Asymmetric Scattering of Polarized Electrons by Organized Organic Films of Chiral Molecules

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Electron transmission experiments demonstrate a large asymmetry in the scattering probability of polarized electrons by thin organized films of chiral molecules. This large asymmetry results from the interaction of the electron's wavefunction with many scatterers (molecules) in the organized monolayer structure and represents a manifestation of quantum interference on the scale of supramolecular lengths.

Since the time of Pasteur (*1*), the presence of chirality in nature and enantiomeric selectivity in chemical and physical processes has intrigued the scientific community. Although enantiomeric selectivity is well established for optical interactions (for example, circular dichroism), such selectivity in electron molecule interactions is less well established. We describe experimental results that demonstrate a large asymmetry (of the order unity) in the scattering probability of polarized electrons by thin organized films of chiral molecules. The large asymmetric scattering occurs despite the fact that the molecules used are simple amino acids and not molecules specially designed to exhibit large spin-orbit coupling, as was the case in recent gas-phase scattering experiments (*2, 3*). The data show that the large enhancement in the asymmetry (10^3 to 10^4 times larger than observed in molecular vapors) results from the interaction of the electron's wavefunction with many scattering centers (molecules) in the organized monolayer structure.

The scattering of low-energy electrons from chiral molecules in the gas phase has been the subject of many theoretical and experimental studies (*4–12*). The asymmetry in electron molecule scattering may be characterized by an asymmetry parameter A,

$$A = \frac{I(+) - I(-)}{I(+) + I(-)} \qquad (1)$$

where $I(+)$ and $I(-)$ are the intensities of the electron beam whose spin angular momentum is oriented parallel (+) and antiparallel (–) to its velocity vector. Recently, an asymmetry in the scattering was observed for a gas composed of camphor lanthanoid (Yb, Eu, Er, Pr) complexes (*2, 3, 13*). Although these molecules were designed to display a large asymmetry, A was found to be only 10^{-4} over an electron energy range of 0.5 to 10 eV. Theoretical studies (*9, 12*) indicated that scattering of spin-polarized electrons from oriented molecules should result in larger asymmetry parameters.

We determined the scattering asymmetry by measuring the transmission of polarized and unpolarized photoelectrons, which were ejected from a Au substrate, through Langmuir-Blodgett (LB) thin films deposited on the Au (*14*). The LB films consist of either L- or D-stearoyl lysine $[(CH_3(CH_2)_{16}C(O)NH(CH_2)_4CH(NH_3^+)CO_2^-]$. Three film assemblies, each containing five monolayers, were used in this study: (i) all molecules had the same handedness (5L or 5D layers), (ii) three monolayers of one handedness were followed by two of the other (3L2D or 3D2L), and (iii) one layer of L (or D) handedness was followed by two of D (or L) handedness and then two of L (or D) handedness (1L2D2L or 1D2L2D). The amphiphilic α-amino acids (stearoyl lysine) were deposited as Z-type LB films (*15*) and then transferred to a glass microscope slide that was coated with a Au film 100 nm thick. For each film type, the grazing angle Fourier transform infrared (FTIR) spectrum was measured. The ratio between the absorption peak at about 2920 cm^{-1} ($-CH_2$ asymmetric stretch) and the peak at 2852 cm^{-1} ($-CH_2$ symmetric stretch) provides a measure of the film order and the orientation of the organic chain relative to the surface (*16*). It was found to be similar for the different samples, indicating the same conformational structure for all films (Table 1). This observation indicates that the geometric difference between the two enantiomers is localized about the carbon center and does not modify the film's structure in a significant way. We conclude that the differences observed in the energy distribution of the photoelectrons for the different samples (see below) are not attributable to changes in the order or packing of the monolayer, but rather are correlated to the local change in geometry of the asymmetric carbon unit.

The Au slides coated with the monolayers were inserted into an ultrahigh vacuum chamber that was pumped to a pressure of $<10^{-4}$ Pa. Polarized photoelectrons were ejected from the substrate using a laser beam at 247- nm wavelength that was produced by mixing the output from a frequency-doubled Nd:Yag pumped-dye laser (320-nm wavelength) with the Nd:Yag (Nd: yttrium-aluminum-garnet) laser fundamental (1064-nm wavelength) and using a λ/4 plate to create either left- or right-handed circularly polarized light. It is known that circular polarized light induces spin polarization in the ejected photoelectrons, whereas linearly polarized light at normal incidence does not (*17–19*). An earlier study (*18*) found that the polarization of the photoemitted electrons from Au was positive (spin vector parallel to the electron's velocity) when the photon was right-handed circularly polarized and that the polarization ranged from 5% for photoelectrons with kinetic energy of 0 eV to 15% at 2 eV. Unpolarized photoelectrons were ejected, using linearly polarized light at either 193 nm or 247 nm. After they had passed through the film, the kinetic energy of the electrons was measured using a time-of-flight electron energy spectrometer.

