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Electron Paramagnetic Resonance Investigations of Biological Systems by Using Spin Labels, Spin Probes, and Intrinsic Metal Ions

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Preface

Electron Paramagnetic Resonance (EPR, or Electron Spin Resonance, ESR) spectroscopy is one of the few methods that selectively and directly detects species containing unpaired electrons (e.g., organic radicals, metal ions) and characterizes their interactions with the surrounding environment. EPR has long been used to investigate contributions of molecular structure and dynamics to function in biological systems, via characterizing paramagnetic species intrinsically present (e.g., metal centers, reaction intermediates) or extrinsically introduced (e.g., covalently-attached spin labels or freely-diffusing spin probes). The field continues to advance in response to the needs of the biomedical, biomaterials, and biotechnology communities for molecular-level information that ranges on spatial scales from macromolecules through whole cells to organisms, and on temporal scales from solvent fluctuations to physiological processes.

In organizing these two volumes, we aim to present to the EPR practitioners, as well as the broader scientific community, state-of-the-art EPR methodologies for studying relationships among structure, dynamics and function in biological systems. It is challenging to distinguish categories, such as advances in technique, hardware, and software, from the applications and systems that drive development, which is a sign of the synergistic interplay of EPR spectroscopy and the science it enables. Thematic threads that run through the chapters, that reflect recent progress in EPR studies, include the following: (1) Developments in instrumentation, experimental and analytical approaches, particularly the use of multiple frequencies/magnetic fields outside of traditional X-band (e.g. 95 GHz), which expand the information content obtainable; (2) Advances in incorporating stable paramagnets into biological targets, which expand the scope of systems and questions tractable by EPR approaches; (3) Progress in characterizing structure and dynamics of biological molecules, and in particular, methods utilizing distances measured via dipolar

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interactions and efforts to improve the related data analysis and interpretation; (4) Methodologies combining EPR and nuclear magnetic resonance (NMR), in the general area of sensitivity enhancement that enables access to previously veiled structural and dynamic information; (5) EPR in the area of cellular, or *in vivo*, measurements, including the march toward EPR oxymetry and imaging of radical reactions and tumors in humans.

The chapters present the principles and practices that underly the various EPR approaches in the “hands-on” format, a hallmark of *Methods in Enzymology*. We sincerely hope that they promote understanding and straightforward application, for the continued impact of EPR methods on the understanding of biological structure, dynamics and function.