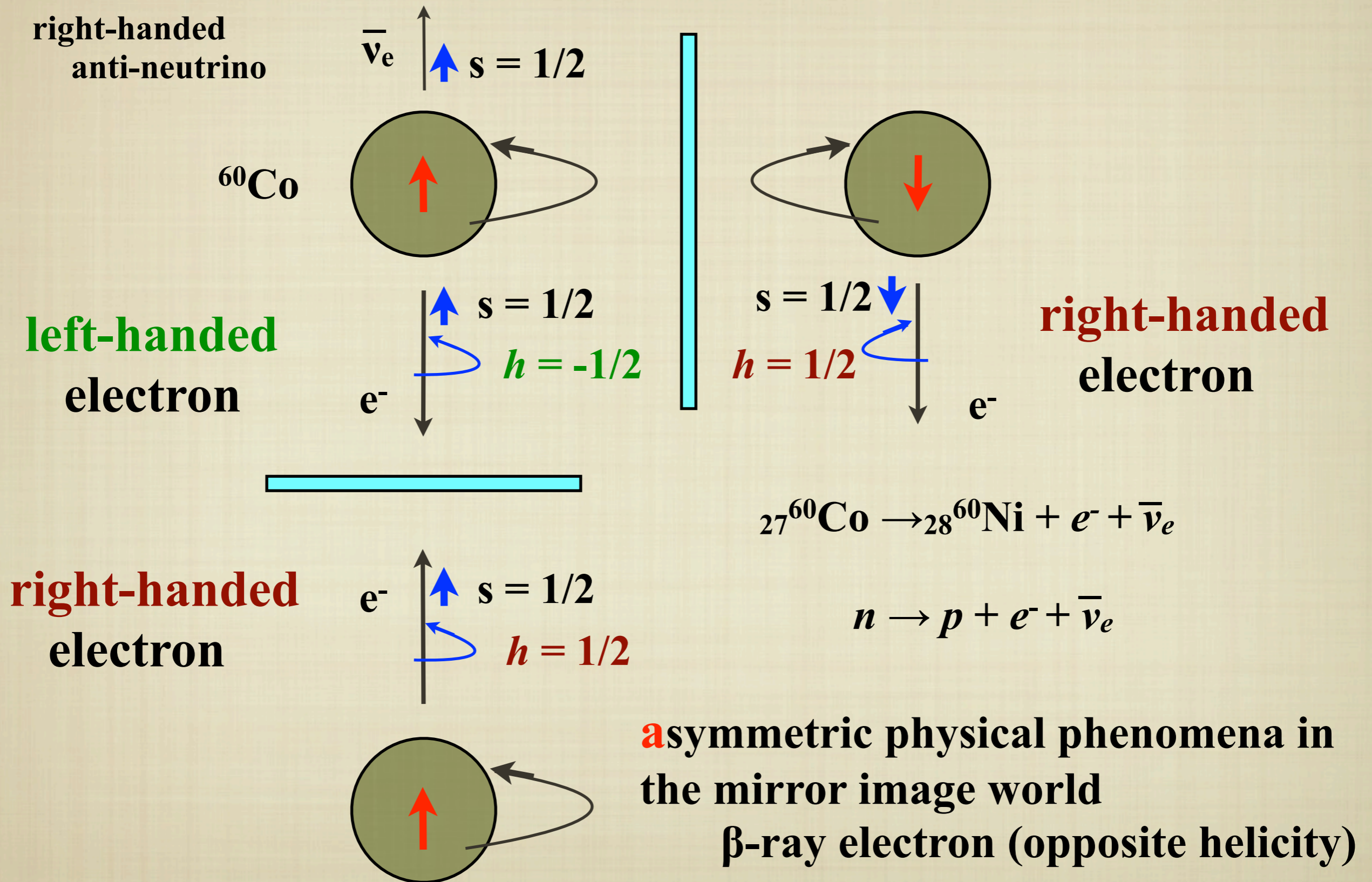
Spin polarized radiation **in nature**



e^- ; β^- -ray electron
 ν_e ; electron neutrino
 (only **negative** helicity,
left-handed)

positive helicity (right-handed)
negative helicity (left-handed)

Symmetry breaking in β -decay



Spin polarized electrons in space

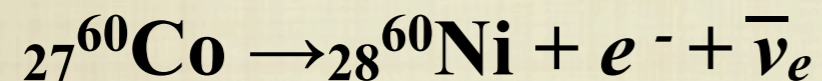
(Generation) Decay of radioactive nuclei and neutron

(Interaction with molecules) Perturbation of wave function by spin-orbital coupling

(Examples of spin polarized electron in space)

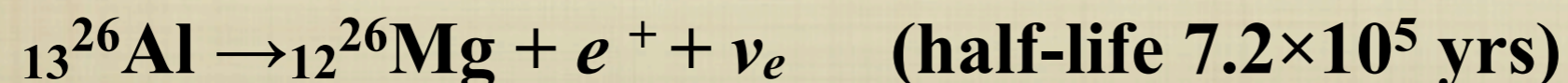
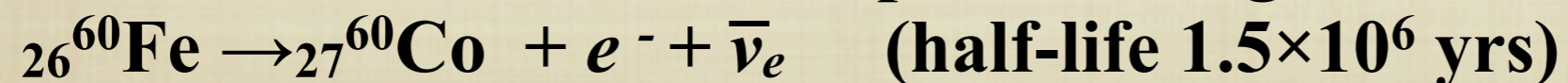
β^- -decay ($n \rightarrow p + e^- + \bar{\nu}_e$) electrons from
neutron star or neutron fireball with super nova explosion

