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

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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

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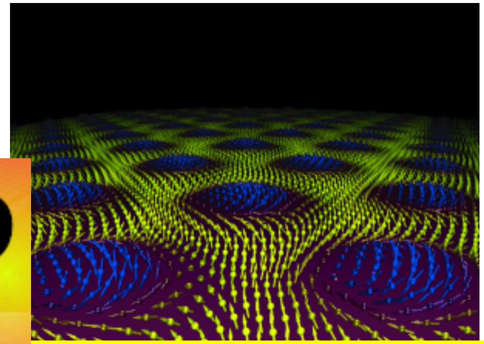
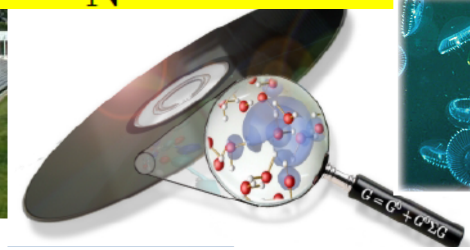
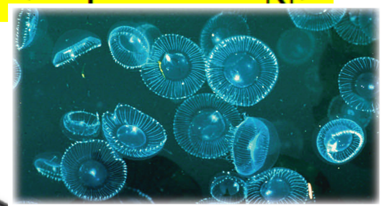


$$H\psi(x_1, \ldots . x_N) = E\ \psi(x_1, \ldots . x_N)$$





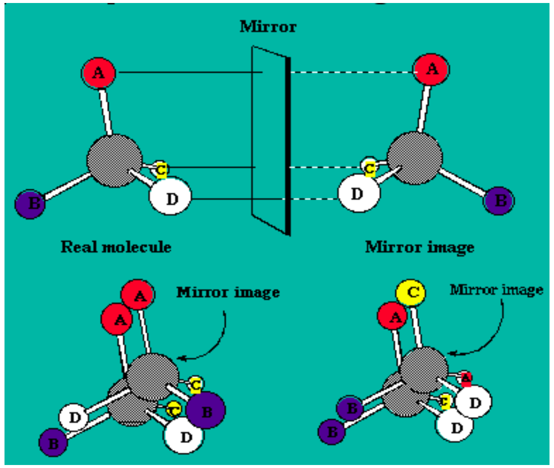
68 research teams across Europe and the United States

a condensed matter community working on

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

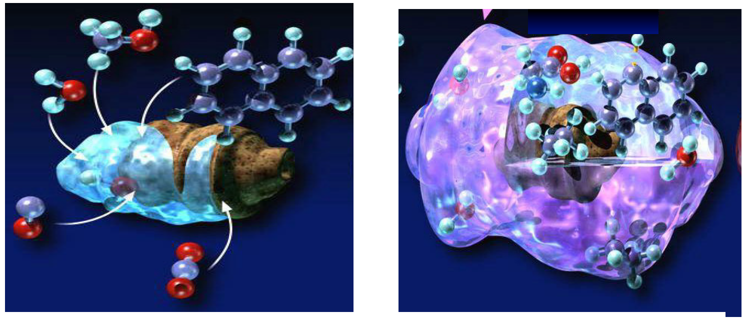
Homochirality of amino acids

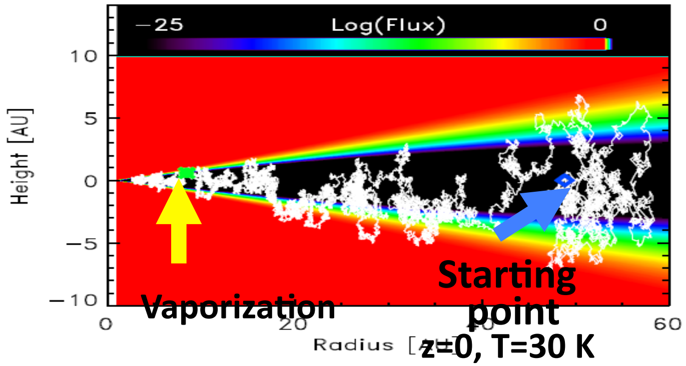
Chirality



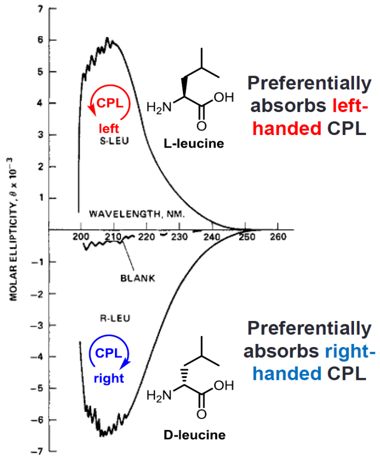
formation

by accretion

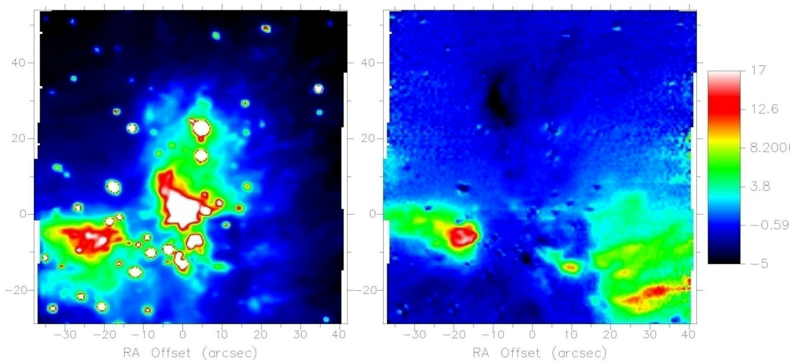




Enantioselective Photolysis via circular dichroism



CPL in Orion star formation region



F. Ciesla and S. Sandford, Science 336, 452 (2012)
J. Kwon et al, The Astrophys. Journal 765, 1 (2013)
G. Munoz Caro et al., Nature 416, 403 (2002)
M. P. Bernstein et al., Nature 416, 401 (2002)
M. Nuevo et al., Astron Astrophys 457, 741 (2006)

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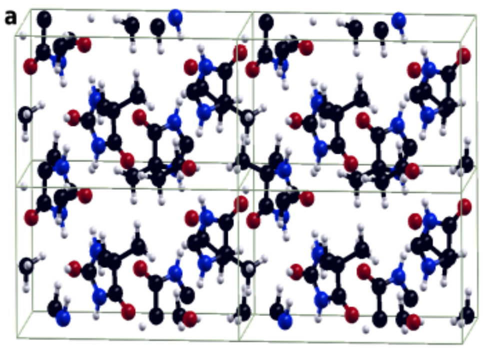
- Initial composition of the interstellar ices in the molecular cloud
- Estimation of the excitation energies and CD
- Role of precursors ?

