Konferenssin osanottajia Aulangon edustalla, vasemmalta tri Anthony Bullock, Aberdeen, dos. Franciska Sundholm, Helsinki, prof. Johan Lindberg, Helsinki, prof. Geoffrey Luckhurst, Southampton, prof Edward Janzen, Guelph, prof. Gerz Likthtenshtein, Moskova, tri Tadeausz Sarna, Krakova, prof. Jack Freed, Ithaca, rouva Geoffroy, (takana) Genéve rouva Freed, prof. M. Geoffroy, Genéve, tri Takahasi Doba, Tukholma, prof. Hayes Griffith ja hänen edessään Helinä ja Robert Brotherus, rouva Ulla Brotherus, tri David Matkin, Southampton, prof. Leonid Volodarski, Novosibirsk ja tri Alexander Wasserman, Moskova.

Ohjelmaan kuului viisi plenaariesitelmää, yksitoista luentoa ja kahdeksantoista posterjulkaisua. Plenaariesitelmät sisälsivät viimeisimpiä tuloksia nitroksidien sovellutuksista sekä biokemian, orgaanisen että fysikaalisen kemian aloilta.

Keskustelu ja ideoitten vaihto oli vilkasta luentojen ja posteresityksien yhteydessä. Koska kokouksen kaikki osanottajat olivat majoitettuina Aulangolla, virallisen ohjelman ulkopuolella käydyt keskustelut ja kanssakäyminen oli myös

antoisaa. Tärkeänä pidettiin henkilökohtaisten kontaktien solmiminen Atlantin takaa tulleiden kutsuvieraiden ja neuvostoliittolaisten välillä. Kehityskelpoisia yhteistyöaiheita löydettiin m.m. polymeerikemian ja nestekiderakennekemian alueilta. Koska näihin liittyviä tutkimuksia tehdään myös Suomessa kokous oli erittäin tärkeä kotimaisille osanottajille. Ilmoituksista huolimatta kotimaiset tutkijat eivät kuitenkaan käyttäneet tilaisuutta hyväkseen kuulla ESR-spektroskopian maailmanhuippujen esityksiä. Tämä on sitä valitettavampaa, koska matkakustannukset estänevät alan kokouksen järjestämistä Suomessa lähitulevaisuudessa.

Kokouksen järjestelytoimikuntaan kuului allekirjoittaneen lisäksi professori J. Johan Lindberg, apulaisprofessori Pertti Törmälä, ja edesmennyt dosentti Jaakko Brotherus. Järjestelytoimikunta on saanut taloudellista tukea Committee for EUCHEM Conferences:ltä, Neste Oy:n Säätiöltä ja Alko Oy:ltä. Lisäksi Kemira Oy järjesti illanvieton Aulangolla kaikille osanottajille. Näistä järjestäjät lausuvat parhaat kiitoksensa.

Osanottajilla oli ekskursiolla mahdollisuus tutustua Sibeliusmuseoon ja linnaan Hämeenlinnassa sekä Hattulan kirkkoon. Meillä oli myös ilo joukossamme nähdä rva Ulla Brotherus lapsineen.

Franciska Sundholm

Nitroxides and Chemical Physics

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The availability of stable nitroxide free radicals has proved a boon for the application of ESR to a number of fields in chemical physics.

We have been using small nitroxide spin probes for studying molecular dynamics in liquids, and have shown the kind of detailed information which one may obtain from ESR studies.[1,2] In general, we have been exploring experimental evidence for the breakdown of simple Brownian motional models for rotational reorientation. One particular problem we have considered is the limitation of the simple Stokes Law: $\tau_R^{SE} = 4\pi\eta a^3/3kT$ for the rotational correlation time τ_R. Our previous results have all been consistent with a linear relation between τ_R and η/T, although a variety of non-ESR experiments have implied deviations.[3,4] We have completed spin relaxation studies on the system perdeuterated tempone (PDT) in toluene as a function of both temperature and pressure[5] using previously reported methods,[6] and we have obtained systematic de-

viation between τ_R and τ_R^{SE} which could be represented in the form $\tau_R/\tau_R^{SE} = A - BT + CT^2 + DT/\varrho$, where ϱ is the density, and A, B, C, and D are constants independent of T and ϱ. These deviations represent the differences between the molecular details of reorientation and the hydrodynamic behavior of a Stokes-Einstein model. They appear to be inconsistent with recent molecular and hydrodynamic models. The very precise and detailed ESR results seem particularly useful for such studies.

An anomaly previously reported[1,2] viz. the breakdown of a Debye spectral density $j(\omega) = \tau_R/(1 + \omega^2\tau_R^2)$ for analyzing the ESR relaxation data was studied with PDT probe both as a function of solvent and of temperature and pressure.[5] We have found that the empirical form $j(\omega) = \tau_R (1 + \varepsilon\omega^2\tau_R^2)$ generally represents the experimental data well. A value of the empirical parameter $\varepsilon = 5.4$ previously found for PDT in toluene,[2] is found to remain constant independent of how a particular τ_R is obtained by varying both T and P

(*i.e.*$\tau_R = \tau_R(T,P)$ while ε is essentially independent of T and P). This encourages us in the belief that ε can be related to a fundamental property of the molecular dynamics such as is represented in a fluctuating torque model[2] or one of a slowly-relaxing local structure.[7] We have also found a good inverse correlation between ε and E_T (the molar transition energy scale), which is a measure of the solvent polarity.[8,9]