β^- -decay of radioactive nuclei



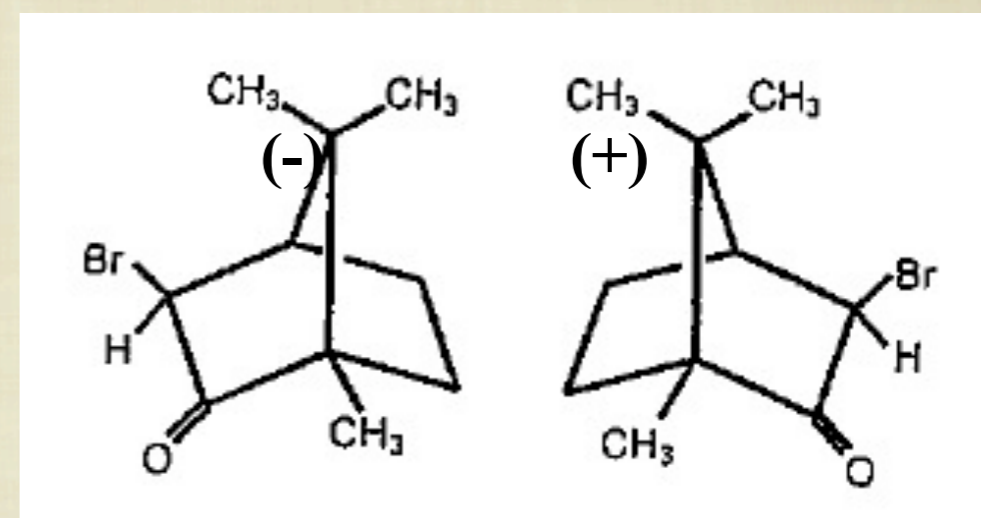
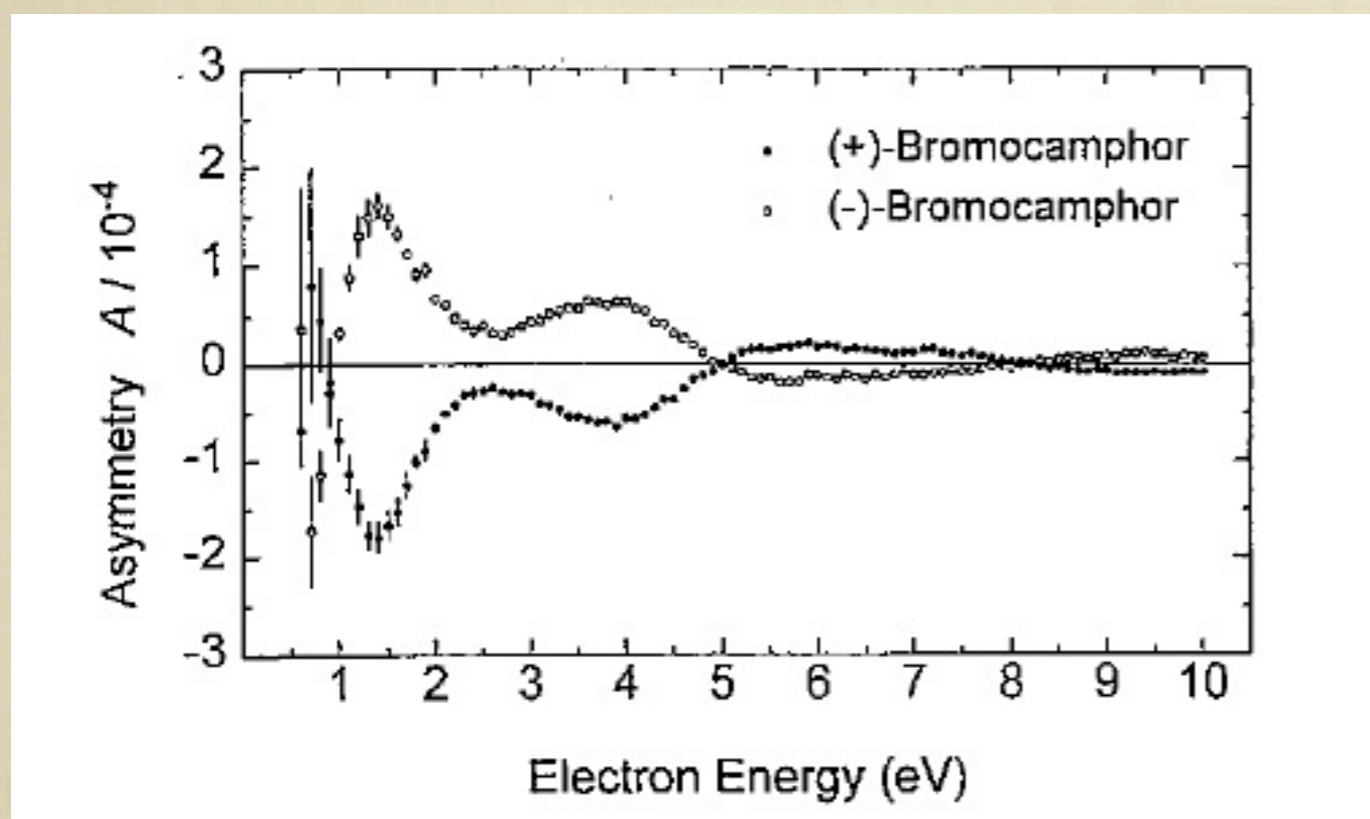
β^- -decay or β^+ -decay ($p \rightarrow n + e^+ + \nu_e$) of short lifetime nuclei in
parent bodies of planets or asteroids

(factors of thermal metamorphism of organic compounds)



Polarized Electron Dichroism (PED)

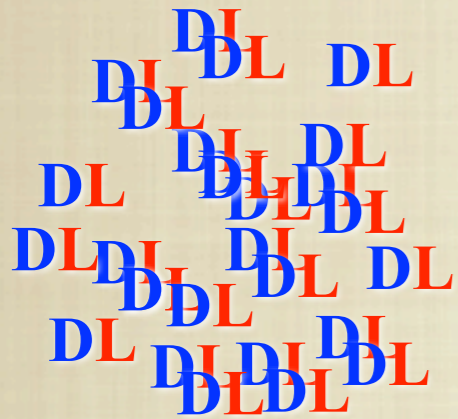
Chiral molecules show asymmetric absorption with electron helicity
 $\sigma(\text{positive helicity}) - \sigma(\text{negative helicity})$



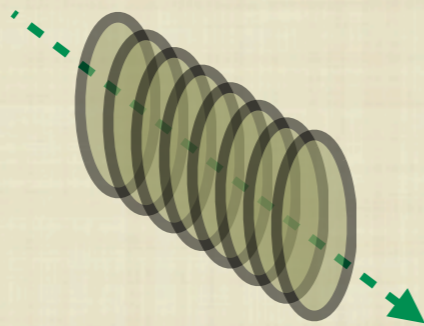
”Electron dichroism: Interaction of polarized electrons with chiral molecules”
Kessler, J.; Phys. Essays Vol.13 p.421 (2000)