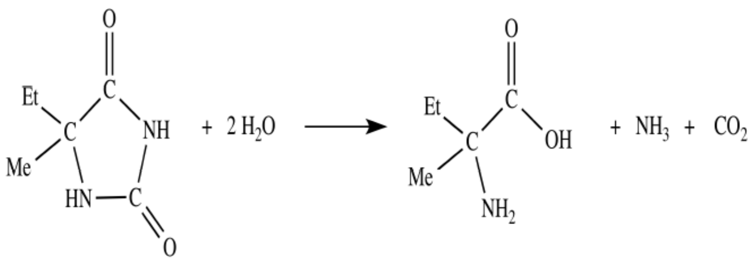
The case of isovaline

1) precursor, cold environment

5-ethyl-5-methylhydantoin

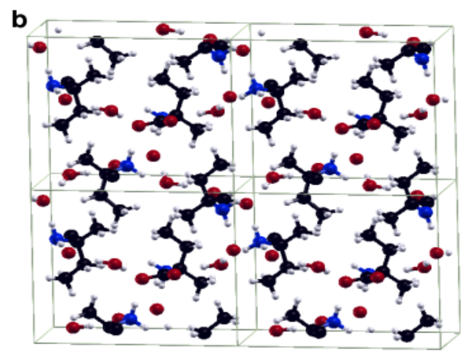


2) warming phase,
formation of the amino acid



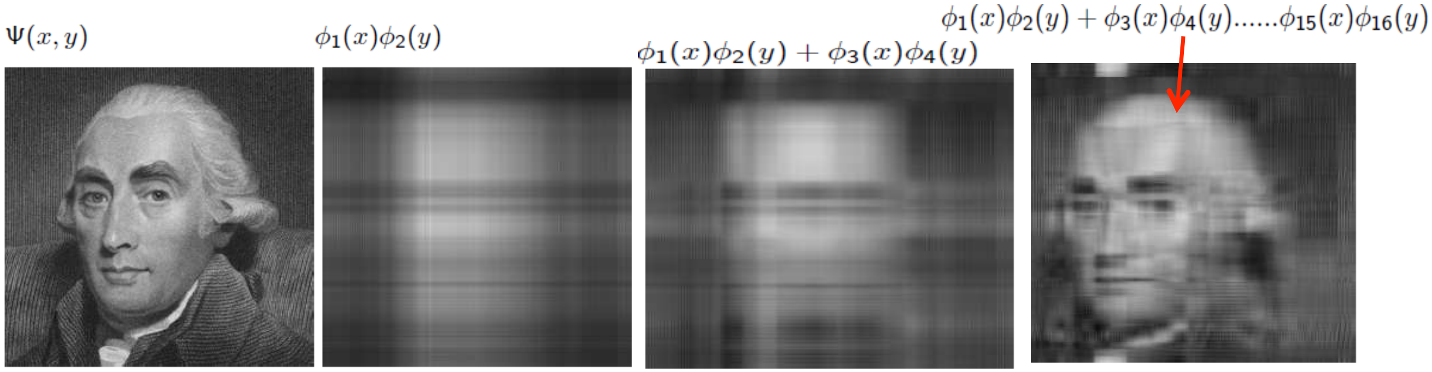
3) Isovaline,

recondensation within ice



Which theoretical approach ?

Wave-function approaches : unaccurate and unpractical in solids



Which theoretical approach ?

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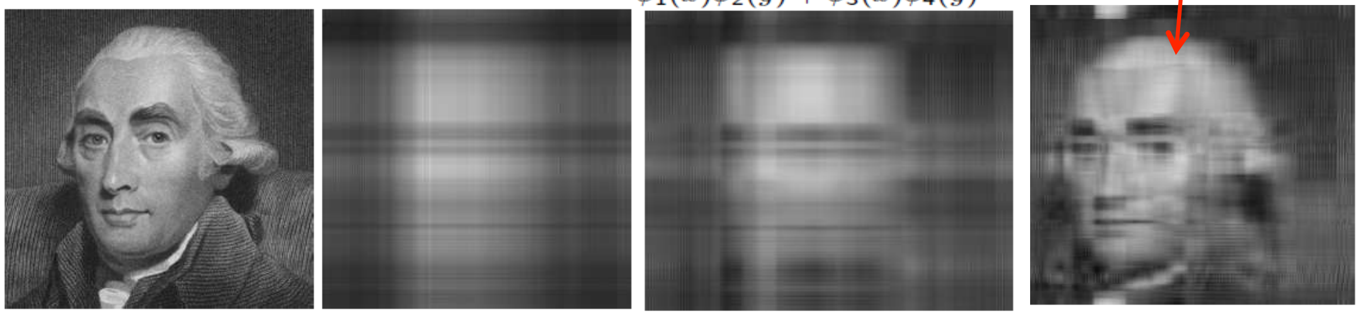
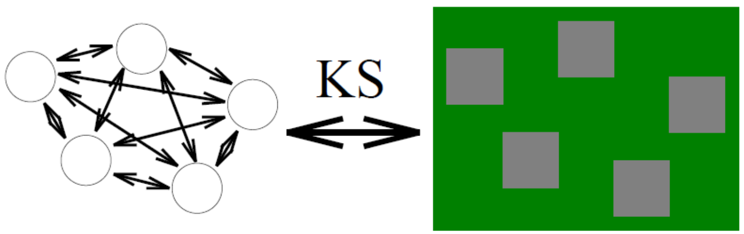
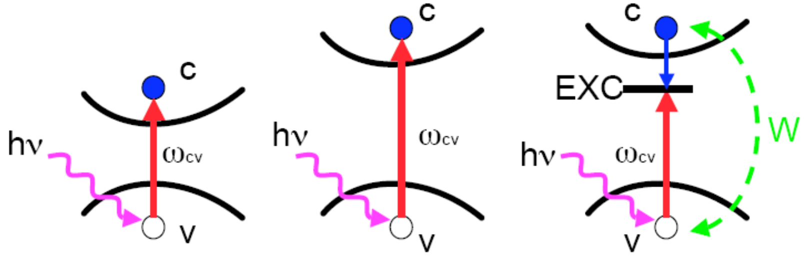


