On the Influence of Microwaves and Static Magnetic Fields on the Recombination of Radical Ions in Reaction Centers of Photosynthetic Bacteria

Wilhelm Lersch, Alexander Ogrodnik, and M. E. Michel-Beyerle

Institut für Physikalische und Theoretische Chemie, Technische Universität München, D-8046 Garching

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Recombination of the bacteriochlorophyll dimer cation and the bacteriopheophytin anion depends on the spin multiplicity of this radical ion pair and can be studied by optical spectroscopy in an external static magnetic field in the absence (MARY) and presence of microwaves (RYDMR). Model calculations of MARY- and RYDMR-spectra are discussed.

Interaction of pigments involved in the first fast electron transfer steps in photosynthetic reaction centers can be studied by a variety of methods focussing on different electronic states as e.g. radical ion pairs. Considering the bacteriochlorophyll dimer cation, (BChl)_2+, and the bacteriopheophytin anion, BPh−, in quinone depleted reaction centers of Rhodopseudomonas spheroides, strain R-26, it has been established [1, 2] that the recombination pathway is spin selective leading with a much higher rate k₆ to the triplet state 3[(BChl)_2]* than via k₅ to the singlet ground state of (BChl)_2 and BPh. Since singlet and triplet phased radical pair states are coupled by hyperfine interaction (HFI), the product yield in the two spin states can be manipulated by external magnetic fields (a static magnetic field H₀ and/or a microwave field H₁) as indicated in the kinetic scheme:

\[ \begin{align*}
\text{singlet product} & \quad \text{triplet product} \\
[(\text{BChl})_2]^+ \ldots \text{BPh}^- & \quad \text{MARY} : \quad [3((\text{BChl})_2)^+ \ldots \text{BPh}^-] \\
\text{k}_5 & \quad \text{k}_6 \\
\end{align*} \]

It is the purpose of this paper to discuss the kinetic and structural information which can be derived from the experimental dependence of the triplet yield on static magnetic fields, in the absence and in the presence of microwaves.

\[ \text{Magnetic field dependent Reaction Yields (MARY)} \]

Reprint requests to Prof. Dr. M. E. Michel-Beyerle, Institut für Physikalische und Theoretische Chemie der TU München, Sonderforschungsbereich 143, Lichtenberg-straße 4, D-8046 Garching.

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action is neglected, nuclear Zeeman interaction can be ignored, too. Thus, the nuclear configuration is a constant of motion, the index \( k \) running over a statistical distribution of initial nuclear arrangements. The z-component of the effective magnetic field in the rotating frame is given by \( h \Delta \omega(k)/\hbar \beta \) consisting of the residual Zeeman contribution and the hyperfine contribution:

\[
\Delta \omega(k) = g \beta H_0 - \hbar \omega + \frac{1}{2} \left( \sum A_n^{(1)} m_{n,k}^{(1)} + \sum A_n^{(2)} m_{n,k}^{(2)} \right).
\]

Hyperfine coupling data for the various nuclei (n) on the two radicals, (1) and (2), were taken from [4]. Transitions from the initial singlet state to the sublevel of the radical pair proceed with the mixing frequency \( a(k) = \frac{1}{2} \left( A g \beta H_0 + \sum A_n^{(1)} m_{n,k}^{(1)} - \sum A_n^{(2)} m_{n,k}^{(2)} \right) \).

At moderately high external magnetic fields \( (H_0 \approx 3 \text{ kG}) \) the contribution from the hyperfine interaction dominates the one from the difference of the magnetic g-factors \( (\Delta g = -0.001) \). Microwaves with a field strength \( H_1 \) couple \( T_0 \) and \( T_{\pm 1} \) triplet sublevels. The exchange interaction \( J \) and the contribution \( D_{zz} \) of the spin dipolar cause energy splittings thus hindering transitions between the states involved \((S, T_0, T_{\pm 1})\). \( D_{zz} \) is the component of the dipole tensor parallel to the external field \( (D_{zz} = \hat{z} \cdot \hat{D} \hat{z}) \) given by

\[
D_{zz}(\theta, \psi) = (\cos^2 \theta - \frac{1}{2}) \cdot D - \sin^2 \theta \cos 2 \psi \cdot E.
\]

The Euler angles \( \theta \) and \( \psi \) describe the orientation of the dipolar main axis system in the laboratory frame. The operators \( P_S \) and \( P_T \) project out the singlet state and triplet states, respectively. The triplet yield is calculated numerically by solving the stochastic Liouville equation in the rotating frame

\[
\frac{d\hat{\sigma}(t)}{dt} = -\frac{i}{\hbar} [\hat{\mathcal{H}}_{\text{rot}}, \hat{\sigma}(t)] - k_S \{P_S, \hat{\sigma}(t)\} - k_T \{P_T, \hat{\sigma}(t)\}.
\]
recombination processes \((J \geq \hbar (k_s + k_T)/2)\). For \(D = 0\) the exchange interaction \(J\) cannot be much stronger than \(\hbar (k_s + k_T)/2\). Otherwise, the RYDMR spectrum at low microwave powers as well as the MARY spectrum would consist of two distinct resonance lines in contradiction to the experimental results. For \(D \neq 0\), however, \(J\) may well exceed this limit. For instance, in the case of \(J = -D/3\), the triplet sublevels \(T_x\) and \(T_y\) are (approximately) degenerate with the singlet level at zero magnetic field. The MARY spectra then remain unsplit for any value of \(J\) and moreover for any orientation of the dipole tensor. For such a case of non vanishing dipolar interaction \((J = 20 \text{ G}, D = -60 \text{ G})\) the RYDMR spectrum is shown in Figure 2. The transition moments of probing and excitation were assumed to be parallel to the symmetry axis of the dipole tensor while the polarisation vectors \(\vec{E}_{\text{exc}}, \vec{E}_{\text{prob}}\) of the exciting and probing light were chosen parallel to the external field. As to its inversion with increasing microwave power the RYDMR spectrum of Fig. 2 qualitatively resembles the spectrum observed by Bowman et al. [3]. Similar spectra, however, can be obtained for vanishing dipolar interaction and \(J\) comparable to or slightly exceeding \(\hbar (k_s + k_T)/2\). The most significant manifestation of a strong dipolar interaction is expected to occur in the angular dependence of RYDMR (and also of MARY) spectra as depicted in Fig. 1, b–d for \(J = 20 \text{ G}\) and \(D = -60 \text{ G}\). To clearly establish the participation of dipolar interaction in RYDMR and MARY spectra it is therefore indispensable to test their angular dependence. First attempts to measure the anisotropy of MARY have been reported by Boxer et al. [5].

The apparent discrepancy between the finding that our experiments [2] were consistent with \(J = 0, D = 0, k_s = 3.9 \cdot 10^{7} \text{s}^{-1}\) and \(k_T = 7.4 \cdot 10^{8} \text{s}^{-1}\) and the fact that the (calculated) RYDMR spectrum for this set of parameters does not show the behaviour observed by Bowman et al. [3] may be resolved by taking into account the wide range of reaction center quality due to preparation and aging. Such variations seem to be especially pronounced in the case of quinone depleted reaction centers. Besides the very narrow MARY spectrum published [2] we observed as well much broader spectra depending on preparation and age. This implies that results derived from experiments on different samples are not necessarily consistent.

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