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LIGHT-INDUCED DYNAMICS OF CHLOROPHYLL SYSTEMS STUDIED BY NEUTRON SPECTROSCOPY

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Abstract

Energy spectra of three chlorophyll-protein systems and of chlorophyll-a in solution were measured using the inelastic neutron scattering technique. The intensities of the observed energy spectra changed significantly when the sample was irradiated by light. This effect is interpreted in terms of electronic-vibrational relaxation mechanisms giving rise to radiationless transitions which enhance the population of the vibrational modes of all the constituents forming the sample either directly or by dissipation.

1. Introduction

Most of the chlorophylls and other pigments in photosynthetic chlorophyll-protein complexes of green plants and bacteria function as molecular antennae absorbing solar energy and conveying it to the specialized chlorophylls of the reaction center complexes. When the chlorophyll molecule of an antenna

complex absorbs light of a particular wavelength, it is electronically excited. The excited molecule has two possible fates. It may loose an electron to the chlorophyll molecule of the reaction centre, in which case a photochemical energy transfer is realized. The excited molecule may also return to its ground state. The corresponding relaxation mechanism can be either radiative, resulting in the emission of a photon, or radiationless, in which case a number of vibrational modes are excited, which are dissipated as heat into the surrounding medium. Relaxation mechanisms generally take place through the simultaneous occurence of both photon and phonon processes subject to energy conservation.

We have performed inelastic neutron scattering experiments for chlorophyll in protein and non-protein environments in order to study the dynamical response as a function of light irradiation. The observed energy spectra exhibit significant changes of the intensities when the sample is irradiated by light. In particular, light irradiation produces a decrease of the intensity of the elastic line, whereas the intensities in the inelastic part of the spectrum increase. These findings may be understood on the basis of radiationless relaxation mechanisms.

2. Experimental

The majority of the experiments were performed on a suspension of membranes of the photosynthetic bacterium Rhodopseudomonas viridis (Rh.v.) in D_2O buffer at a protein concentration of roughly 20mg/ml. The bacterium Rh.v. is a suitable system since it has only one photosystem. Moreover its photosynthetic membranes form a highly ordered intracytoplasmic membrane system which can easily be isolated in large quantities. The membranes themselves form extensive two-dimensional lattices the structure of which has been investigated by electron micro-

scopy and image processing methods (1,2,3).

The samples were filled into cylindrical containers consisting of an aluminium ring of 1 mm height and two very thin mica windows of 25 mm diameter. The sample was mounted in a closed-cycle He refrigerator. The light source was a halogen lamp with a maximum intensity of 2 MLux. Various broad-band filters were used to yield wavelengths between 400 nm and 1000 nm.

The inelastic neutron scattering experiments were performed at the reactor Saphir in Würenlingen using a triple-axis spectrometer. In the experiments the scattered neutrons were analyzed according to the energy transfer

$$\hbar\omega = \frac{\hbar^2}{2m} (k_o^2 - k_1^2) \quad , \tag{1}$$

while the momentum transfer

$$\hbar\vec{Q} = \hbar (\vec{k}_o - \vec{k}_1) \tag{2}$$

was kept constant. m denotes the neutron mass, and $\vec{k}_o$ and $\vec{k}_1$ are the wave vectors of the incoming and outgoing neutrons, respectively. The measurements were carried out both in the neutron energy-loss ($\hbar\omega>0$) and neutron energy-gain ($\hbar\omega<0$) configuration with the analyzer or monochromator energy kept fixed at 15 meV. A pyrolitic graphite filter was inserted into the scattered or incoming neutron beam in order to reduce higher-order contamination. To gain intensity a doubly bent graphite monochromator and a horizontally bent graphite analyzer were used.

Fig. 1 shows a typical energy spectrum observed for Rh.v. at T=28 K and Q=4.15 Å^{-1} with and without light irradiation. The spectrum of the incoming light was very broad ($400\leq\lambda\leq800$ nm). Apart from the intense elastic line there is considerable inelastic scattering on the neutron energy-loss side of the spectrum which corresponds to creation of vibrational excitations in the system. The energy distribution is peaking at $\hbar\omega$=7 meV.