Density Functional Theory (DFT) and its time extension



Interacting electrons + real potential

Non-interacting, fictitious particles + effective potential



Real time TDDFT: flowchart

(a) apply a perturbative electric field along three directions

$$E_\nu(t) = \frac{k_0 \hbar}{e}\delta(t) \qquad E_\nu(\omega) = \frac{k_0\hbar}{\sqrt{2\pi}e}$$

$$\psi_n(t=0^+) = \exp\left\{-\frac{i}{\hbar}\int_{0^-}^{0^+} H(\hat{t'})dt'\right\}\psi_n(t=0^-) = e^{-ik_0 r_v}\psi_n(t=0^-)$$

(b) propagate the TDKS wavefunctions

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

$$d_\mu(t) = \sum_i \langle\psi_i(t)|\boldsymbol{r}_\mu|\psi_i(t)\rangle,$$

$$L_\mu(t) = \sum_i \langle\psi_i(t)| - \mathrm{i}(\boldsymbol{r}\times\nabla_\mu)|\psi_i(t)\rangle$$

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

$$S_{\mu\nu}(E) = \frac{2mE}{\pi\hbar^2 e^2} Im\alpha_{\mu\nu}(E)$$

$$\beta_\mu(E) = \frac{e^2\hbar i}{2mck_0}\int_0^\infty \mathrm{e}^{(E+\mathrm{i}\delta)t/\hbar} L_\mu(t)\mathrm{d}t$$

$$R_\mu(E) = \frac{Im\beta_\mu(E)}{\pi}.$$

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **24** (2012) 233202 (11pp) doi:10.1088/0953-8984/24/23/233202

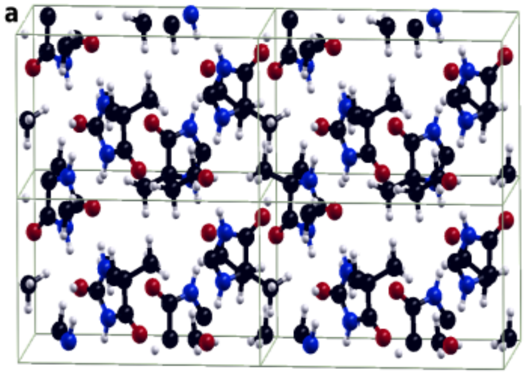
TOPICAL REVIEW

Time-dependent density-functional theory in massively parallel computer architectures: the OCTOPUS project

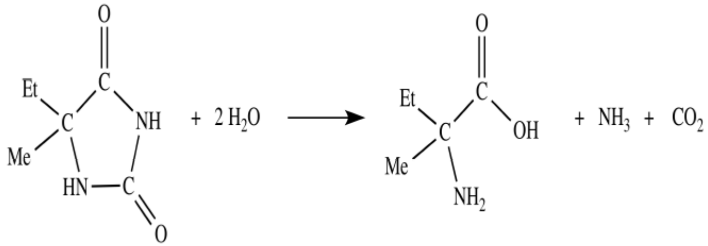
Xavier Andrade[1], Joseba Alberdi-Rodriguez[2,3], David A Strubbe[4,5], Micael J T Oliveira[6], Fernando Nogueira[6], Alberto Castro[7], Javier Muguerza[3], Agustin Arruabarrena[3], Steven G Louie[4,5], Alán Aspuru-Guzik[1], Angel Rubio[2,8] and Miguel A L Marques[9,10]

Preliminary studies on crystallized amino acids and precursors

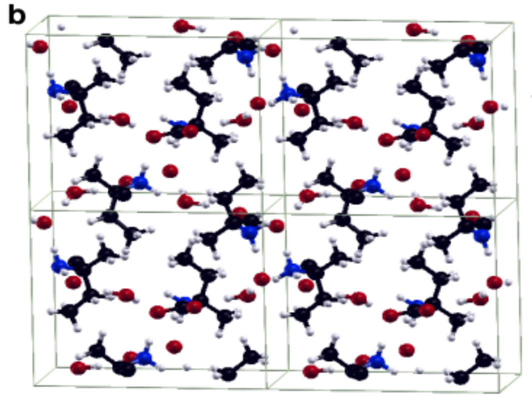
1) precursor, cold environment
5-ethyl-5-methylhydantoin

