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LOW TEMPERATURE TIME DEPENDENT RESONANCE RAMAN SPECTRA OF CO BOUND TO SPERM WHALE MYOGLOBIN, Mb AT pH 3: I E T Iben, J Friedman (AT&T Bell Labs & NYU (chem)) B Cowen, H Frauenfelder (U of Illinois, CU (phys)) and R Sanches (U Sao Paulo, Brazil (phys))

Cryogenic samples of MbCO at pH 3 were studied using ns and ps time resolved resonance Raman spectroscopy. Using a 10ns, 423nm, excitation-probe laser pulse, we observed a predominantly CO bound spectrum even at 10K, whereas a pH 7 sample is completely photolyzed. The values of the core markers are similar at pH 3 and pH 7, indicating a 6-coordinated, low-spin species; however, the Fe-CO stretch frequency is decreased from 507cm⁻¹ to ~490cm⁻¹, revealing a more open heme pocket. Shifting the pulse to 430nm results in an enhanced contribution from the photoproduct population. The relative amplitude of the 10ns photoproduct spectrum decreases with increasing temperature. Despite adequate S/N, the Fe-His(F8) stretch is not observed showing that the Fe-His(F8) bond is broken by 10ns. We also measured the time evolution of the photoproduct Raman spectrum from 30ps to 3ns at 80K and 100K. 50% recombines non-exponentially in time by ~300ps, supporting the flash photolysis rebinding data of Cowen et al (1989, Biophys J. 55.M- PM-E11)

Tu-Pos56

THEORY OF LIGHT SCATTERING FROM SMALL SPHERULITIC DOMAINS OF SICKLE HEMOGLOBIN POLYMERS. J. R. Wheeler and Marilyn F. Bishop, Dept. of Physics, Virginia Commonwealth Univ. 1020 West Main St., Richmond, VA 23284-2000.

We have calculated the light scattering from spherulitic domains of sickle hemoglobin (HbS) polymers, where the domains are well separated and small compared with the wavelength of incident light. Inside a spherulite, we have used a model uniform anisotropic effective medium dielectric tensor. This effective medium is composed of polymers, monomers, and solution, and the anisotropy results from polymer alignment within the domain. Outside the spherulite, we assume an isotropic effective medium composed of monomers and solution. The results depend on the average length of polymers, which we have obtained from the double nucleation mechanism as a function of the extent of polymerization.

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CONFORMATIONAL DISORDER AND REACTIVITY: PHOTODISSOCIATION QUANTUM YIELD STUDIES IN OxyHb(Mb)

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Transient absorption studies by several groups suggest that the low quantum yield of photodissociation of O₂Hb(Mb) at ambient temperatures is due to geminate recombination occurring from picoseconds to nanoseconds. We have extended these studies to cryogenic temperatures where we find, using both cw and 30 ps pulses, that a sizable fraction (60% at 8K) of an O₂Hb(Mb) sample can not be photodissociated even with extensive optical pumping. These findings in conjunction with transient absorption measurements with 50 ps resolution, together indicate that at 10K or lower, the low quantum yield is due to a population of conformational substates that undergoes either an ultra fast (<<10ps) geminate recombination process or a photophysical process that results in the recovery of the oxy species. Line shape comparisons of the photoproduct absorption in the region of the inhomogeneously broadened band III (~760nm) for CO and O₂ form of Hb(Mb) indicate that the "unphotolyzable" part of the distribution of substates for oxy photoproducts resembles the fast recombining population of carboxy photoproducts observed in kinetic hole burning experiments. A structural model incorporating the iron displacement and the tilt and rotational degrees of freedom of His(F8) is used to explain the mapping of ligand reactivity onto the inhomogeneous line shape of band III.

Tu-Pos57

RESONANCE RAMAN STUDIES OF STEADY STATE HEME REDUCTION AND PHOTOREDUCTION IN CYTOCHROME b₆f and bc₁ COMPLEXES.

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The heme sites of the isolated cytochrome b₆f complex in various stages of reduction have been studied using resonance Raman techniques. The spectra are interpreted in terms of Raman spectra for the related bacterial cytochrome bc₁ complex and the isolated turnip cytochrome f. Transient photoreduction behavior of these complexes has been observed using electron transfer inhibitors and oxidation/reduction mediators. Rapid photoreduction of the oxidized heme c₁ and f has been observed in a nanosecond time scale using high laser fluxes. High power 410 nm laser excitation yields a spectrum similar to that observed for the sodium ascorbate reduced complexes. (Supported by NIH GM33330.)

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