Photolysis of *rac*-Leucine with Circularly Polarized Synchrotron Radiation

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Dedicated to *André Brack*

Amino acids that pass the RNA machinery in living organisms occur in L-configuration. The question on the evolutionary origin of this biomolecular asymmetry remains unanswered to this day. Amino acids were detected in artificially produced interstellar ices, and L-enantiomer-enriched amino acids were identified in CM-type meteorites. This hints at a possible interstellar/circumstellar origin of the amino acids themselves as well as their stereochemical asymmetry. Based upon the current knowledge about the occurrence of circularly-polarized electromagnetic radiation in interstellar environments, we subjected *rac*-leucine to far-UV circularly-polarized synchrotron radiation. Asymmetric photolysis was followed by an analysis in an enantioselective GC/MS system. Here, we report on an advanced photolysis rate of more than 99% for leucine. The results indicate that high photolysis rates can occur under the chosen conditions, favoring enantioselective photolysis. In 2014, the obtained results will be reexamined by cometary mission *Rosetta*.

Introduction. – The origin of cellular life [1], including the evolution of genes and enzymes, is based on biopolymers that are strongly selective towards the chirality of their monomer subunits [2]. Proteins are composed of amino acid monomers of L-configuration. The evolutionary origin of life's molecular asymmetry remains yet unanswered; one approach among others focuses on asymmetric interstellar phenomena inducing an enantiomeric excess (ee) into organic molecules by enantioselective photolysis or asymmetric synthesis. This hypothesis is supported by the fact that more than 16 different amino acids have been identified in simulated interstellar ices [2–4], and achiral glycine has been detected in a cometary dust sample returned by Stardust [5]. Besides, enantiomerically enriched amino acids [6–8] and *rac*-diamino acids [9] were found in CM type meteorites – a comprehensive summary of these amino acids can be found in [10] – and among them no chiral amino acid shows an excess of the D-enantiomer. Amino acids' asymmetry might have been induced by circularly-polarized (CP) electromagnetic radiation that has been detected in interstellar environments and star-forming regions [11][12]. These data and indications point towards the fact that biomolecular asymmetry might have been induced photochemi-

cally in interstellar amino acids long before these amino acids were delivered to the early Earth and triggered the origin of life on our planet [13][14]. Such a scenario will be probed (and challenged) in the near future since the Cometary mission *Rosetta* is designed to land on a comet nucleus in 2014 and should analyze cometary ice *in situ* [15]. The COSAC (Cometary Sampling and Composition) instrument aboard *Rosetta*'s Lander will focus on the enantioselective analysis of chiral organic molecules including amino acids by the application of a *Chirasil*-L-*Val*, a *Cyclodextrin G-TA*, and a *Chirasil-Dex CB* stationary phase [2]. The COSAC experiment is a combined GC/MS aboard the Philae cometary surface probe of the *Rosetta* Lander.

To better understand a possible photochemical origin of biomolecular asymmetry, we studied *a*) the asymmetric formation of amino acids [16][17] and biological cofactors [18] under interstellar conditions using CP light, and *b*) the asymmetric photolysis of amino acids subjected to CP electromagnetic radiation at the synchrotron SOLEIL. Here, we report on recent experiments subjecting the amino acid *rac*-leucine to CP synchrotron radiation [19] in the far-UV. It is well-known that due to the chiral interaction with a 'chiral' CP photon, the enantiomers have different absorption cross sections at certain wavelengths resulting in a non-zero circular dichroism (CD) $\Delta\varepsilon = \varepsilon_{\text{L-leucine}} - \varepsilon_{\text{D-leucine}}$, whose intensity varies with the photon energy. The chosen photon energy was higher than the leucine dissociation energy, and, therefore, an absorbing leucine enantiomer will undergo photodissociation, mainly by decarboxylation. An increasing photolysis rate will induce an increase in ee in the remaining non-photolyzed leucine sample [20] following a hyperbolic tangent function given in [21]. The optical yield is moreover dependent on the optical anisotropy factor $g = \Delta\varepsilon / \varepsilon$. The aim of the present study was to induce photolysis rates of 99% and above in leucine at a wavelength that corresponds to a large CD value. Irradiation experiments were performed on solid-state samples at irradiation wavelengths below 200 nm. CD Measurements show remarkably high values in this region [22], much higher in fact than above 200 nm in aqueous solution. We assume moreover that our amorphous leucine samples better represent the occurrence of amino acids under interstellar conditions than the previously studied aqueous solutions [23][24] or a microcrystalline phase [22].