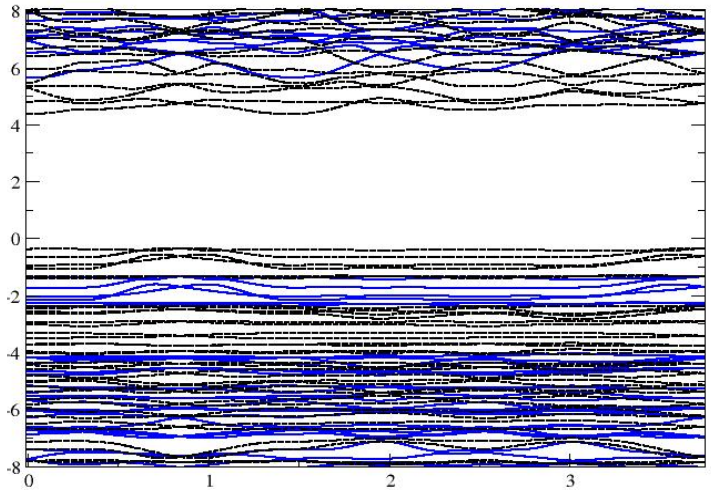


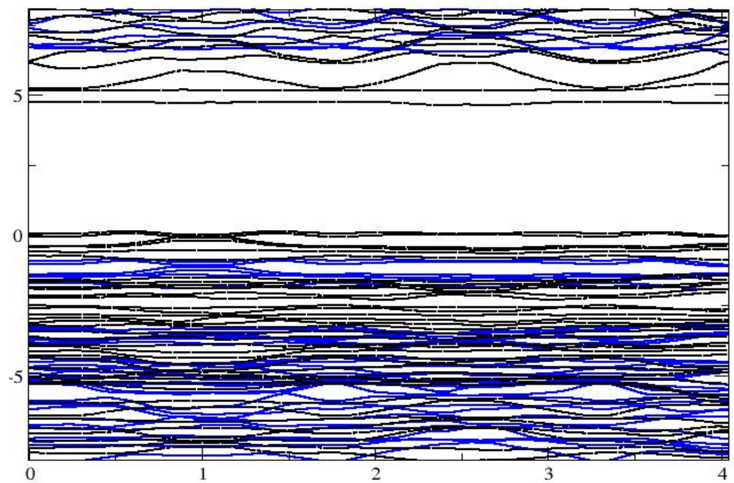
2) warming phase,
formation of the amino acid



3) Isovaline,
recondensation within ice

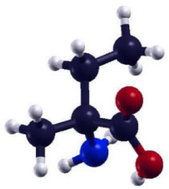


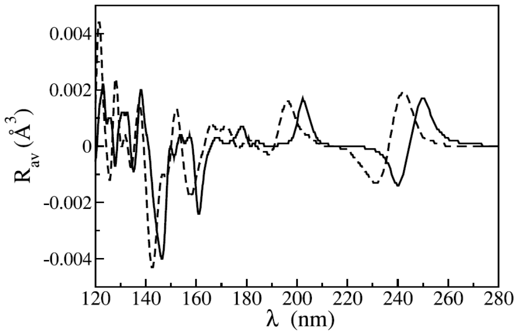




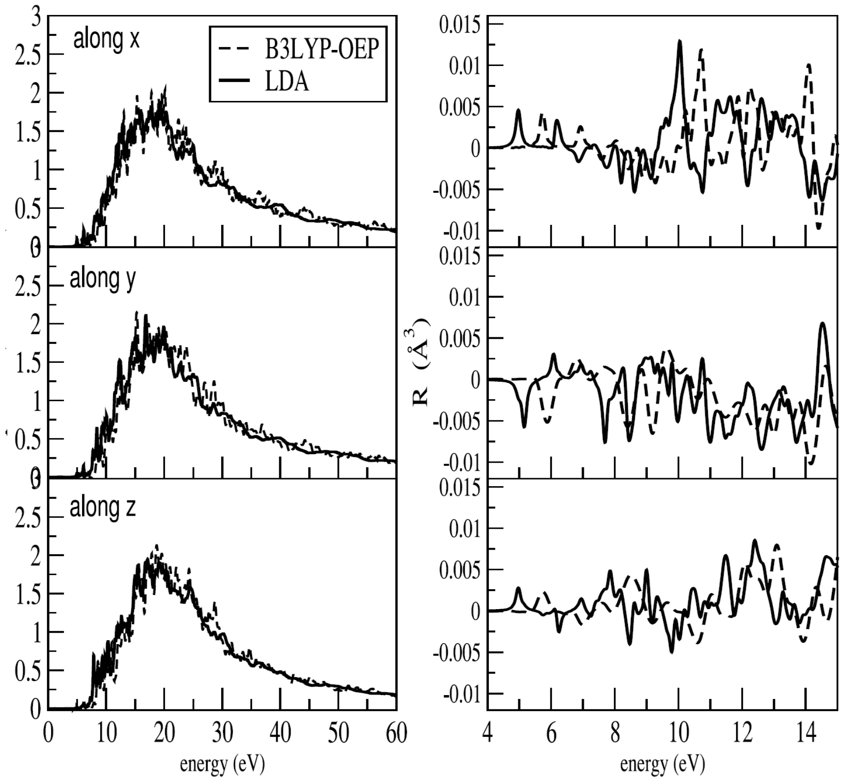
DFT-LDA	**4.894 eV**	**4.697 eV**
DFT-B3LYP	**6.801 eV**	**7.412 eV**

CD absorption for gas-phase isovaline using different approximations





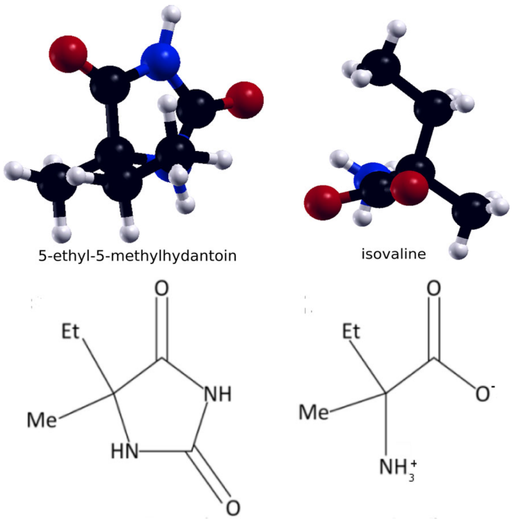
CIRCULAR DICHROISM =
absorption of left CPL – absorption of right CPL

