Circular dichroism on condensed amino acids and precursors: results from Time Dependent Density Functional Theory

Fabiana Da Pieve

Laboratoire des Solides Irradiés,
École Polytechnique, Palaiseau, France

interest born during a one-day “illegal” participation to the NASA workshop: “Water, Ice and the origin of life in the Universe” Reykjavik, Iceland, 2012
ETSF
European Theoretical Spectroscopy Facility

www.etsf.eu

68 research teams across Europe and the United States

a condensed matter community working on

- light-matter interaction
- a better description of the electron
- electron/nuclear dynamics

\[ H\psi(x_1, \ldots, x_N) = E\psi(x_1, \ldots, x_N) \]
Homochirality of amino acids

Chirality

formation by accretion

Enantioselective Photolysis via circular dichroism

F. Ciesla and S. Sandford, Science 336, 452 (2012)
Key questions

• Initial composition of the interstellar ices in the molecular cloud

• Estimation of the excitation energies and CD

• Role of precursors?
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- Initial composition of the interstellar ices in the molecular cloud
- Estimation of the excitation energies and CD
- Role of precursors?

The case of isovaline

1) precursor, cold environment
   5-ethyl-5-methylhydantoin

2) warming phase, formation of the amino acid

3) Isovaline, recondensation within ice
Which theoretical approach?

Wave-function approaches: unaccurate and unpractical in solids
Which theoretical approach?

Wave-function approaches: inaccurate and unpractical in solids

Density Functional Theory (DFT) and its time extension
Real time TDDFT: flowchart

(a) apply a perturbative electric field along three directions

\[ E_\nu(t) = \frac{k_0 \hbar}{e} \delta(t) \quad E_\nu(\omega) = \frac{k_0 \hbar}{\sqrt{2\pi} e} \]

\[ \psi_n(t = 0^+) = \exp \left\{ -\frac{i}{\hbar} \int_{0^-}^{0^+} H(t') dt' \right\} \psi_n(t = 0^-) = e^{-ik_0 r_\nu} \psi_n(t = 0^-) \]

(b) propagate the TDKS wavefunctions

\[ \psi_n(t) = \hat{S}^{-1/2} \hat{T} \left[ \exp \left( -\frac{i}{\hbar} \int_0^t dt' S^{-1/2} \hat{H}(t') \hat{S}^{-1/2} \right) \right] \hat{S}^{1/2} \psi_n(0) \]

\[ d_\mu(t) = \sum_i \langle \psi_i(t) | r_\mu | \psi_i(t) \rangle, \]

\[ L_\mu(t) = \sum_i \langle \psi_i(t) | -i(r \times \nabla_\mu) | \psi_i(t) \rangle \]

\[ \alpha_{\mu\nu}(\omega) = \frac{-ed_\mu(\omega)}{E_\nu(\omega)} \]

\[ S_{\mu\nu}(E) = \frac{2me}{\pi \hbar^2 e^2} \text{Im} \alpha_{\mu\nu}(E) \]

\[ \beta_\mu(E) = \frac{e^2 \hbar}{2mc k_0} \int_0^\infty e^{(E+i\delta)/\hbar} L_\mu(t) dt \]

\[ R_\mu(E) = \frac{\text{Im} \beta_\mu(E)}{\pi}. \]
Preliminary studies on crystallized amino acids and precursors

1) precursor, cold environment
5-ethyl-5-methylhydantoin

2) warming phase,
formation of the amino acid

3) Isovaline,
recondensation within ice

DFT-LDA  4.894 eV
DFT-B3LYP  6.801 eV
CD absorption for gas-phase isovaline using different approximations

CIRCULAR DICHROISM = absorption of left CPL – absorption of right CPL

- Energies are different
  (even more when you consider the directional dependence)

- But sign and shape of the CD is ok

- Agreement with literature

FDP et al., MNRAS 2014
CD on molecular units as extracted from the solid matrix

Orientationally averaged CD for precursor in agreement with liquid solutions

No big influence of surrounding ice, agreement with thin film of isovaline:

