INTRODUCTION

Visual pigments are composed of a small chromophore (absorption center) called retinal (the aldehyde of vitamin A) covalently linked to surrounding protein, called opsin. The pigments are situated in specialized membranes. The best studied, rhodopsin, is found in vertebrate rods, the cells of the retina responsible for low light level vision as opposed to color vision. The purple membrane protein of a bacterial cell called halobacterium halobium also contains retinal as its chromophore surrounded by a colorless protein. The absorption of light by visual pigments causes, eventually, a neural response giving rise to vision. Light absorption by the purple membrane results in protons being pumped across the cell wall of the bacterium; the energy of this electrical gradient is then used to produce available chemical energy for the cell in terms of high energy chemical bonds (formation of ATP).

After light absorption by the chromophores of the two pigments, a successive set of spectrally distinct, temperature-dependent states are produced. The only action of light absorption by rhodopsin is to form a spectrally red shifted pigment, called bathorhodopsin, in less than 6 picoseconds. Rhodopsin has a lower free energy than bathorhodoosin. Photon energy is converted to chemical energy in the rhodopsin to bathorhodopsin transition; this chemical energy is then available to drive subsequent chemical reactions finally producing neural excitation. Another pigment, isorhodopsin, is not found in nature but also forms bathorhodopsin upon light absorption. Its chromophore is composed of a different geometric form of retinal, i.e. 9-cis retinal, than that of rhodopsin, i.e. 11-cis retinal (see Figure 1). The purple membrane
pigment of halobacterium halobium is often called bacteriorhodopsin since its chromophore is the same as rhodopsin and since its chromophore is covalently joined to surrounding protein by a Schiff base linkage, i.e. a \(-\text{C}=\text{N}-\) bonding (see Figure 1). In some sense, the function of both chromophores can be said to be the same, namely to convert a significant fraction of light energy to chemical energy. Several excellent review articles have written on these systems (Ebrey and Honig, 1975; Honig, 1978).

Resonance Raman spectroscopy has provided a great deal detailed information concerning the structure and structural changes of the chromophore in these two pigment systems (for reviews see Callender and Honig, 1977; Mathies, 1979). The Raman cross-section of the chromophore vibrational modes are greatly enhanced when the incident light frequency lies in the visible, since the light is in resonance with the absorption structure of the chromophore, relative to protein modes, as the surrounding protein is colorless. Five to seven orders of magnitude in enhanced Raman cross-section can be realized. In addition, water (the ubiquitous biological medium) has a very low Raman cross section and thus does not give a troublesome background spectrum. Thus the observed Raman signal is due to modes of the chromophore only and can be analyzed in terms of structure. As will be apparent below, the Raman structure is quite sensitive to the geometric form of retinal. In addition, our results below are key, we believe, in pointing towards the molecular mechanism by which light energy is initially converted to chemical energy. Resonance Raman spectroscopy has found wide applicability in the study of other biologically interesting chromophores (for reviews