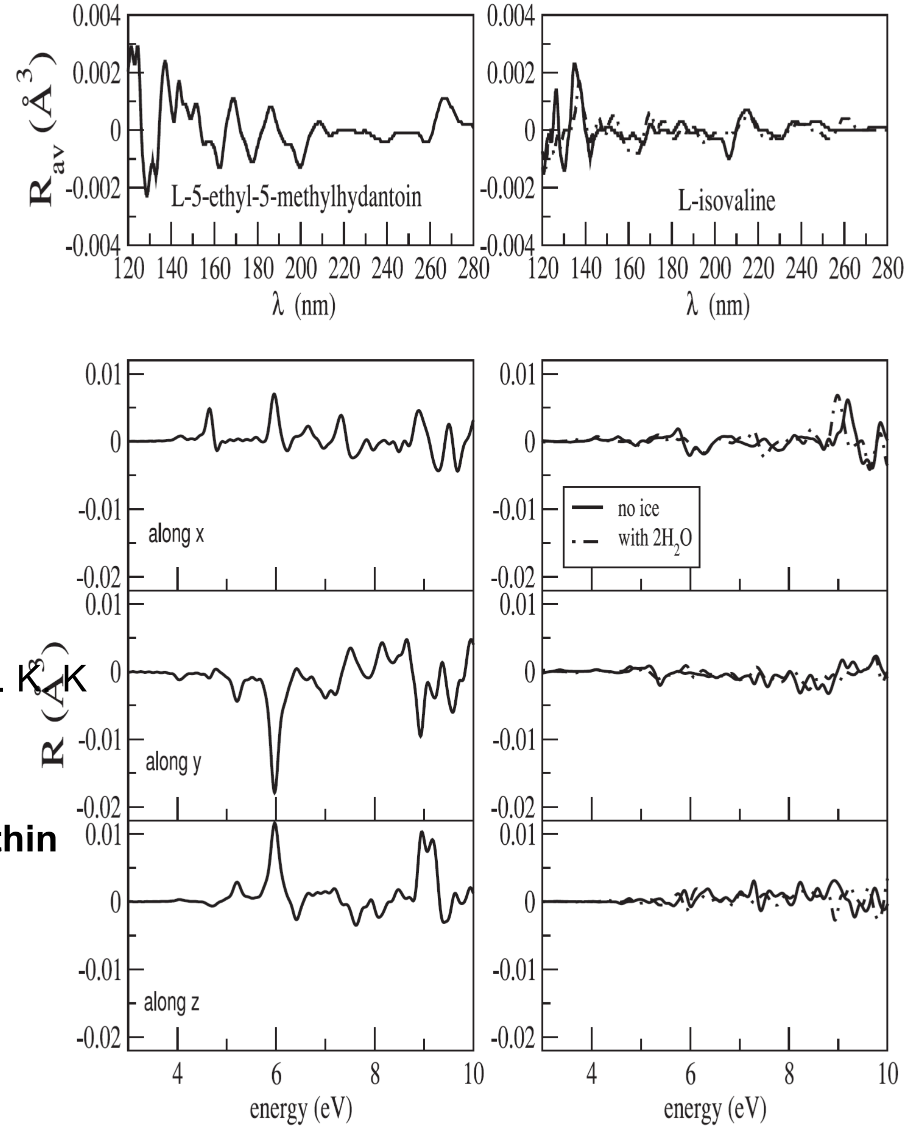


- **Energies are different**
  (even more when you consider the directional dependence)
- **But sign and shape of the CD is ok**
- **Agreement with literature**
  (Adrian-Scotto M., Antonczak S., Bredehoft J., Hoffman S., Meirehenrich, U., 2010, Symmetry, 2, 935)

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

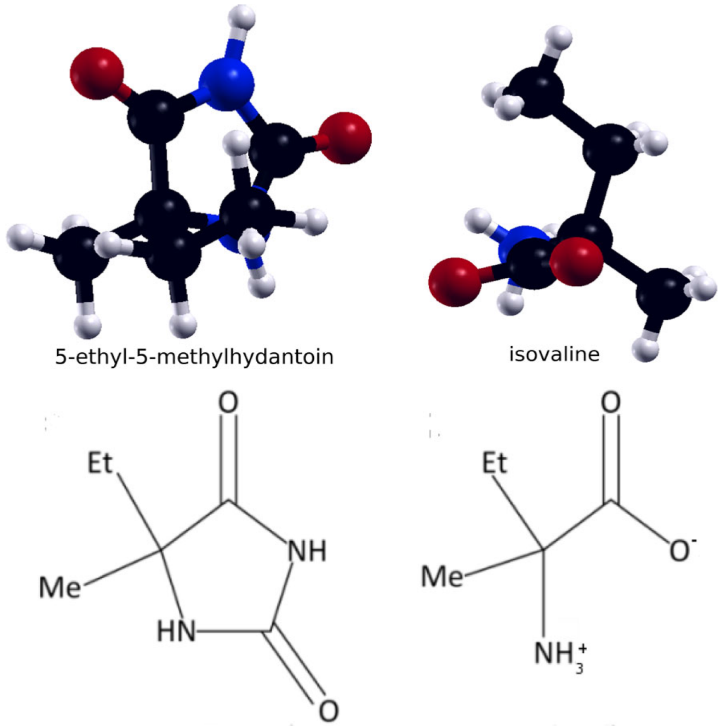
Sarker K. P., Takahashi J.-i., Kawamoto Y., Obayashi Y. T. K. K K., 2012, Int. J. Mol. Sci., 13, 1006