The study of molecular ordering and dynamics in liquid crystals is also important. We have completed a study of the isotropic-nematic and nematic-smectic A phase transitions using PDT in liquid crystal 40-6.[5] The critical exponent on the linewidth parameters B and C were again found to be $\gamma = -\frac{1}{2}$ as in our previous study on another liquid crystal.[10] This is consistent with Landau-de Gennes mean-field theory.[10] On the nematic side of the N-S_A phase transition, $\gamma = -\frac{1}{3}$, a result which is in direct contradiction to predictions of Brochard[11] in terms of order-director fluctuations and dynamic scaling. Our model to explain this is based upon the existence of small domains of local smectic organization (*i.e.* cybotactic clusters) just above this phase transition with finite lifetime, which will have greater nematic ordering and packing and is consistent with expelling the PDT out from the central aromatic region of the clusters.[8]

Recent work on viscous liquid crystals studied with the deuterated spin probe: $C_4H_9O - C_6H_6 - CONH$-PDtempone (PD-4) as a function of angle of tilt of nematic director with respect to magnetic field have uncovered some intriguing features.[12] The unusual observations were obtained for liquid crystals in the class that tends to form bilayers in the smectic phase because of end-CN groups.[8] The orientation-dependent slow-motional ESR spectra could only be interpreted in terms of a cooperative distortion mode yielding a two-dimensional type of distribution of local directors that is slow (or static) on the ESR timescale. This is similar to the interpretation recently given for the ESR spectra from oriented spin-labeled lipid multilayers fo low water content.[13]

The rigorous analysis of the slow-motional ESR spectra required powerful new computational algorithms developed by Moro and Freed.[14] These algorithms are expected to play an important role in the serious interpretation of complex ESR spectra. They have recently been successfully applied to a series of previously published nitroxide ESR spectra pertinent to the protein-lipid interaction in membranes to demonstrate a case for the model of a single type of lipid molecule subjected to microscopic ordering, which is enhanced and modified by addition of protein, while the overall sample is characterized by a microscopic disorder of the bilayer fragments.[15] This model, requiring extensive spectral simulation, is offered as an alternative to the familiar two-site model of "fluid" and "immobilized" lipids.

The advent of time-resolved ESR techniques[16] will be very important in the future of nitroxide ESR. Recent applications of electron spin echo (ESE) spectroscopy to nitroxide ESR have been reviewed by Stillman and Schwartz.[17] We have studied a model system Tempone in 85 % glycerol-water by ESE both in the fast motional and slow tumbling regions.[18] This work illustrated its potential value especially for slow motional studies, since we found that the phase memory time, $T_M \alpha \tau_R$ with the proportionality constant interpreted by theory to be dependent on the model for molecular reorientation. The general slow motional lineshape theory for nitroxides has now been converted into a useful theory for spin echoes in the slow motional regime.[19] The relatively simple theory, in terms of eigen-modes excited by the 90° and 180° pulses, should be useful in explaining the T_M for slow motions and also for analyzing motional effects on echo modulation patterns.[17, 18] Present experimental technique[17, 18] allows us to measure $T_M \gtrsim 50$ nsec.

A new application of nitroxides has been to the study of surface adsorption and of molecular dynamics on surfaces. Di-tertiary-butyl nitroxide (DTBN) enables us to explore the nature of the interaction of a paramagnetic probe with a clean metal surface.[20] The ESR cavity is an integral part of the UHV system.[21] Fresh metal films are evaporated onto the interior surface of a TE 011 mode cyclindrical cavity at a vacuum of about 10^{-10} torr. The DTBN is then leaked into the UHV system and is adsorbed on the interior surface. When an air-oxidized Cu surface is used, strong signals from chemisorbed DTBN immobilized on the surface are observed. However, when clean Cu and Ag surfaces are used, there is no ESR signal from the chemisorbed DTBN, except when cooled to below −100°C. We know that the DTBN is chemisorbing because of a different resonance phenomenon we observe in the ESR cavity under high vacuum. We call it CREMSEE or cyclotron resonance from microwave-induced secondary electron emission. It is due to the electron-cyclotron resonance (ECR) of secondary electrons emitted from the surface. When electrons absorb enough successive microwave quanta before colliding with the cavity walls, there will then be a large secondary electron yield. This yield is a function of the surface preparation. The threshold microwave power P_t required to excite CREMSEE is reduced by nearly an order of magnitude by air-oxidizing the metal surface. The proof that DTBN is chemisorbing on the surface comes from observing the drop in P_t as the DTBN is leaked in; (this can also be reversed by heating the surface to drive off the DTBN). It is concluded that DTBN does form a substantial complex to these metals in which its paramagnetic resonance signal is lost. This loss might be due to a diamagnetic bond with fractional ionic character between the O atom of the DTBN and a surface metal atom(s) or possibly because of a resonance between a paramagnetic complex of DTBN chemisorbed on the surface and the charge transfer complex with the surface metal, so that the latter could lead to a strong enough coupling of the unpaired electron with the conduction electrons of the metal and a consequent broadening ot the ESR signal.

Further surface studies have been performed with the simple nitroxide: NO_2. It is useful for studying molecular dynamics on insulator surfaces[22] and for reaction mechanisms on clean metal surfaces.[21]

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