



Laboratory for Condensed Matter Theory: Molecular Spectroscopy : Resonance Raman Scattering of Metal Complexes and Heme Proteins / Vibrational Optical Activity of Metal Porphyrins and Proteins

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1. Current Research and Principal Research Interests

I have investigated biophysical properties of heme proteins in terms of vibrational spectroscopy in order to elucidate the physiological functions by which the mutual interactions between protein, heme iron and porphyrin work cooperatively. Recently, I have been focusing on two topics, one is the electronic properties of metal porphyrins themselves, the other is the interactions between ligands and the porphyrin ring through the heme iron. I also try to apply the spectroscopy not only to bio-related chemistry but a wide range of inorganic chemistry and material science.

1)*Electronic States of Porphyrins and Porphycenes:* Porphycene, a tetrapyrrolic structural isomer of porphyrin, is a new type of porphyrinoid chromophore. Resonance Raman spectra of reduced porphycenes were measured in an effort to characterize structural changes concomitant with chemical reduction. Frequency shifts were observed for reduced porphycenes in certain skeletal modes. The observed RR behavior was generally consistent with the results of vibrational analysis by quantum chemical calculations based on density functional methods. In the course of porphycene studies, I found it worthwhile studying thoroughly resonance Raman spectra for metal-free compounds such as N-deprotonated- and N-protonated porphyrinoid chromophores: Some marker Raman bands shift systematically upon deprotonations, suggesting that a coulomb interaction should be predominant for the Raman frequencies rather than MO type interactions - electron delocalization, between a central metal ions and porphyrin ligands. The results provided a sort of theoretical background to the empirical rules so far believed undoubtedly.

2-1)*Photodissociation and Photoreduction:* Photodissociation has been utilized to investigate the association and dissociation rate constants for ligand binding to hemoproteins to provide insight into the relationship between structure and dynamics. I reported the first example of photodissociation in a ferric low-spin porphyrin complex. The fact that photolysis of 1-MeIm is initiated by π^* excitation of the porphyrin suggests that there is at least one delocalized molecular orbital in the metal complex which is responsible for the photodissociation. I would like to elucidate the phenomenon such as photoreduction in terms of the same discussion applied to photodissociation.

2-2)*Vibrational Optical Activity:* Vibrational circular dichroism studies of ligands bound to hemoproteins have been reported, the results of which give valuable new insights into the electronic states as well as the coordination geometry of hemoproteins. The results indicate that the chiral environment produced by the peripheral substituents on the porphyrin ring, which give rise to a diastereotopic plane, is responsible for the generation of strong VCD of the ligands in hemeproteins, whereas specific interactions of distal residues with the porphyrin ring and the

ligands in halo-proteins are not always necessary. However, there still remain a couple of problems to be solved, different VCD signs for some ligands and the origin of the magnetic transition dipole moments.

2. Selected Publications

Related to research interest 1:

1. "Electronic and Vibrational Properties of Porphycene Anions", R. M. Gulam, T. Matsushita, and J. Teraoka, *J. Phys. Chem. A*, **107**, 2172-2178 (2003).
2. "Resonance Raman Characterization of Porphycene Anions", R. M. Gulam, T. Matsushita, S. Neya, N. Funasaki, and J. Teraoka, *Chem. Phys. Lett.*, **357**, 126-130 (2002).

Related to research interest 2:

3. "Photodissociation of 1-Methylimidazole Ligand in Ferric Low-Spin Iron Porphyrin", J. Teraoka and K. Nakamoto, *J. Am. Chem. Soc.*, **122**, 6301-6302 (2000).
4. "Loop Structure in Human Serum Albumin from Raman Optical Activity", J. Teraoka, A. F. Bell, H. Lutz, and L. D. Barron, *J. Raman Spectrosc.*, **29**, 67-71, (1998).
5. "What is the Crucial Factor for Vibrational Circular Dichroism in Hemo-protein Ligands?", J. Teraoka, N. Yamamoto, Y. Matsumoto, Y. Kyogoku, and H. Sugeta, *J. Am. Chem. Soc.*, **118**, 8875-8878 (1996).
6. "UV Resonance Raman Saturation Spectroscopy of Tryptophan derivatives; Photophysical Relaxation Measurements with Vibrational Band Resolution", J. Teraoka, P. A. Harmon, and S. A. Asher, *J. Am. Chem. Soc.*, **112**, 2892-2900 (1990).
7. "Structural Implication of the Heme Linked Ionization of Horseradish Peroxidase Probed by the Fe-Histidine Stretching Raman Line", J. Teraoka and T. Kitagawa, *J. Biol. Chem.*, **256**, 3969-3977 (1981).

The others:

8. "Cytochrome c-Crown Ether Complexes as Supramolecular Catalysts: Cold Active Synzymes for Asymmetric Sulfoxide Oxidation in Methanol", A. Suzumura, D. Paul, H. Sugimoto, S. Shinada, R. R. Julian, J. L. Beauchamp, J. Teraoka, and H. Tsukube, *Inorg. Chem.*, **44**, 904-910 (2005).
9. "Mechanism of Superconductivity in the Polyhedral-network semiconductor Ba₈Si₄₆", J. Teraoka, Y. Morimoto and S. Yamanaka, *Nature Mater.*, **2**, 653-655 (2003).
10. "Chemical Activation of Cytochrome c Proteins via Crown Ether Complexation: Cold-Active Synzymes for Enantiomer-Selective Sulfoxide Oxidation in Methanol", D. Paul, A. Suzumura, H. Sugimoto, J. Teraoka, S. Shinoda and H. Tsukube, *J. Am. Chem. Soc.*, **125**, 11478-11479 (2003).