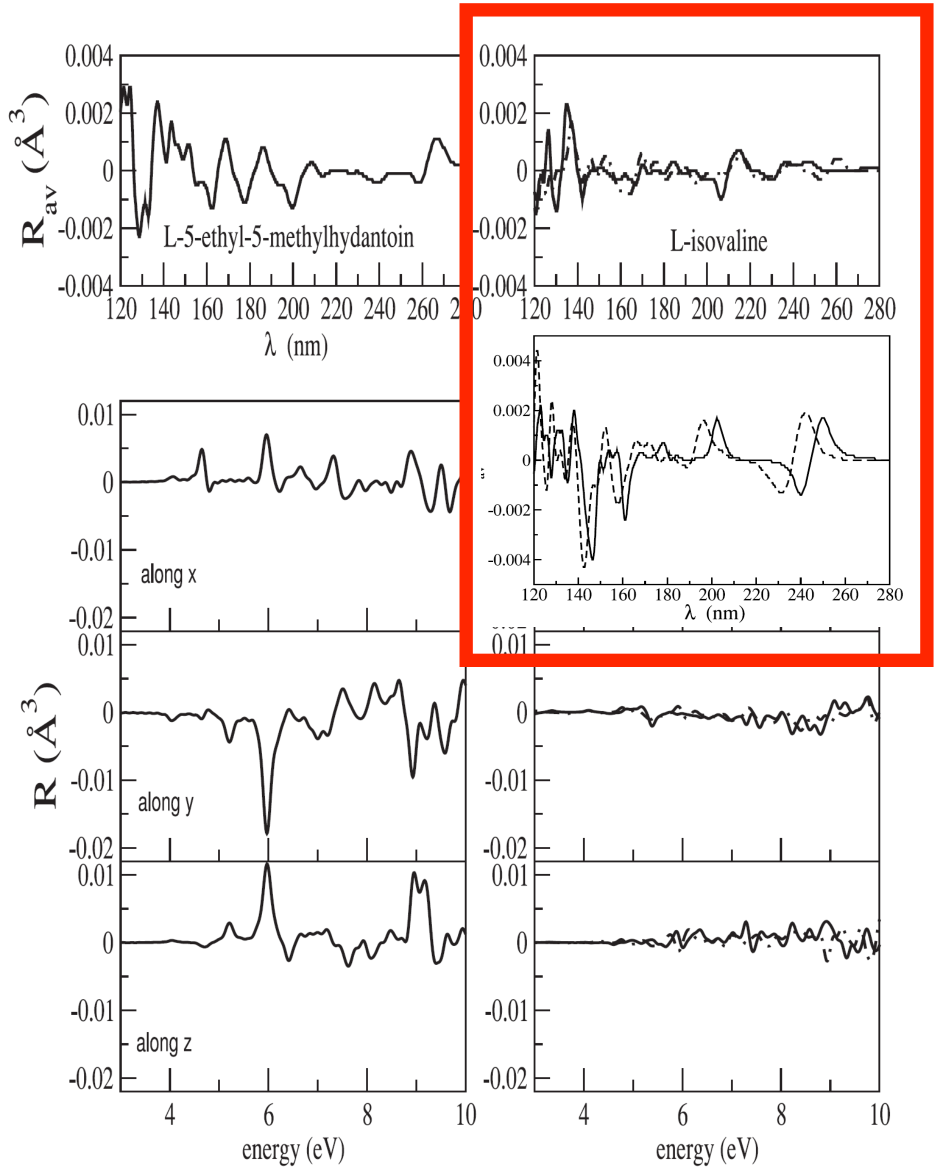
No big influence of surrounding ice, agreement with thin film of isovaline:

Takahashi J.-I. et al., 2009, Int. J. Mol. Sci., 10, 3044

FDP *et al., MNRAS 2014*

CD on molecular units as extracted from the solid matrix (OEP-EXX)