Results and Discussion. – By using an ultra high vacuum (UHV) sublimation chamber, an amorphous L-leucine sample of 150-nm film thickness was deposited onto a MgF_2 window by heating the leucine reservoir to 132° for 16 min at 10^{-8} mbar. VUV/CD spectra of this film were recorded between 130 and 330 nm at the Institute for Storage Ring Facilities, University of Aarhus, Denmark, using the synchrotron beamline UV1 at the ASTRID storage ring. The obtained CD spectrum is given in *Fig. 1*. As expected, it depicts an interesting CD signal below 200 nm: a positive band at 184 nm and a negative band at 163 nm noticeably different from the solid state CD spectrum recorded from microcrystalline D-leucine reported in [22].

A first preliminary test of enantioselective photolysis at beamline DESIRS of the synchrotron SOLEIL was performed to determine the dimensions of the *rac*-leucine film, the obtained photon transmission, the optical density, the alignment of the setup *etc*. To this end, an amorphous film of *rac*-leucine with 2.0 mm × 5.4 mm lateral dimensions and a thickness of 987 nm was condensed onto a MgF_2 window using the

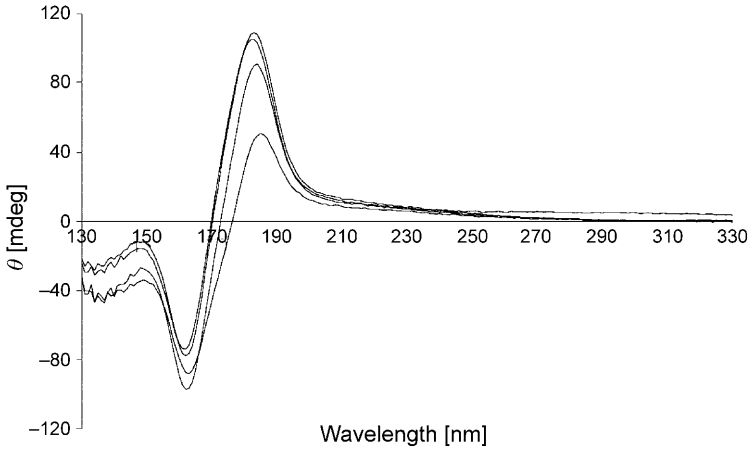

Fig. 1. *VUV CD spectra of an amorphous* L*-leucine film of 150-nm thickness recorded at the synchrotron facility ISA, University of Aarhus, Denmark.* To avoid contributions to the signal from VUV birefringence and linear dichroism, the sample was rotated around the light axis in steps of 90° leading to the four visible traces. CD spectra of D-leucine show signals of opposite sign. Signal is given in millidegrees of ellipticity θ, which can be converted to circular dichroism by the equation θ [mdeg] = 3298.2 $\Delta\varepsilon$.

UHV sublimation chamber in which the amino acid reservoir was heated to 145° for 50 min. Under inert conditions, this sample '*A*' was taken out of the sublimation chamber and immediately installed in the UHV irradiation chamber. It was subjected to right CP synchrotron radiation of 181 nm (6.85 eV). The footprint of the synchrotron radiation was 2.5 mm × 6.75 mm and thus larger than the deposited leucine film. During the first hours of irradiation, the transmission monitored by a photodiode downstream of the irradiation chamber increased as expected due to photolysis of the amino acid. Then, as assumed, the transmission normalized to the beam current reached a quasi-constant value. After 17 h, irradiation was stopped; the remaining leucine was extracted with ultra-pure H_2O and derivatized to form a volatile (ethoxycarbonyl)leucine ethyl ester (Leu-ECEE) derivative [25]. The D,L-Leu-ECEE enantiomers were separated on a *Chirasil*-L-*Val* stationary phase and individually quantified in the single-ion monitoring mode on mass trace *m*/*z* 158 using a GC/MS system *Agilent 6900*/*5973* setup at the synchrotron facilities. With the help of an additional non-irradiated 981 nm *rac*-leucine film that had been sublimated for 52 min at 145°, extracted, derivatized, and analyzed identically, a total photolysis rate of 84.6 ± 0.5% was determined for sample *A*. Sample *A* and the non-irradiated sample were alternately injected eight times to minimize the error in photolysis rate and ee determination. An ee value of 0.0 ± 0.5% was found (see also *Table*).