Polarized beam irradiation experiments

simulated ISD surface formation



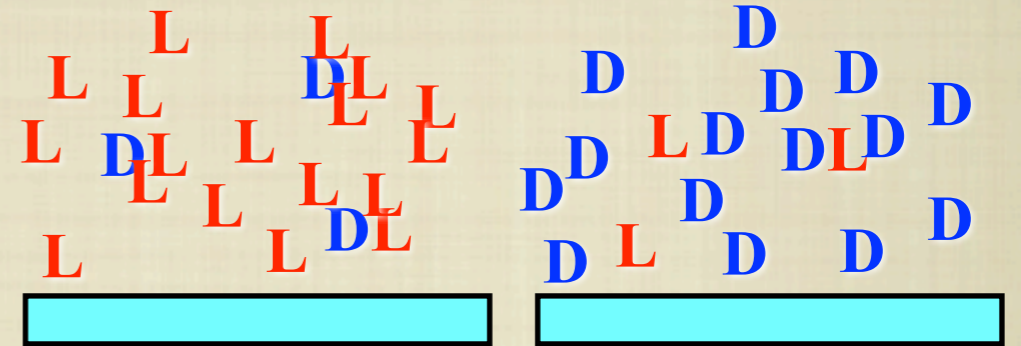
chiral impulse irradiation



polarized quantum beam irradiation
spin polarized electron beam (β -ray)

optical anisotropy measurement

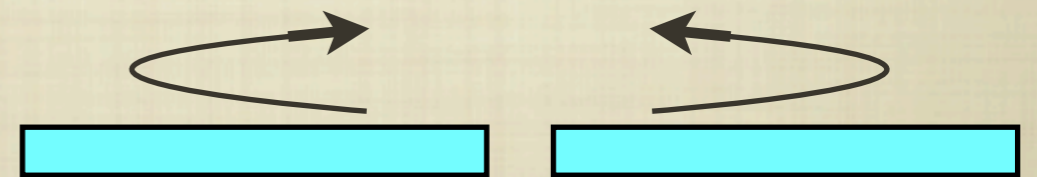
(a) preferential photolysis



(b) chiral polymerization



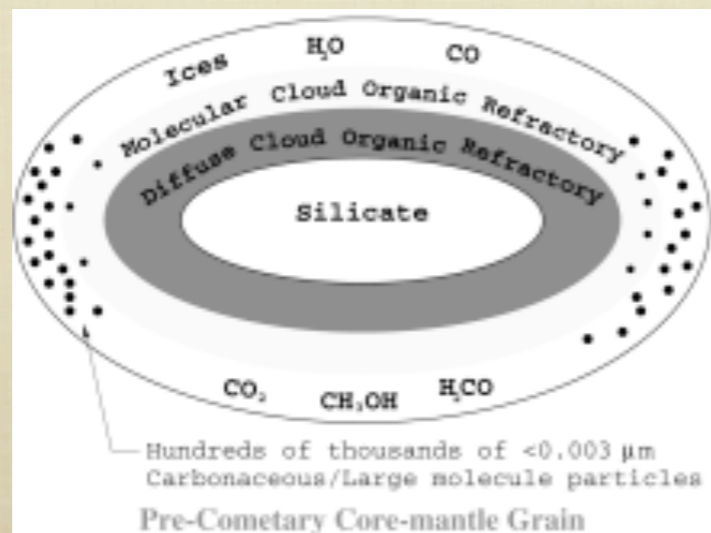
(c) chiral conformation change or structural distortion



circular dichroism (CD) spectra
 σ (Left-CPL) - σ (Right-CPL)

Solid films of **racemic organic compounds** on glass substrate

amino acids
Alanine
Isovaline



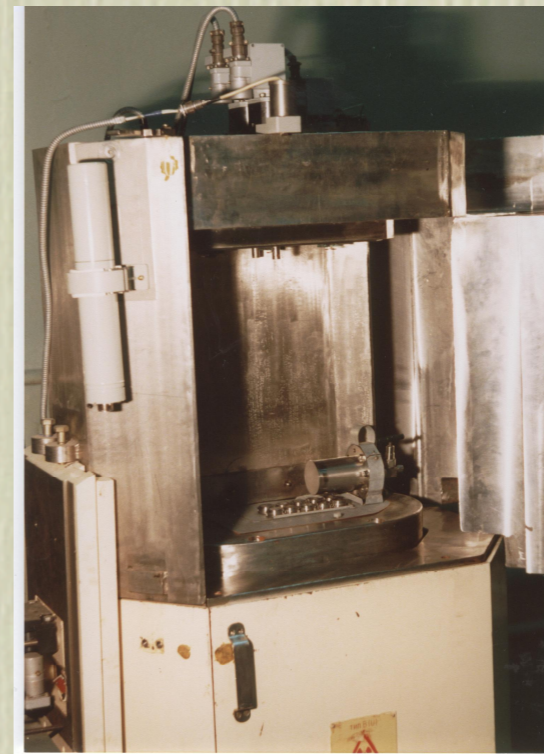
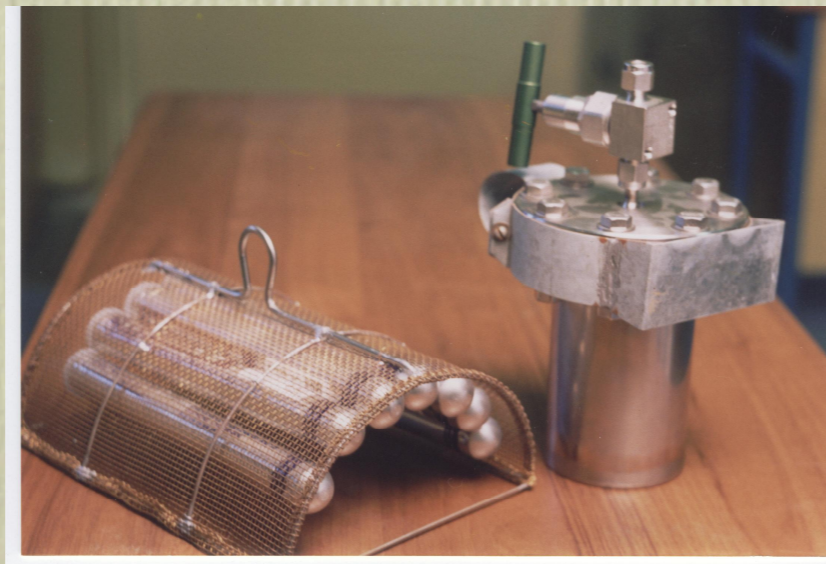
Spin polarized electron (β -ray) irradiation

β -ray Source: Russian Federal Nuclear Center
Chelyabinsk-70 (Snezhinsk)

$^{90}\text{Sr} - ^{90}\text{Y}$ (50 Ci) Electron energy 0.5 MeV

Irradiation Dose 2.5×10^5 Gy

β -Rays Irradiation
in Snezhinsk, Russia



- Amino acid metal complexes or amino acid precursors were irradiated with high flux β -rays from a ^{90}Sr - ^{90}Y source (50 Ci) at Snezhinsk, Russia.