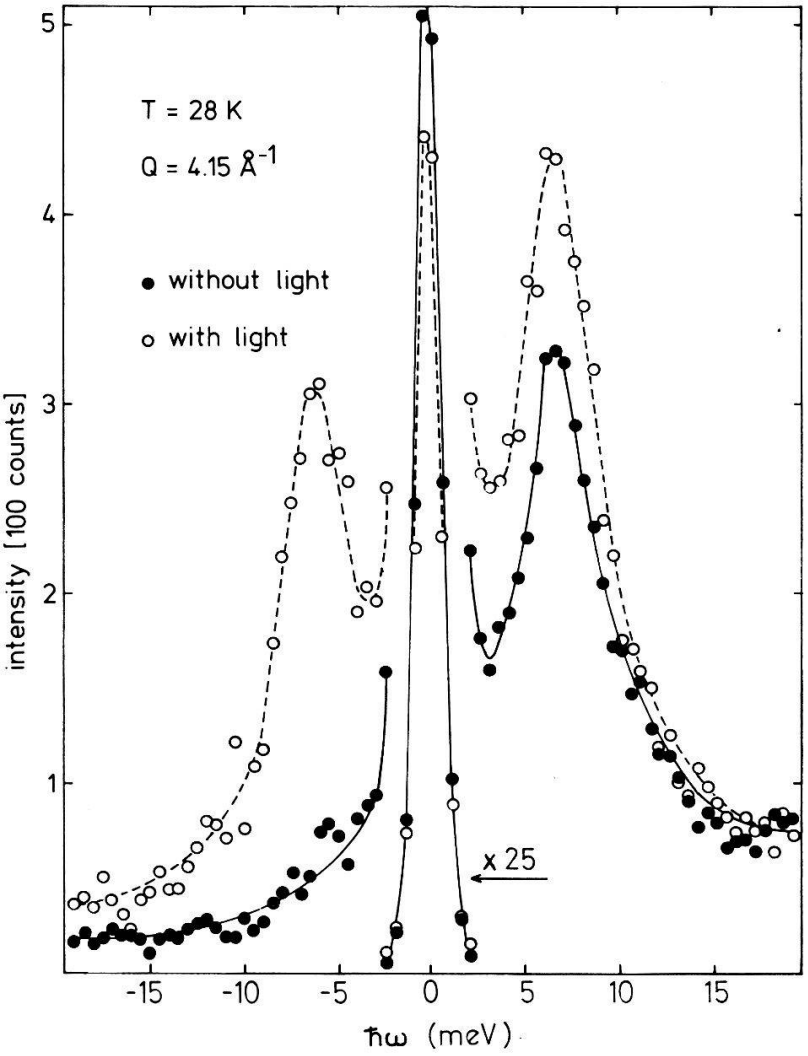

Figure 1

Energy spectra of neutrons scattered from a suspension of membranes of the photosynthetic bacterium Rhodopseudomonas viridis in D_2O buffer. The lines are drawn as guides to the eye.

The energy-gain side of the spectrum taken for the non-irradiated sample exhibits little scattering. This is expected, since the system is essentially in its ground state at low temperatures. Under light irradiation the spectrum exhibits a significant change of intensities; in particular , the intensity of the elastic line decreases, whereas the intensities in the inelastic part of the spectrum increase. The light effect shows up most clearly on the energy-gain side of the spectrum. Light irradiation appears to increase the thermal population of the vibrational excitations from n to n+Δn, so that the system behaves as if it were in thermal equilibrium at a hypothetical higher temperature T*>T.

A quantitative measure of the observed light effect is

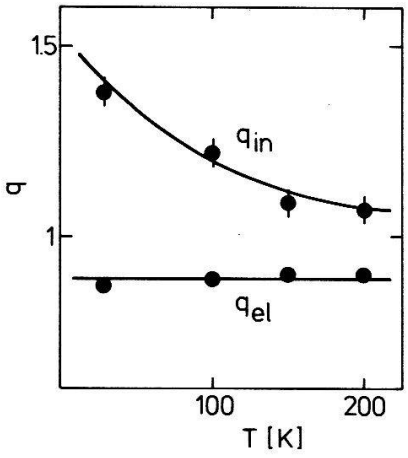

Figure 2

Observed and calculated ratios of the elastic and inelastic peak intensities for Rh.v. as explained in the text. Q = 4.15 $Å^{-1}$.

btained by the following ratios of the elastic and inelastic eak intensities:

$$q_{el} = \frac{\text{Intensity } (\hbar\omega=0, \text{ with light})}{\text{Intensity } (\hbar\omega=0, \text{ without light})} , \qquad (3)$$

$$q_{in} = \frac{\text{Intensity } (\hbar\omega=7\text{meV, with light})}{\text{Intensity } (\hbar\omega=7\text{meV, without light})} . \qquad (4)$$

he intensity ratios q observed at various temperatures are shown n Fig. 2.