For sample *B*, a 301-nm film of *rac*-leucine was prepared by 13-min sublimation at 145°. At the synchrotron, sample *B* was irradiated with right-handed CP synchrotron radiation at 187 nm (6.63 eV) for 55 h. The circular polarization rate of the synchrotron radiation was *ca.* 99%. The wavelength was slightly increased compared to sample *A* in order to better match the maximum of the CD spectrum (*Fig. 1*), and to avoid

Table. *Photolysis Rates and ee Values of Leucine Samples Obtained by Enantioselective Photolysis Applying CP Synchrotron Radiation*

Sample	Film thickness [nm]	Irradiation time [h]	Circular polarization	Photolysis rate [%]	ee L-leucine
A	987	17	right	84.6	0.0
B	301	55	right	99.23	5.2
C	300	56	left	99.875	–[a])

[a]) The amount of remaining amino acid was too low to precisely determine the ee.

irradiation at a wavelength close to a zero CD value. After comparison with a non-irradiated *rac*-leucine sample of 300 nm that was deposited for 22 min at 145°, a total photolysis rate of 99.23% was obtained for sample *B* as depicted in *Fig. 2*. An ee value of $5.2 \pm 0.5\%$ of the D-leucine enantiomer was recorded in the remaining leucine film (*Fig. 3*). This is to date the highest reported ee value introduced in an amino acid by means of photochemistry. It is in accordance with theoretical predictions of *Kagan et al.* who calculated an ee of 4.6% for a photolysis rate of 99.0% on the basis of an anisotropy factor of $g = 0.02$, typical for amino acids under the chosen conditions [21]. The measured ee value of 5.2%, however, needed to be confirmed by irradiation of a *rac*-leucine film with opposite-handed synchrotron radiation.

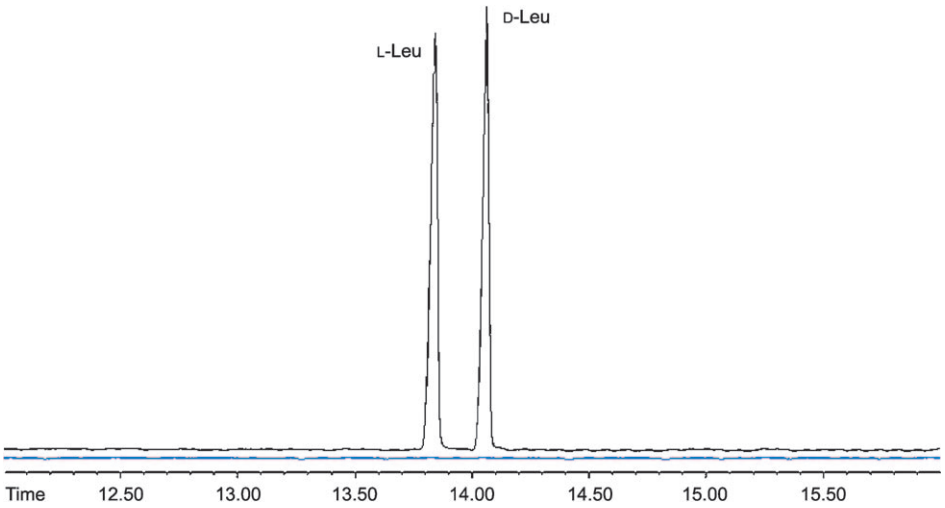

Fig. 2. *Enantioselective gas chromatogram of sample* B (blue line). The upper black line represents the chromatogram of the non-irradiated *rac*-leucine sample illustrating the photolysis rate of 99.23%. In sample B (blue line) the ee value was determined. Leucine enantiomers were extracted with H_2O and derivatized to form (ethoxycarbonyl)leucine ethyl ester (ECEE) prior to GC analyses.