Optical anisotropy (circular dichroism) measurement

Light Source:

HiSOR (Hiroshima Univ., Japan)

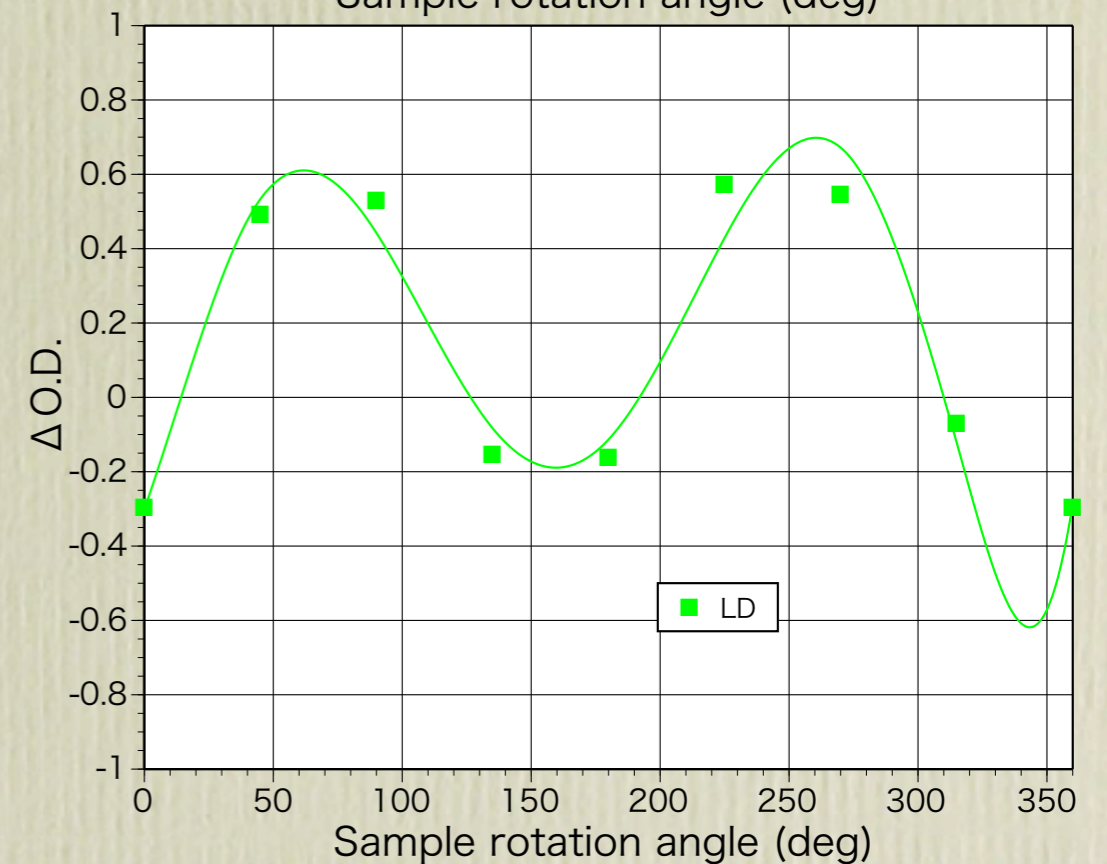
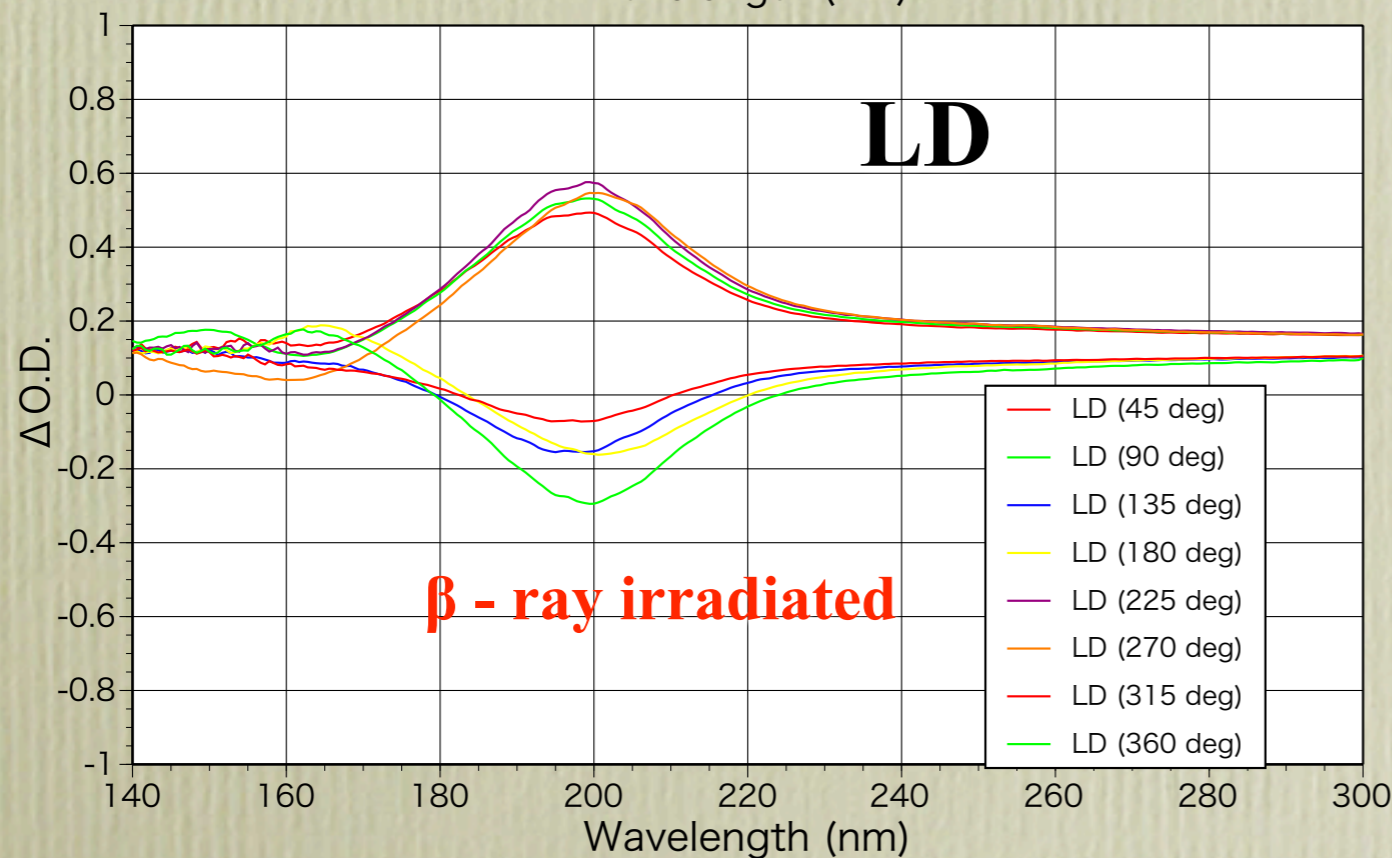