The transmission of unpolarized photoelectrons as a function of the photoelectron kinetic energy (Fig. 1) and the relative quantum yields of photoelectrons (Table 1) show that the electron transmission probability is higher through films composed of identical

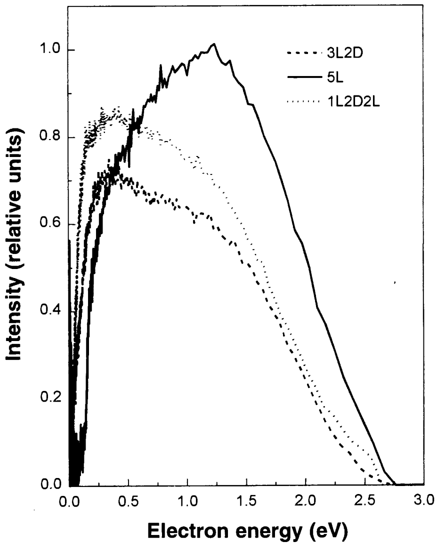

Fig. 1. Electron energy distribution for the transmission of unpolarized photoelectrons for three layer types.

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monolayers (5L and 5D). The similar yield for the 5L and 5D layers is consistent with an unpolarized initial electron beam. The transmission efficiency through the 1D2L2D monolayer structure is similar (*20*) to the transmission through the 3D2L film (Table 1). These results indicate that the number of L- to D-monolayer interfaces does not control the transmission probability.

The unpolarized electron beam, which is generated from the Au by the linearly polarized light, may be viewed as an equal combination of two spin-polarized beams $[I_0(+) = I_0(-) = I_0/2]$ that have different interactions with the layer. According to the bound helical electron model (*4*), the predominant contribution to the asymmetry in the electron scattering cross sections arises from the spin-orbit interaction. For chiral molecules, the combination of unequal perturbation of the spin orbitals and the asymmetry of the spatial wavefunctions results in chiral electron scattering and a net helicity. The asymmetry can be expressed as

$$X = \frac{\sigma_+ - \sigma_-}{\sigma_+ + \sigma_-}$$

where σ_+ and σ_- are the total cross sections for a "spin up" electron to be scattered from L and D molecules, respectively. For a "spin down" electron, the same values are expected for the cross sections, but in the reverse order.

In order to estimate the cross sections, we shall assume that the transmission depends only on the attenuation factor and has no phase component (*13*). This approximation does not account for orientational effects in the scattering (*11*). The intensity of the beam after one layer is given by

$$I = I_0(+)\exp(-\sigma_+N) + I_0(-)\exp(-\sigma_-N) \qquad (2)$$

where the number density of molecules in a monolayer is $N = 4 \times 10^{14}$ molecules/cm^2 and $I_0(+)$ and $I_0(-)$ are the initial intensities of the electron beam polarized parallel and antiparallel to the velocity vector, respectively. Using the quantum yield data for the unpolarized transmission through the three different monolayer assemblies, the difference in scattering cross-sections (δ) is found to be $\delta = |\sigma_+ - \sigma_-| = 8 \times 10^{-16} \pm 1 \times 10^{-16}$ cm^2. Determination of the individual cross sections from Eq. 2 requires knowledge of the absolute quantum yield. Although not measured explicitly here, they can be estimated by comparison to the photoemission yield on bare Au surfaces (*21*). Using a quantum yield of 0.61 for the 5L layers, cross sections of 1.7×10^{-16} and 9.7×10^{-16} cm^2, and $|X| = 0.7 \pm 0.2$ are found. The magnitude of $|X|$ depends weakly (logarithmically) on the choice of quantum yield. For example, a decrease in the quantum yield by a factor of 8 would reduce $|X|$ by a factor of 2. These parameters characterize the asymmetry in the electron molecule scattering on a "per molecule" basis.