Sample *C* was sublimated for 18 min at 145° giving a 300-nm film of *rac*-leucine. Sample *C* was irradiated for 56 h with the opposite-handed light, *i.e.*, left-handed CP synchrotron radiation at 187 nm, also CP at 99%. Our strategy was again to obtain a high total photolysis rate with the opposite ee in the remaining amino acid residue. In

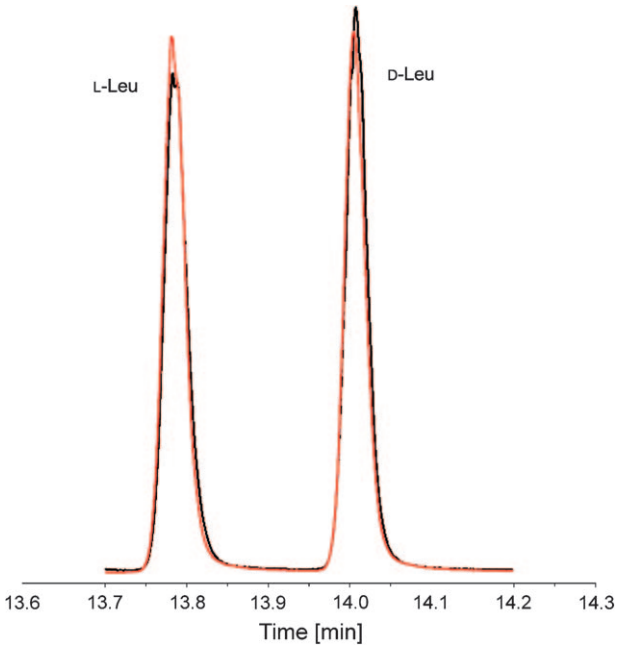

Fig. 3. *Overlaid enantioselective gas chromatograms of baseline-separated leucine enantiomers in sample* B (black line) *and in the diluted non-irradiated racemic sample* (red line). For each chromatogram, four samples that were analyzed alternately were averaged. Sample *B* shows an ee value of 5.2% of the D-enantiomer compared to the non-irradiated sample. Leucine enantiomers were extracted with H_2O and derivatized to form (ethoxycarbonyl)leucine ethyl ester (ECEE) prior to GC analyses.

sample *C*, we recorded a photolysis rate of 99.875 $(+0.125-0.5)\%$. The ee value however, proved difficult to determine, since the accuracy and precision of the applied enantioselective GC/MS method is dependent upon the amount of sample reaching the detector, considering that, after irradiation, the remaining amino acid film is even thinner than a monolayer. As expected, the standard deviation increases with decreasing sample quantity. Even after tweaking various GC/MS instrument parameters such as threshold values, solvent trapping, and others in order to determine the ee value of sample *C* with high precision, the standard deviation of 5% in the ee determination of this sample remained higher than the obtained ee. In summary and after a multitude of enantioselective analyses, we cannot establish that an opposite significant ee was induced into sample *C*. For future analyses, an enantioselective multidimensional GC × GC system will be applied providing higher sensitivity and improved detection limits. Here, the combination of a *Chirasil*-L-*Val* phase in the first dimension with a *Carbowax* phase in the second dimension will allow both the high-resolution chromatographic separation of enantiomers in the first dimension and the separation of matrix, such as solvent and column bleeding, from the amino acid enantiomers in the second dimension. For this application, the GC × GC technique provides higher signal-to-noise ratios and thus more precise ee measurements.

Promising results obtained for the amino acid leucine in terms of high photolysis rates allow us to assume that asymmetric interstellar photochemical processes might have initiated the origin of molecular asymmetry manifested in living organisms. The obtained results let us envisage future experiments that will include the amino acid isovaline which is dialkylated at C(α). Isovaline has been identified in various meteorites with high ee values of the L-enantiomers [6], but also in many fungal peptides [26–28]. Isovaline is predicted to be more inert against potential photo-racemisation reactions. For upcoming experiments, the amino acid films' irradiation chamber will be installed closer to the focal point of the DESIRS beamline so that a higher photon/molecule ratio is reached in order to shorten irradiation times (ideally 10–15 h per sample).

Cometary mission *Rosetta* has been designed to deposit the Lander Philae on comet *67P/Churyumov-Gerasimenko* in 2014 aiming to enantioselectively analyze organic molecules including amino acids in cometary matter *in situ* [2][15][29–34]. A comet nucleus sample return mission was also proposed recently [35]. Expected results on the occurrence of amino acids including an eventual ee value will further elicit whether or not interstellar photochemistry might have induced an asymmetry in biomolecules which was possibly required for the origin of life on Earth.