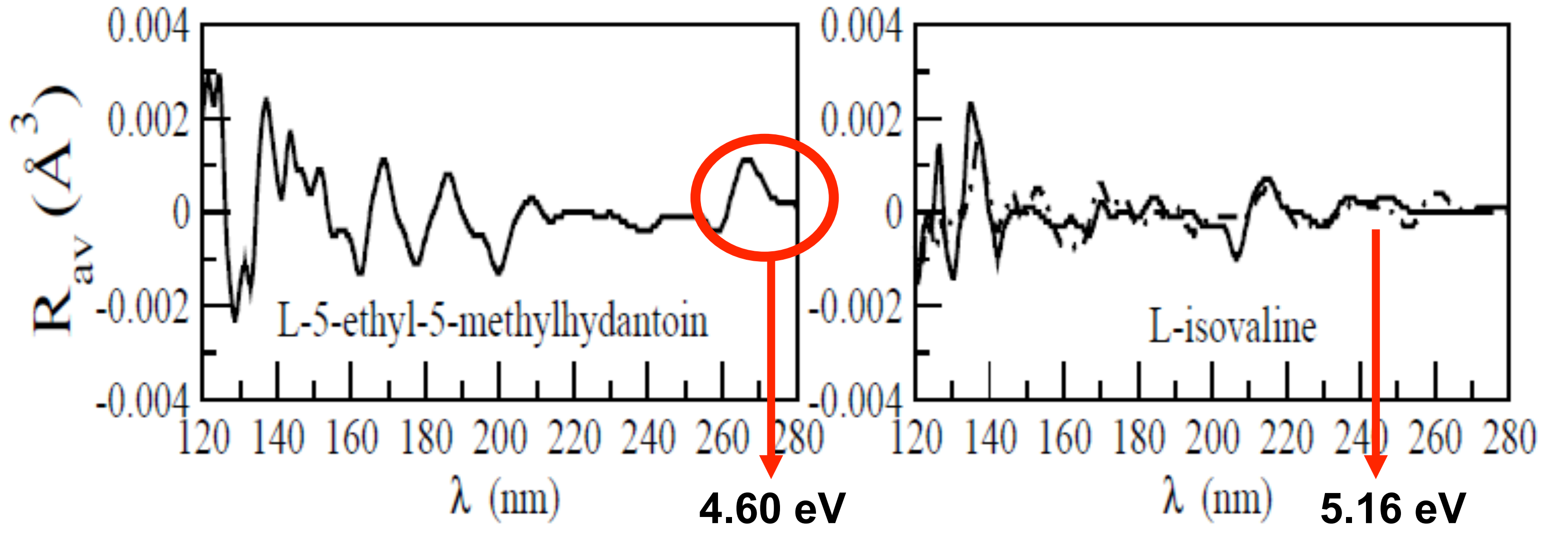




Big difference between gas-phase and "solid state" molecule

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

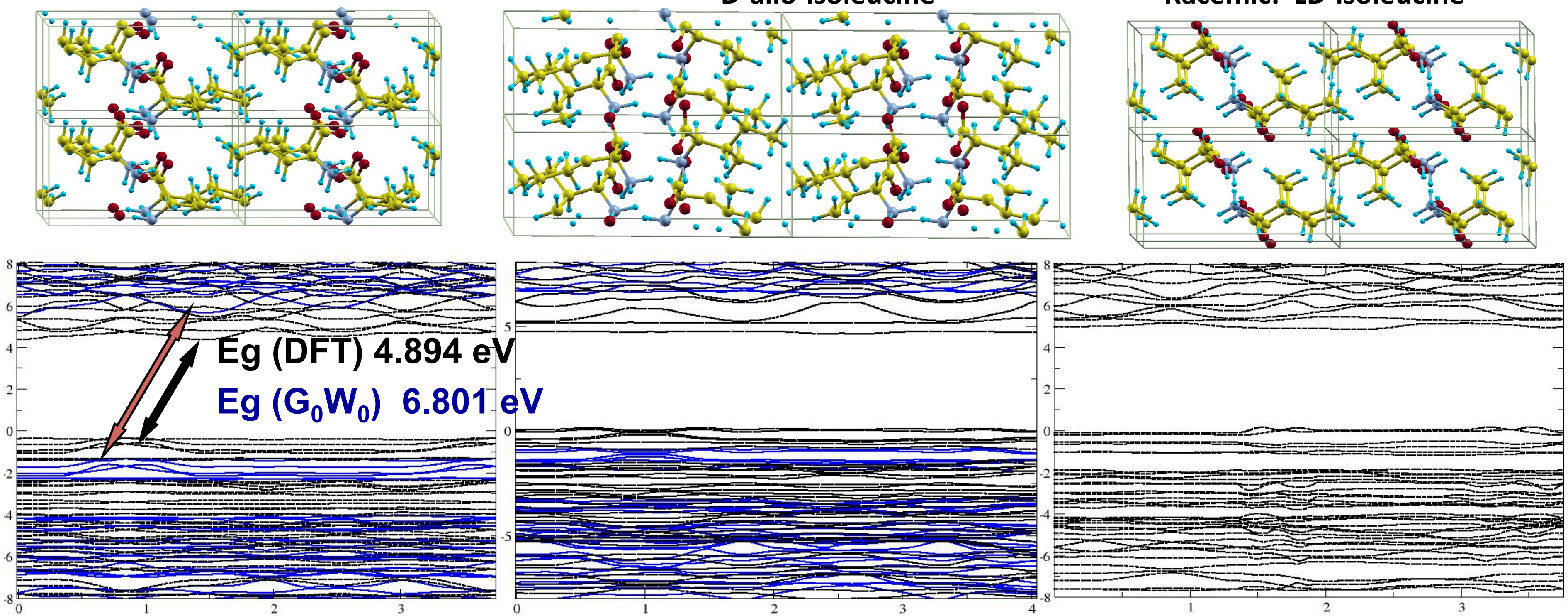
The VUV region is characterized by stronger CD

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

FDP *et al., MNRAS 2014*

Future: the Isoleucine serie

L-isoleucine — D-allo-isoleucine — Racemic: LD-isoleucine



Very little dispersion

E_g = 4.894 eV — E_g = 4.697 eV — E_g = 4.831 eV

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

	L-isoleucine	D-allo-isoleucine	Racemic: LD-isoleucine
DFT-GGA	4.894 eV	4.697 eV	4.831 eV
G0W0	6.801 eV	7.412 eV	7.256 eV
TB-mBJ	6.307 eV	6.818 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:

ABINIT : ***X. Gonze, B. Amadon, P.-M. Anglade,et al., Comp. Phys. Commun. 180, 2582 (2009)***

WIEN2K: ***K. Schwarz, P. Blaha:, in: "Practical Aspects of Computational Chemistry I", Springer Science, ISBN: 978-94-007-0918-8, 191 (2012)***

OCTOPUS : ***X. Andrade et al., J. Phys. Cond. Matt. 24, 233202 (2012)***

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(b) propagate the TDKS wavefunctions

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

First-order Crank-Nicholson integration method

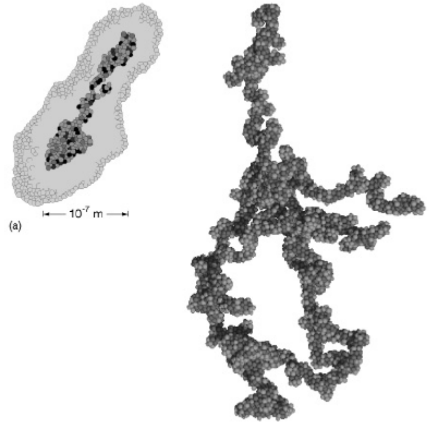
$$\left[\hat{S} + \frac{i}{2\hbar}\hat{H}(t)\Delta t\right]\psi_n(t+\Delta t) = \left[\hat{S} - \frac{i}{2\hbar}\hat{H}(t)\Delta t\right]\psi_n(t)$$

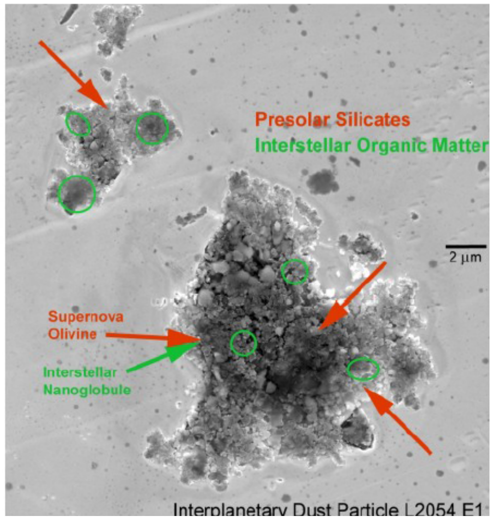
A x = b : solved by conjugated-gradient squared method (CGS)

Δt = 2 attosecond. Integration for 20 fs (→ 0.2 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?