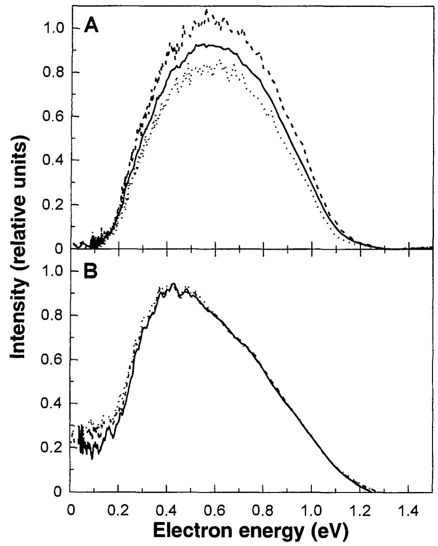

Fig. 2. Electron energy distribution for five layers of L-stearoyl lysine (**A**) and for a five-layer structure in which the monolayers were 99% L-stearoyl lysine and 1% D-stearoyl lysine (**B**). The photoelectrons were ejected with linearly polarized light (solid line), right-handed circularly polarized light (dashed lines), and left-handed circularly polarized light (dotted lines).

The transmission of polarized electrons through five layers of L-stearoyl lysine show an increased yield of photoelectrons when right-handed circularly polarized light is used for the photoemission, as compared to the yield when left-handed circularly polarized light is used (Fig. 2A). The energy distribution of the photoelectrons retains the same general shape when the polarization of the light is changed. If right-handed circularly polarized light creates positively polarized electrons (*18*), then a film containing L-type molecules transmits positively polarized electrons more efficiently than negatively polarized electrons. A film composed of five D-layers displays the opposite behavior—as expected for a change in the sense of electron polarization with a change in the sense of light polarization.

The value for δ, obtained from the data in Fig 1, can be considered with the transmission yield data from Fig. 2A to determine the initial polarization that is generated by the circularly polarized light. We obtained a polarization of 18% for the photoelectrons emitted from the Au by the circularly polarized light, in reasonable agreement with earlier work (*18*). Using this value of the polarization, we computed an asymmetry factor $|A|$ of 0.12, which is 10^3 larger than that reported in gas-phase studies (*2, 3, 13*).

The electron energy distributions were also determined for a sample containing five layers of L-stearoyl lysine that had each monolayer doped with a 1% impurity of D-stearoyl lysine. The FTIR data (Table 1) show that this level of dopant did not modify the film structure. The energy profiles reveal no dependence of the transmission yield of photoelectrons on the polarization of the light (Fig. 2B). This low level of impurity would not have such a large effect on the asymmetry if the electron molecule scattering in the layer could be treated as incoherent. In such a case, a reduction in the asymmetry of only 5% for five layers would be expected. However, if the asymmetric scattering requires the coherent interaction of the electron wavefunction with many molecules (scattering centers) in the layer, then the fluctuations of the electron molecule potential that are introduced by the impurity can dephase the electron wavefunction and reduce the asymmetry. The significant increase in the number of low-energy electrons in Fig. 2B, as compared to Fig. 2A, illustrates the increase in scattering for the doped monolayers.

The enhanced scattering of one electron spin polarization over another by a chiral layer is related to the intrinsic structure of monolayer films. First, the low-energy electrons used in this study are at energies close to known resonances of the electron film system (*22*). These resonances should reflect the underlying chirality in the molecules and are expected to enhance the asymmetry factor. Second, the molecules in the films are aligned with respect to the electron source. This alignment restricts the angular averaging and may enhance the effect (*12*). Finally, the slow electrons we used have a

Table 1. Relative electron quantum yields and infrared spectral ratios for different monolayer assemblies. The relative electron quantum yields Φ are scaled to 1 for an unpolarized beam passing through a 5L layer. The error in the quantum yields between samples is estimated to be 5 to 10%, whereas the error in the quantum yield as a function of polarization within a given sample is 1%.

Parameter	5L	5(99% L;1% D)	5D	3D2L	3L2D	1D2L2D	1L2D2L
I_{asym}/I_{sym}	3.7	3.7	3.3	3.1	3.5	3.1	3.5
Φ (193 nm)	1	–	1.05	0.59	0.67	0.70	0.79
Φ (247 nm)	1	1.05	1.07	–	0.69	–	0.82
	1.11(+)	1.05(+)	0.92(+)				
	0.89(–)	1.05(–)	1.21(–)				

long wavelength (a 0.5-eV electron has a wavelength of about 2 nm) and may therefore interact coherently with a large area of the monolayer (*21*), hence, many chiral centers. This last effect is evident in the rapid loss of asymmetry when the monolayer film has a 1% dopant of its enantiomer. The results in Fig. 2B suggest that the latter effect is dominant for this system.