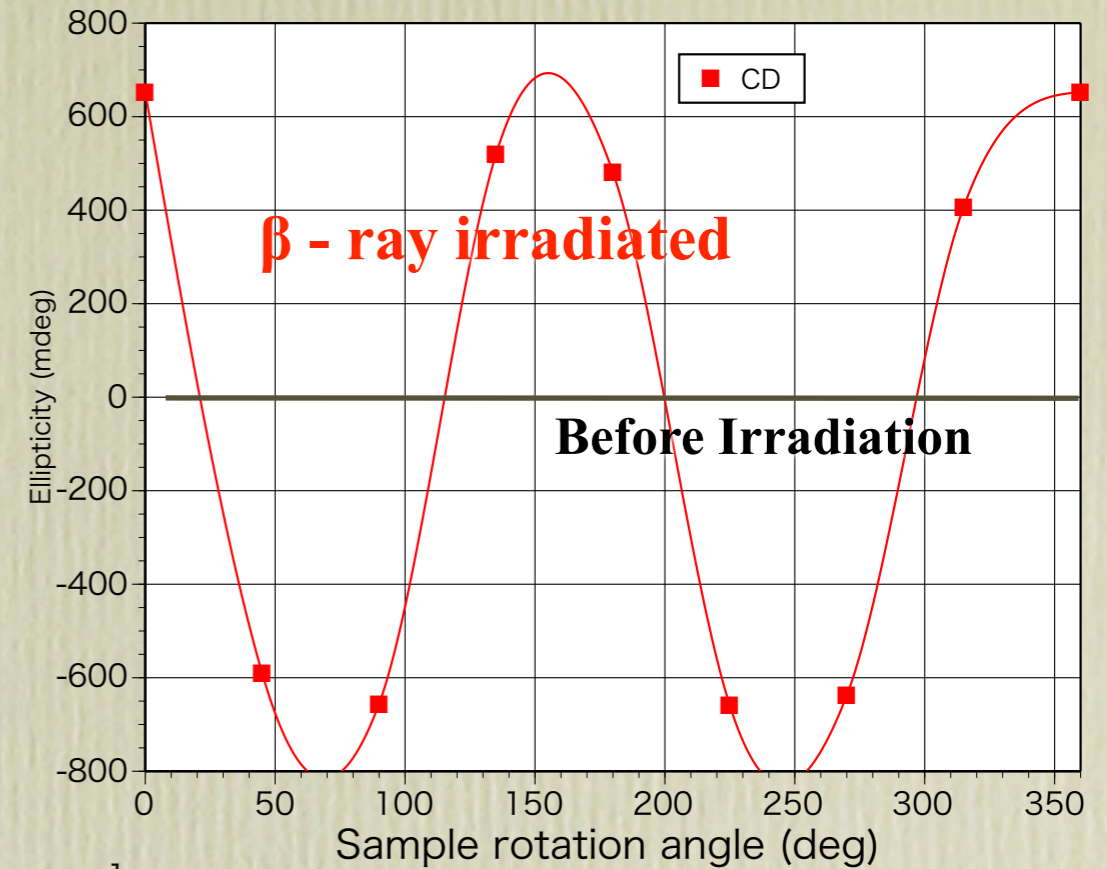
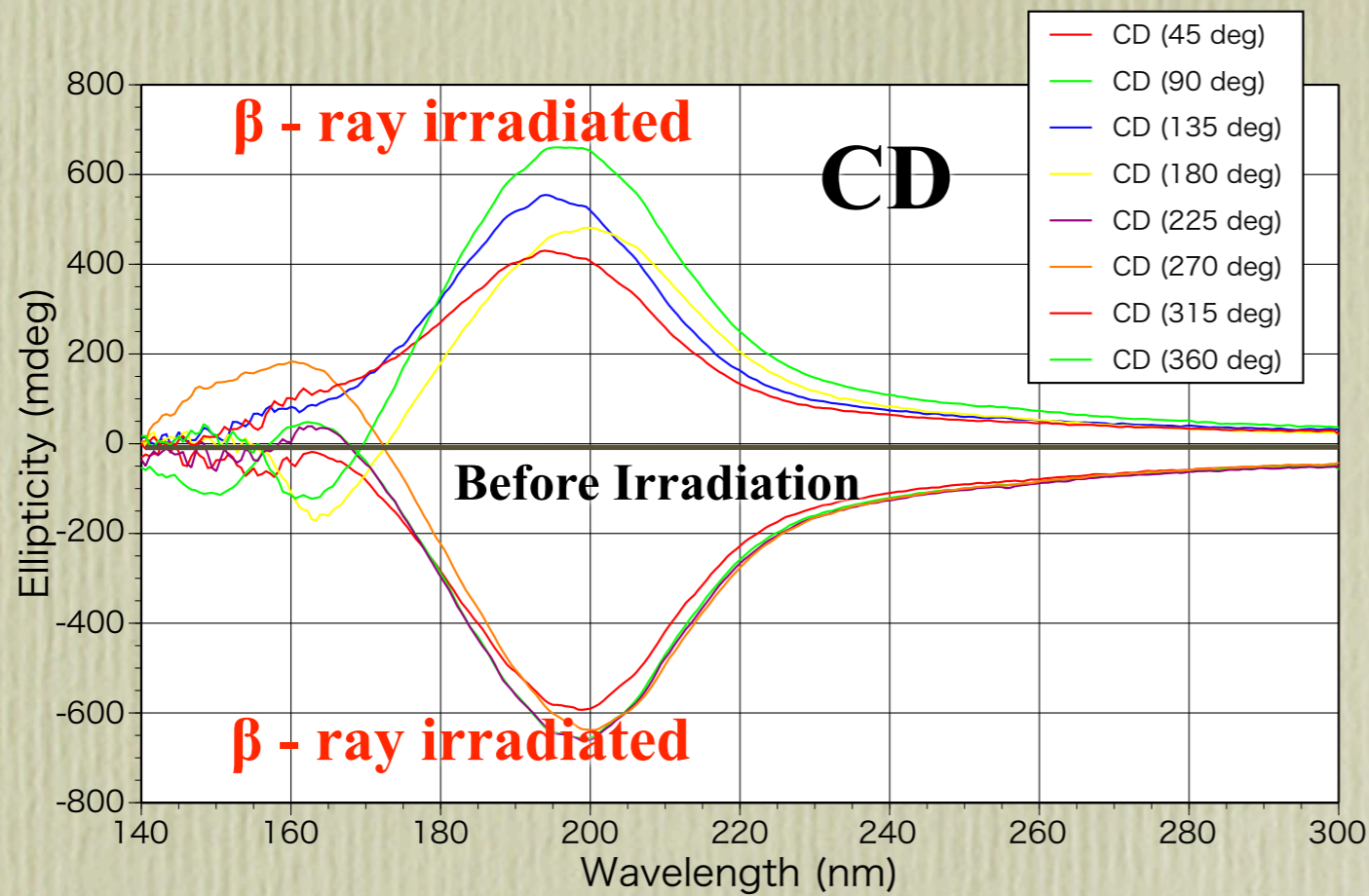
Synchrotron Radiation Circular Dichroism (SR-CD) Beam Line BL-15

