Photodissociation Dynamics of Tryptophan

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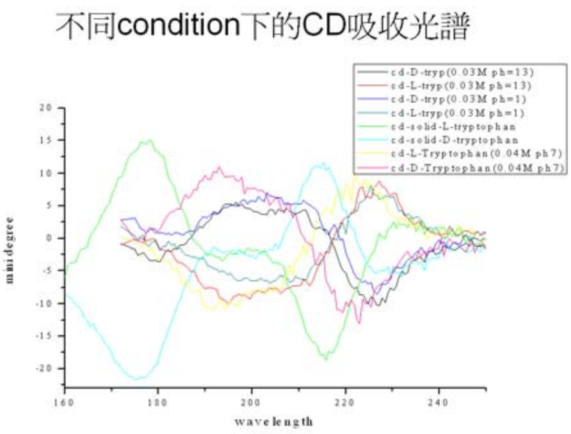
Life uses only L enantiomers of amino acids to form proteins, and D enantiomers of riboses for DNA and RNA. The origin of this property, called biomolecular homochirality, has been a puzzle since it was discovered in the 19th century. A number of processes have been proposed to produce enantiomeric excess (1,2), including the action of circular polarization light (CPL) from daylight sky, the effects caused by the parity-violation aspect of the electroweak interaction, and the extraterrestrial mechanism. The difficulty with any proposed Earth-based mechanism (2) and the discoveries of enantiomric excesses of L-amino acids in the Muchison and Murray meteorites (3-5) as well as the observation of CPL in start formation region (6) support the extraterrestrial mechanism.

The excesses of L-amino acids in these meteorites range from several per cent up to 15%. Engel and Macko (4) suggested the possibility that the amino acid excesses "may have resulted from the alternation of initially abiotic, racemic mixtures by a process such as preferential decomposition by exposure to circularly polarized light.' The excess can be increased by increasing the fraction of material photolyzed, but it will be reduced in proportion to the CPL for circularization of less than 100%. They are not though to have produced completely by asymmetric photolysis, since the circular dichroism of the amino acids is too small to produce such a large excess without dissociating >99% of the molecules. However, it is very possible that asymmetric photolysis introduces a smaller enantiomeric excess, which is then amplified by another physical or chemical mechanism. Experiments performed with CPL and elliptically polarized light (EPL) in laboratory on racemic leucine in solution at single wavelength (212.8 nm) showed that polarized light induces asymmetric photolysis.(7-8) Enantiomeric excess (e.e.) from 1.98 to 4.68% with CPL and from 2.56 to 3.88% with EPL were observed from photo-decomposition..

Mason (9-12) has recently criticized the CPL explanation of Engel and Macko, claiming that since the circular dichroism bands of an optically active molecule alternate in sign along the wavelength axis, they cancel one another over the entire spectrum due to the Kuhn-Condon zero sum rule (13-14), thus white CPL like sunlight cannot effectively discriminate between enantiomers. However, Bonner (14) argues that even though the CD bands of a chiral molecules do alternate in sign and their rotational strengths taper off and sum to zero over the entire spectrum, it does not follow that an enantioselective photochemical effect caused by CD at one photochemically active wavelength will necessarily be cancelled by an opposite CD at a different wavelength. This is simply because photochemical reactions are wavelength dependent. As a result, it is necessary to understand the photochemical reactions for different CD bands in order to find out whether broadband CPL is relevant for enantioselective photochemistry.

We plan to investigate this problem by measuring the VUV absorption spectrum and CD spectrum of amino acids, and then study the photodissociation mechanism for each electronic state. Figure 1 shows the tryptophan UV absorption spectrum and CD spectrum measured in SRRC. In the future, photodissociation study will be performed in IAMS, Academia Sinica. The combined data will publish in the near future.



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