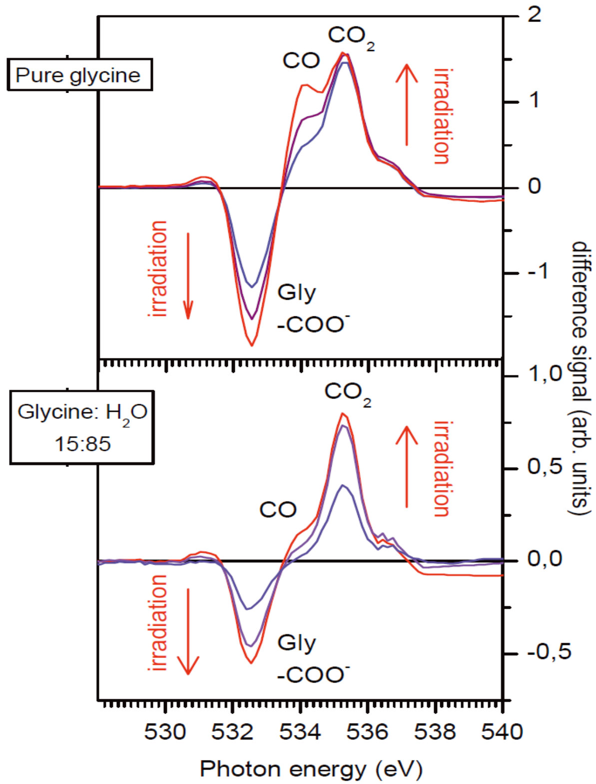
Above: fractal models for interstellar grains, with and without ice mantles.

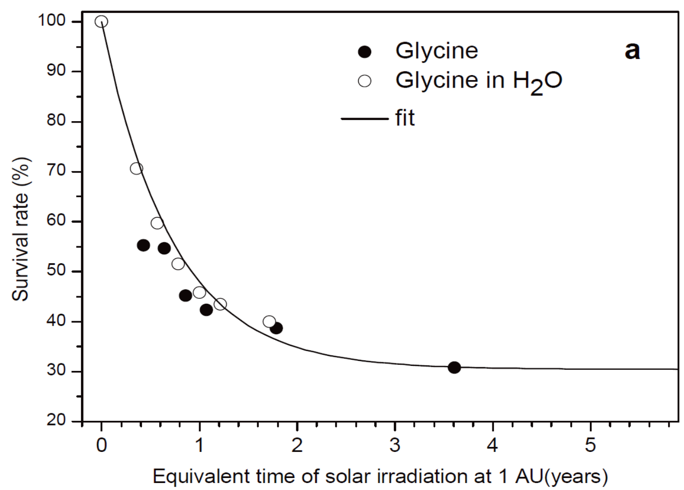
Right: presolar solids in an interplanetary dust particle.

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 ?***





- **TEMPO beamline, SOLEIL**
- ***A. Pernet et al,***
- ***Astronomy and Astrophysics 552, A100 (2013)***

CPL in Orion star formation region

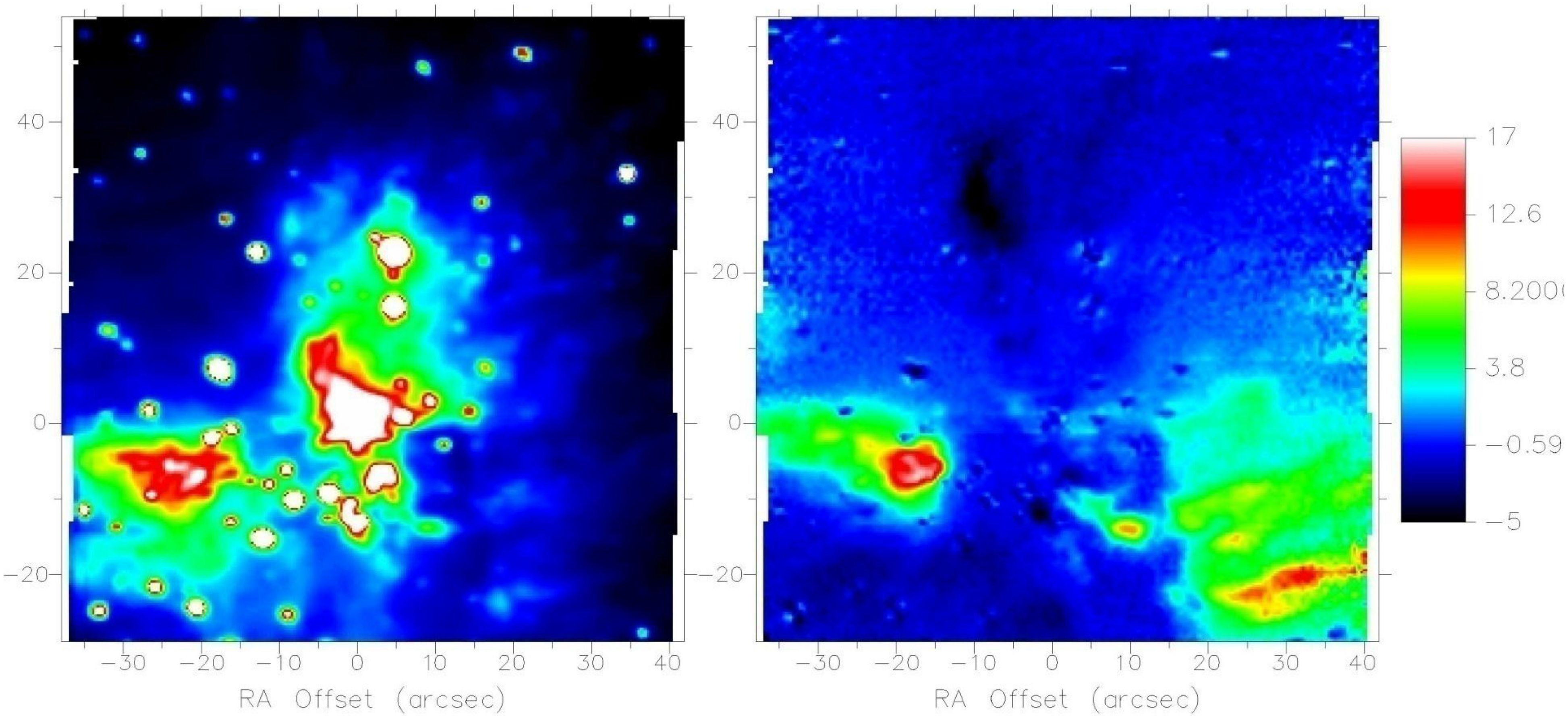


Fig.6: Circular polarization image of the OMC-1 star formation region in Orion at 2.2 µm. (Right) Percentage circular polarization ranging from – 5 % (black) to +17 % (white). Polarization accuracy ranges from about 0.1 % in the brighter regions to 1 % in the fainter regions. By convention, positive 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