Simultaneous measurement of

Circular Dichroism (CD) and Linear Dichroism (LD)

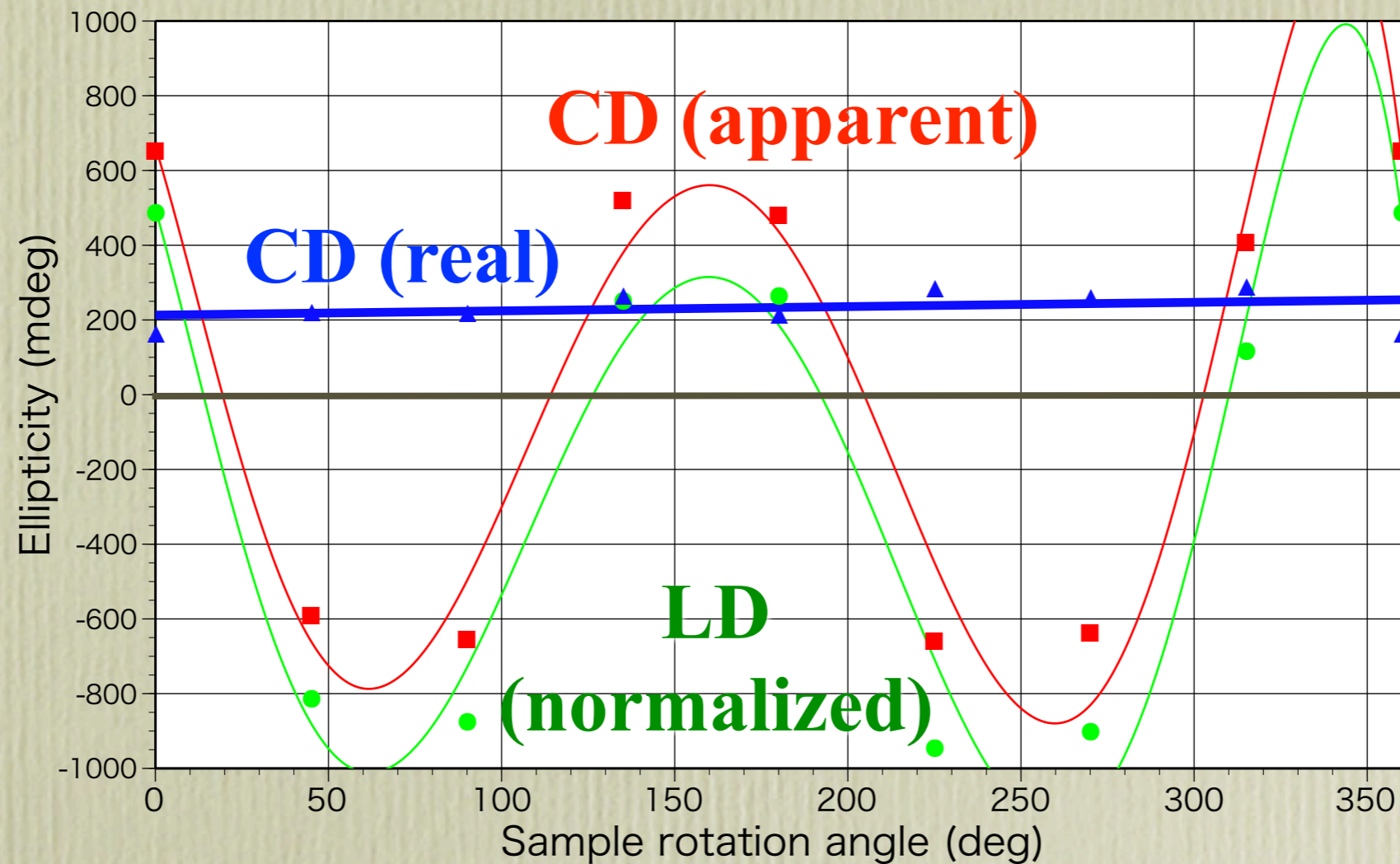


β - ray irradiation (DL-Isovaline film)



β - ray irradiation (DL-Isovaline film)

$$\text{CD (real)} = \text{CD (apparent)} - \text{LD (normalized)}$$



Beta-ray electron irradiation on racemic amino acid (Isovaline)