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Experimental Part

The amino acid sublimation chamber is equipped with an amino acid sublimation source, a quartz microbalance and a holder for the MgF_2 substrates onto which the amino acids are re-condensed (*Fig. 4*). Two types of MgF_2 substrates can be fitted. Either a disc with a diameter of 22 mm, which can be used for synchrotron radiation CD measurements, or a 5×8 mm rectangular substrate, which can be used for photolysis experiments. The rectangular substrate is fitted with a *Teflon* and a Cu mask allowing for the deposition of a 2.0×5.4-mm film. In the sublimation source, the amino acids are filled into a cylindrical 19-mm^3 quartz reservoir which fits inside a metal cylinder. The metal cylinder is resistively heated with a *ThermoCoax* heater (*ThermoCoax S.A.S.*, France) and the temp. is measured with a K-type thermocouple. The sublimation source is mounted on a 1″ retractable bellows, allowing the source-substrate distance to be controlled. An integrated shutter allows opening and interrupting the amino acid flow precisely. The rate of amino acid re-condensation (as an area density change rate) can be monitored by a 5-MHz quartz crystal microbalance (QCM) using an *Inficon-Maxtek 5* silver-coated quartz crystal, mounted on a 2″ retractable bellows. The QCM can be inserted between the source and the MgF_2 substrate before and after sublimation to measure the mass flow rate. Typical deposition rates of the amorphous amino acid films are 10–20 nm min^{-1}, and the error in the leucine film-thickness determination is 5 nm. The UHV vacuum chamber is pumped by a *Varian Turbo-V 81M* turbo pump, backed by a *BOC Edwards XDS 10* scroll pump. The pressure is monitored by a *Balzer Compact Full Range* gauge.

VUV CP Synchrotron radiation was produced by the electromagnetic polarizing undulator *OPHELIE2* (*HU640* type) [36] installed on the French storage ring SOLEIL, feeding the DESIRS beamline [37], whose monochromator was set to zeroth order in order to transmit the full spectrum of the fundamental radiation on the undulator. Such a spectrum has a 7% relative bandwidth around a central photon energy which can be tuned over the whole VUV range (5–40 eV). Absolute circular polarization rates, carefully measured and calibrated with a dedicated VUV polarimeter [38], vary from 90 to 100%

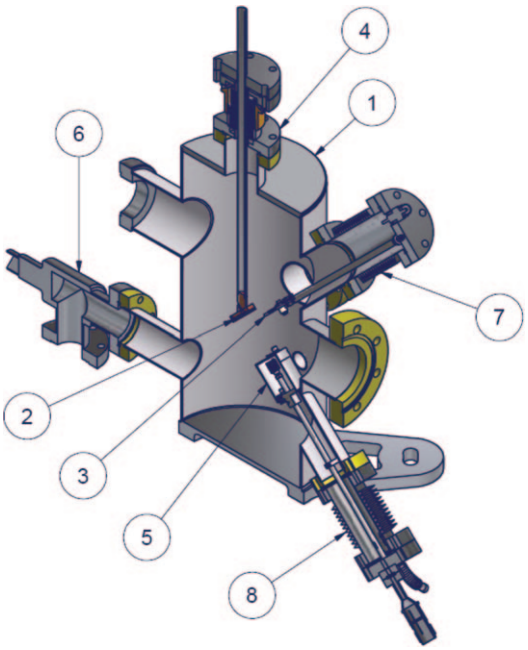

Fig. 4. *Temperature- and pressure-controlled ultra high vacuum (UHV) system for sublimating and re-condensing amino acids designed and constructed at the synchrotron facility ISA, University of Aarhus, Denmark. 1:* UHV chamber, *2:* MgF_2 crystal holder, *3:* QCM, *4:* manipulator, *5:* temperature-controlled reservoir for amino acids, *6:* UHV pump, *7:* QCM support, and *8:* reservoir support.

over the 6 to 35 eV range. Note that high harmonics of the undulator were cut-off by a gas filter [39] filled with Xe. Detailed enantioselective GC/MS conditions were reported in [4][22][25].

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