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Faculty Research

Jack H. Freed

Title: Frank and Robert Laughlin Professor of Physical Chemistry, Director of ACERT

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Educational Background:

PhD, Columbia University, 1962

BChe, Yale University, 1958

Awards:

- Alfred P. Sloan Research Foundation Fellow
- Weizmann Institute Senior Fellow
- John Simon Guggenheim Memorial Foundation Fellow
- Hebrew University Institute for Advanced Studies Fellow
- American Academy of Arts and Sciences Fellow
- American Physical Society Fellow
- ACS Buck-Whitney Award
- International ESR Society Gold Medal
- Irving Langmuir Prize
- International Zavoisky Prize, Zavoisky Institute, Russian Academy of Science
- 2004 Festschrift Issue of Journal of Physical Chemistry

Professor Freed is also Director of The National Biomedical Research Center for AdvanCed ESR Technology (•ACERT)

Research Description:

Our research group focuses on the application of magnetic resonance to problems in chemical physics and biophysics. We study molecular dynamics, reactivity, and structure in condensed media, on clean surfaces, and in model membranes. The understanding of how molecules move, interact, and react with one another in condensed phases is at the heart of nearly all chemistry. Only in recent years, however, have modern techniques been developed that can directly explore such dynamics at the molecular level. We have been active in developing ESR spectroscopy into such a tool. One important area we study is that of molecular reorientational motions in liquids and membranes. We learn about the detailed nature of such motional processes. In particular we find that the molecular reorientation is coupled to a loose dynamic solvent cage. The ability to study the participation of the solvent cage in liquid state dynamics is a unique feature of our modern ESR techniques. Because the comparison between the experiment and theoretical models is challenging the complex modeling and analyses are being performed at the Cornell Theory Center. The spin label technique, wherein one chemically attaches a stable free radical to a macromolecule or

biomolecule to probe its structure and dynamics, can now also be applied with greater effectiveness using our methods. Thus, for example, one can study the complex modes of internal and overall reorientation that are characteristic of many macromolecules, as well as the motions in ordered media such as liquid crystals, surfaces, biological membranes, and lipid systems. The ESR experiments are complemented by X-ray studies of the ordered phases at the Cornell High Energy Synchrotron Source. Our group has pioneered new two-dimensional and Fourier-transform ESR techniques that greatly enhance the sensitivity to motional dynamics. Whereas Fourier-transform and two-dimensional techniques are well known in NMR, their development in ESR is very recent. The shorter time resolution of ESR makes it more suitable for the study of dynamical processes, including the microscopics of chemical reactions in liquids. Our group has also pioneered ESR imaging techniques to study macroscopic diffusion. It is one of the most reliable methods for measuring lateral diffusion in membranes and the anisotropy of diffusion in liquid crystals. Our newer methods of Fourier-transform ESR imaging enable one to study simultaneously microscopic diffusion over molecular length scales and macroscopic diffusion in membranes and complex fluids. Our modern two-dimensional Fourier-transform ESR methods also enable us to study structure in solids. Distances between the unpaired electron and nearby nuclei can be mapped out by observing the coherence cross-peaks. A new double quantum experiment now permits the measurement of distances in macromolecules between two different sites that are spin labeled. Such large-distance measurements of 20-60 ? are expected to be important in structural determinations of large proteins. Further pioneering efforts in our group have included the extension of ESR techniques to higher fields and frequencies. Our new far-infrared ESR spectrometer enhances the study of complex motional processes and holds the possibility of greatly enhanced signal sensitivity.

Selected Publications:

Borbat, P.P., J. H. Davis, S. E. Butcher, and J. H. Freed, Measurement of Large Distances in Biomolecules Using Double-Quantum-Filtered Refocused Electron-Spin-Echoes, *J. Am. Chem. Soc,* **2004,** *126,* 7746-7747.

Liang, Z., Y. Lou, J.H. Freed, L. Columbus, and W.L. Hubbell, A Multifrequency ESR Study of T4 Lysozyme Dynamics using the Slowly Relaxing Local Structure Model, *J. Phys. Chem.,* **2004,** *108,* 17649-17659.

Dzikovski, B.G., Petr P. Borbat, and J.H. Freed, Spin-Labeled Gramicidin A. Channel Formation and Dissociation, *Biophys. J.,* **2004,** *87,* 3504-3517.

Chiang, Y.K., Y. Shimoyama, G.W. Feigenson, and J.H. Freed, Dynamic Molecular Structure of DPPC-DLPC-Cholesterol Ternary Lipid System by Spin-Labeling ESR, *Biophys. J.,* **2004,** *87,* 2483-2496.

Blank, A., C.R. Dunnam, P.P. Borbat, and J.H. Freed, Pulsed 3D Electron Spin Resonance Microscopy, *Applied Phys. Letters,* **2004,** *85,* 5430-5432.

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