FDP et al., MNRAS 2014
CD on molecular units as extracted from the solid matrix (OEP-EXX)

Big difference between gas-phase and “solid state” molecule

FDP et al., MNRAS 2014
Circular dichroism via real time TDDFT (OEP-EXX)

Peaks for the precursor are overall stronger in a region for C-C breaking of the ring

Important role of the CD in precursors
Pizzarello S., Schraderb D., Monroea A., Lauretta D., 2012, PNAS USA, 109, 11949

The VUV region is characterized by stronger CD

A confined VUV CPL induces more efficiently L-ee in both (precursor and amino acid)

FDP et al., MNRAS 2014
Future: the Isoleucine serie

Very localized states, likely to correspond closely to the molecular orbitals

Very little dispersion

\[ E_g = 4.894 \text{ eV} \]

\[ E_g = 4.697 \text{ eV} \]

\[ E_g = 4.831 \text{ eV} \]

DFT-GGA

G0W0

TB-mBJ

4.894 eV

6.801 eV

6.307 eV

4.697 eV

7.412 eV

6.818 eV

4.831 eV

7.256 eV

6.709 eV
Conclusions

Need for accurate energies of absorption peaks in solids

Simple approximations work reasonably for the sign of the CD

Precursors absorb at lower energies, enantioselective photolysis is bigger

Need for fractal generation of amorphous structures

My collaborators in this project:
Dr. G. Avendano-Franco, USA , Prof. P. Geerlings, Belgium

packages used:


Real time TDDFT: flowchart

(a) apply a perturbative electric field along three directions

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\[ \psi_n(t) = \hat{S}^{-1/2} \hat{T} \left[ \exp \left( -\frac{i}{\hbar} \int_0^t dt' S^{-1/2} \hat{H}(t') \hat{S}^{-1/2} \right) \right] \hat{S}^{1/2} \psi_n(0) \]

First-order Crank-Nicholson integration method

\[ \left[ \hat{S} + \frac{i}{2\hbar} \hat{H}(t) \Delta t \right] \psi_n(t + \Delta t) = \left[ \hat{S} - \frac{i}{2\hbar} \hat{H}(t) \Delta t \right] \psi_n(t) \]

\[ A \mathbf{x} = \mathbf{b} \quad \text{solved by conjugated-gradient squared method (CGS)} \]

\[ \Delta t = 2 \text{ attosecond. Integration for 20 fs (} \rightarrow 0.2 \text{ eV resolution)} \]
Key questions

- What is the initial composition of interstellar ices in cold molecular clouds?
- How do they evolve from parent clouds to the envelopes of newly-born stars?
- How much of the icy material from the parent cloud survives the journey to the comet- and planet-forming regions of protoplanetary disks?

Above: fractal models for interstellar grains, with and without ice mantles.
Right: presolar solids in an interplanetary dust particle.
Details

- **What exists in literature until now?**
  - Many studies on gas-phase molecules, none on the condensed phase, none on different energy ranges, none on directional effects of the absorption

- **Which phase?**

  ![Graph showing irradiation effects on different molecules](image)

  - TEMPO beamline, SOLEIL
  - A. Pernet et al,
  - Astronomy and Astrophysics 552, A100 (2013)
Fig. 6: Circular polarization image of the OMC-1 star formation region in Orion at 2.2 μm. (Right) Percentage circular polarization ranging from –5 % (black) to +17 % (white). Polarization accuracy ranges from about 0.1 % in the brighter regions to 1 % in the fainter regions. By convention, positive polarization means that the electric vector is seen to rotate counterclockwise in a fixed plane by an observer looking at the source. (Left) The total IR intensity. The bright source at coordinates (0,0) is the Becklin-Neugebauer object. The size of a typical protostellar disk (100 astronomical units) is less than 1 arc sec at the 450 pc distance of OMC-1 and therefore much smaller than the observed polarization structure.

Bailey et al.: Science 281 (1998), 672