Two important implications of our results are sketched here. A solid substrate coated with a thin layer of chiral molecules could be used to generate highly polarized electron beams. For example, after an unpolarized beam of electrons transverses five layers of L-stearoyl lysine, it will contain twice as many "spin up" electrons as "spin down" ones. The second implication relates to the origin of chirality in nature. Early studies of the asymmetry in electron scattering from chiral molecules was motivated by the suggestion (*23*) that chiral asymmetry may arise through the preferential destruction of one enantiomer in a racemic mixture by spin-polarized electrons produced in β decay (*24*). Our results suggest that the electron mechanism for generating chiral asymmetry in nature may be viable if the molecules are oriented by adsorption or other means at an interface. In such structures, the enhanced asymmetry in the electron molecule scattering cross sections (compared with the gas phase) arises from cooperative phenomena related to the structure of monolayer films. It remains to be seen, however, if these asymmetric interactions can give rise to asymmetric chemical transformations.

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Self-Assembly of Flat Nanodiscs in Salt-Free Catanionic Surfactant Solutions

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Discs of finite size are a very rare form of stable surfactant self-assembly. It is shown that mixing of two oppositely charged single-chain surfactants can produce rigid nanodiscs as well as swollen lamellar liquid crystals with frozen bilayers. The crucial requirement for obtaining nanodisc self-assembly is the use of H^+ and OH^- as counterions. These counterions then form water and lower the conductivity to 10 microsiemens per centimeter. In the case of cationic component excess, a dilute solution of nanodiscs is in thermodynamic equilibrium with a lamellar phase. The diameter of the cationic nanodiscs is continuously adjustable from a few micrometers to 30 nanometers, with the positive charge located mainly around the edges.

Above the chain melting temperature, solutions of single-chain ionic surfactants self-assemble into micelles in water. A large number of stable shapes such as spheres, cylinders, and folded bilayers, but not flat finite discs, have been reported. If anionic and cationic surfactants are mixed (catanionic), the strong reduction in area per head group resulting from ion pairing induces formation of molecular bilayers at low concentrations. Thus, vesicles may form spontaneously. These vesicles are a thermodynamically stable state (*1*). The two counterions of the anionic and cationic surfactant form a dissociated salt. For a catanionic weight concentration of 5%, the resulting ionic strength exceeds 0.1 M. Vesicles as well as flexible cylinders have been identified and described in catanionic surfactant systems (*2, 3*). Because of the high ionic strength between aggregates, electrostatic repulsions are screened. The osmotic pressure of these aggregates is <100 Pa. In the absence of electrostatic repulsion stabilizing the system, the catanionic bilayers spontaneously form closed vesicles (*4*). Hoffmann *et al.* (*5*) have published a pioneering study of catanionic systems without excess salt; they have observed strongly repulsive charged cylinders of limited length.

Catanionic solutions described in the literature usually consist of five components, including the two counterions, with overall electroneutrality. The equilibrium-phase diagram at fixed temperature can then be represented in space in a tetrahedron containing the single-phase and multiple-phase regions (*6*). A highly stable colloidal solution requires a high osmotic pressure induced by unscreened electrostatic repulsions. This condition is met in pure catanionic surfactant solutions that contain only recombining H^+ and OH^- counterions plus counterions of the component in excess. In this case, the phase diagram can be approximated as a triangle, with only two degrees of freedom.

In this study, we obtained catanionic solutions by mixing myristic acid ($C_{13}H_{27}COO^-$-H^+) and the hydroxide-exchanged form of cetyltrimethylammonium chloride [$C_{16}H_{33}N$-$(CH_3)_3^+OH^-$] (*7*). Obtaining a pure carbonate-free surfactant solution requires the use of a glove box under nitrogen to avoid contact with atmospheric CO_2 (*7*). Near equimolarity, at a total surfactant content of 20 g/liter, the conductivity was on the order of 10 μS/cm, which corresponds to an ionic concentration on the order of 10 μM. The Debye screening length associated with this conductivity is about 100 nm, compared with 5 to 15 nm obtained with other counterions (*8*). The pH varied from 7

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