→ **chiral optical anisotropy**

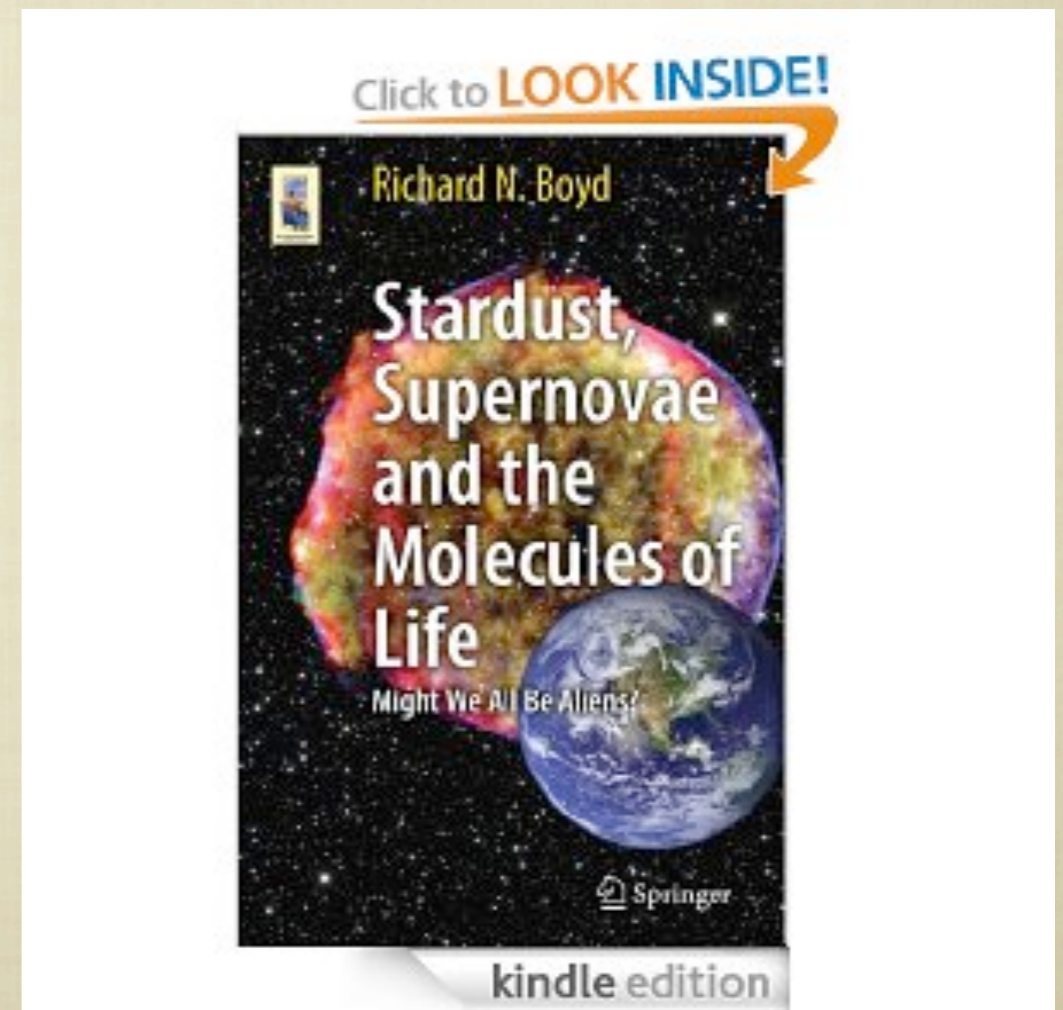
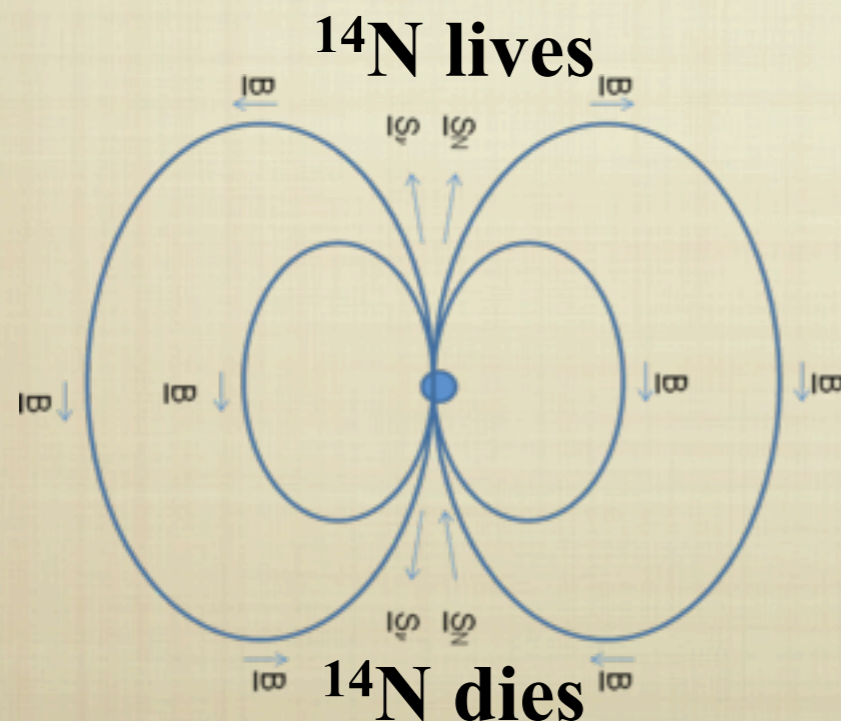
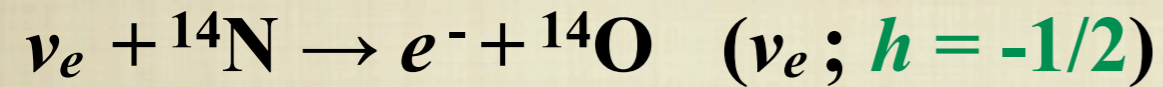
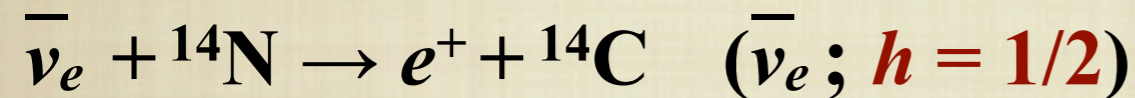
Neutrino radiation in space

“Supernovae, Neutrinos and the Chirality of Amino Acids”

R.N.Boyd, et al. *Int.J.Mol.Sci.* 12 3432 (2011)

“Model for Determining Amino Acid Chirality in the Supernova Neutrino Processing Model”

M.Famiano; *5th Astrobiology Work Shop* (2012)