Similar experiments have also been performed for chlorohyll-protein complexes isolated from pea chloroplasts in D_2O uffers and chlorophyll molecules incorporated into lipid vesicles s well as for chlorophyll molecules dissolved in deuterated enzene. The energy spectra of all these systems exhibited imilar features as those observed for Rh.v. Control experiments ith lipid vesicles without chlorophyll did not show any light ffect.

Some preliminary measurements were performed with seudo-monochromatic light (bandwidth 50 nm). The results for h.v. are interesting in the sense that the light effect appears o be almost uncorrelated with the optical absorption spectrum. In articular, only a very small light effect is observed for λ= 1000 nm corresponding to the most intense absorption line of acteriochlorophyll. This indicates that light absorption at

λ=1000 nm occurs with little energy loss through radiationless transitions, but it efficiently contributes to the photochemical energy transfer from the antenna complexes to the reaction centres.

3. Interpretation

The interaction of the neutrons with the sample may be expressed in terms of a differential cross-section which is related to thermal averages of operators describing the scattering system. Because of the complicated structure of our samples it is at present not possible to rigorously calculate a cross-section formula. Nevertheless we expect that even a very crude approximation should enable us to interprete our observations qualitatively. Assuming only one type of scattering centers in the sample we obtain the following cross-section formula for neutron energy-loss in the incoherent approximation (4):

$$\frac{d^2\sigma}{d\Omega\, d\omega} \sim \frac{k_1}{k_o} \frac{\sigma_{inc}}{M} Q^2 e^{-2W(Q)} \frac{g(\omega)}{\omega} \langle 1+n \rangle, \qquad (5)$$

where σ_{inc} and M denote the incoherent cross-section and the effective mass of the scattering centers constituting the sample, respectively, $g(\omega)$ is the density-of-states of the vibrational excitations, and $e^{-2W(Q)}$ is the Debye-Waller factor with

$$W(Q) = \frac{\hbar}{4M} Q^2 \int_0^{\omega_{max}} d\omega \, \frac{g(\omega)}{\omega} \langle 1+2n \rangle. \qquad (6)$$

For elastic scattering Eq. (5) simplifies to

$$\frac{d\sigma}{d\Omega} \sim \sigma_{inc} e^{-2W(Q)} . \qquad (7)$$

Replacing $g(\omega)$ by a delta function centred at $\hbar\omega_o$ = 7 meV we derive the following intensity ratios from eqs. (5)-(7):

$$q_{el} = e^{-\frac{\hbar Q^2}{M\omega_o}\Delta n} , \qquad (8)$$

$$q_{in} = q_{el}\,(1+\frac{\Delta n}{1+n}) . \qquad (9)$$

A least-squares fitting procedure was applied to the experimental data of Fig. 2 on the basis of Eqs. (8) and (9). Good agreement between theory and experiment is obtained for the model parameters $\Delta n=0.6$ and $M=50$ AMU. The resulting enhancement Δn of the population of the vibrational excitations corresponds to a hypothetical sample temperature $T^*=88$ K which may serve as a measure of the decay rate of the excited chlorophyll molecules via radiationless transitions. The resulting effective mass M is of little physical significance since it is a mean value averaged over all the vibrational modes excited in the system; it may take any value between 1 AMU and several thousand AMU depending on whether a single vibrating hydrogen atom or the vibrational mode of a protein is considered. On the other hand the value of M should not be too far away from the molecular weight of D_2O which constitutes the major part of the sample.

4. Conclusions

Using the inelastic neutron scattering technique we have observed a significant change of the energy spectra of various chlorophyll systems when irradiated by light. The electro-magnetic field introduces an external disturbance, displacing the chlorophyll system from the initial equilibrium conditions and thus giving rise to relaxation effects. A high efficiency of photochemical energy transfer requires that the radiationless processes are minimized. A measurement of the irradiation effect observed by neutron spectroscopy could there-

fore be a useful tool to investigate where, and how much, energy is lost in the initial steps of photosynthesis.

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