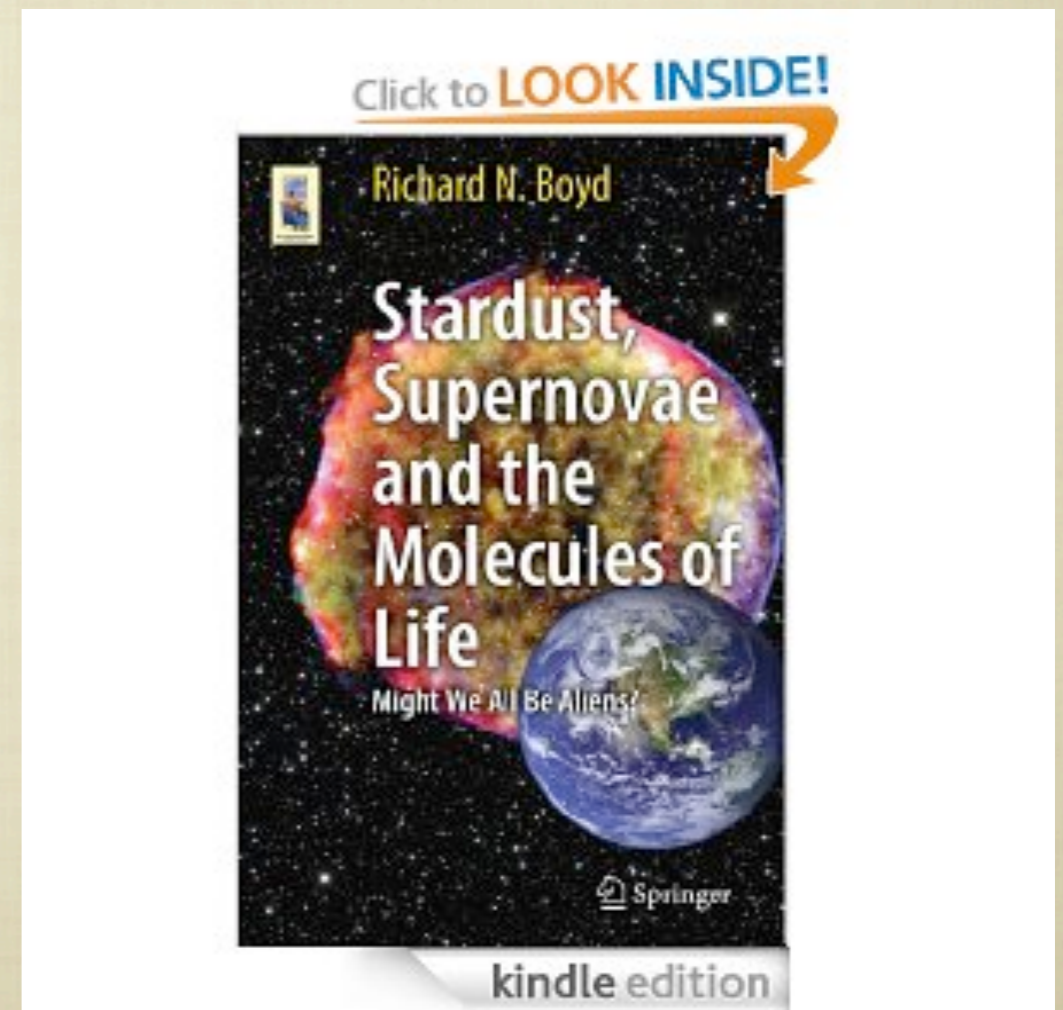
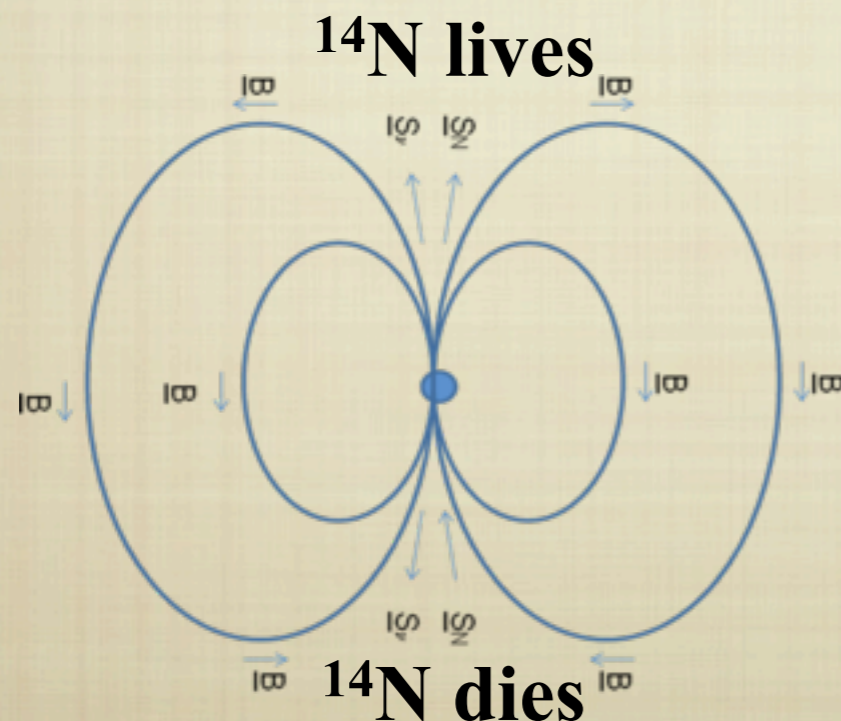
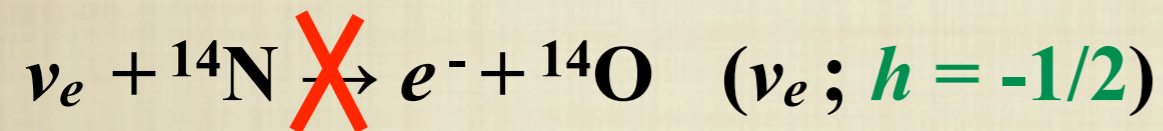
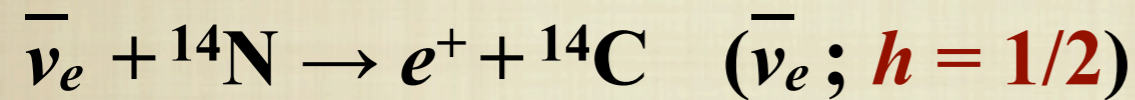
Neutrino radiation in space

“Supernovae, Neutrinos and the Chirality of Amino Acids”

R.N.Boyd, et al. *Int.J.Mol.Sci.* 12 3432 (2011)

“Model for Determining Amino Acid Chirality in the Supernova Neutrino Processing Model”

M.Famiano; *5th Astrobiology Work Shop* (2012)



Summary

1. **Circularly polarized photon** irradiation

racemic amino acids

optical anisotropy (chirality)

achiral amino acid precursors

optical anisotropy (chirality)

2. **Beta-ray electron** irradiation

racemic amino acid

optical anisotropy (chirality)

These results phenomenologically support the **scenarios** for the origin of terrestrial biomolecular homochirality.

Future Plan

1. **Circularly Polarized Photons**

Higher energy circularly polarized photon beams

195 nm UV @ Hiroshima Univ.

Gamma-ray @ UVSOR

2. **Spin Polarized Radiations**

Helicity-controlled (positive, negative, and intermediate)

spin polarized electron or positron beams

Well-tuned electron accelerator @ UVSOR or Nagoya Univ.

Synchrotron radiation circular dichroism spectra @ HiSOR

Neutrino or Anti-neutrino beams @ ???

3. **Circular dichroism spectra**

Synchrotron radiation circular dichroism spectra @ HiSOR

First-principle quantum-chemistry calculations @ SX6i

Collaborators

CPL irradiation

Palash Kumar Sarkers, Yumiko Obayashi,

Takeo Kaneko, Kensei Kobayashi

Yokohama National University (Japan)

Masahiro Adachi, Heishun Zen, Masahiro Katoh

UVSOR (Japan)

Masato Hosaka, Naoto Yamamoto

Nagoya University (Japan)

Hikaru Yabuta

Osaka University (Japan)

Beta-ray irradiation

Natalia Okatyeva, Natalia G. Poluhina,

German A. Gusev, Vladimir A. Tsarev

P.N. Lebedev Physical Institute (Russia)

Takeshi Saito

Institute for Applied Studies (Japan)

SR-CD measurement

Koichi Matsuo, Kunihiro Gekko

Hiroshima Synchrotron Radiation Center (Japan)

Jianhua Xu, Ye Tao

Beijing Synchrotron Radiation Facility (China)

Synthesis of DL-Isovaline and DL-EtMeHydantoin

Hajime Mita

Fukuoka Institute of Technology (Japan)

