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Excited states and electron transfer mechanism in the photosynthetic reaction center of *Rhodopseudomonas viridis*: SAC–CI study

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Abstract

The symmetry adapted cluster (SAC)–configuration interaction (CI) method has been utilized to assign the excited states in absorption and linear dichroism spectra and to clarify the mechanism of the unidirectionality in the electron transfer of the photosynthetic reaction center of *Rhodopseudomonas viridis*. We have calculated the ground, excited, ionized, and electron-attached states of all the chromophores in the reaction center. The protein effects were included with the use of the point-charge model.

1. Introduction

Ab initio electronic structure theory has achieved chemical accuracy even for large molecules [1] and the elucidation of biochemically important phenomena by such methods constitute a challenging frontier of quantum chemistry. In this Letter, the SAC (symmetry adapted cluster)–CI (configuration interaction) method [2–4], which describes almost all kinds of ground and excited states of molecules in good accuracy including electron correlation [1,5], has been applied to the photosynthetic reaction center (PSRC) of *Rhodopseudomonas* (*Rps.*) *viridis* [6] in order to give a definite assignment of the excitation spectrum [7] and to clarify the mechanism of the electron transfer (ET) and the origin of its unidirectionality. This is by far the highest-level calculation modern quantum chemistry can achieve.

Fig. 1 compares the absorption and linear dichroism (LD) spectra of the PSRC of *Rps. viridis* observed by Breton [7] with those calculated by the SAC–CI method. All the chromophores included in the PSRC [6] (bacteriochlorophyll *b* dimer (special pair, P), bacteriochlorophyll *b* in L- and M-branches (B_L and B_M), bacteriopheophytin *b* in L- and M-branches (H_L and H_M), menaquinone (MQ), ubiquinone (UQ), and four different hemes, c-552, c-554, c-556, and c-559, in the c-type cytochrome subunit) were calculated within the environment of proteins, water, and the other chromophores which were dealt with by the point charge electrostatic model. The peaks numbered from I to XIV in the observed spectrum are assigned by the dotted lines to the SAC–CI ones. This assignment was done using

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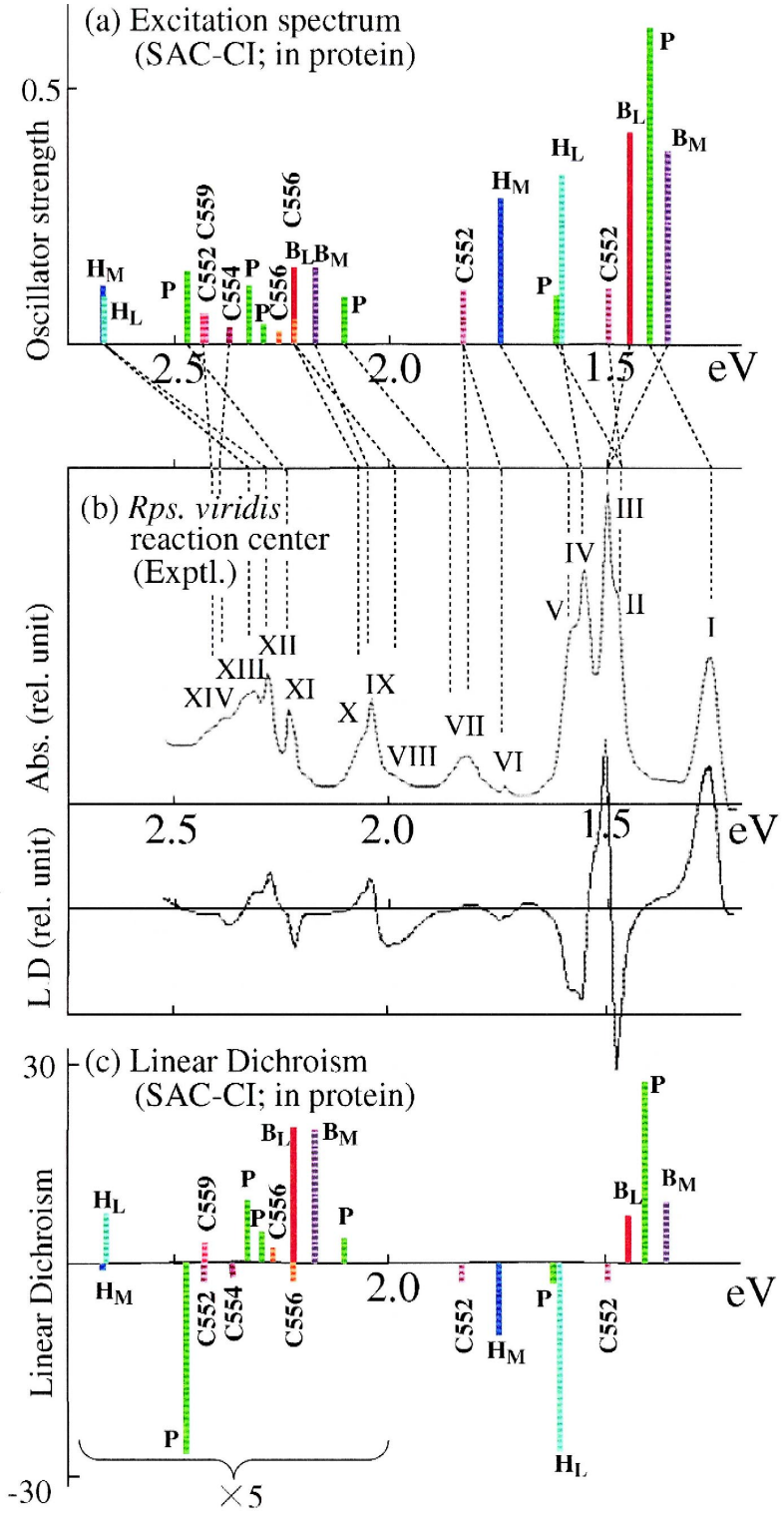
(a) Excitation spectrum
(SAC-CI; in protein)
Oscillator strength
0.5
2.5
2.0
1.5
eV
(b) Rps. viridis
reaction center
(Exptl.)
Abs. (rel. unit)
L D (rel. unit)
(c) Linear Dichroism
(SAC-CI; in protein)
Linear Dichroism
30
-30
×5

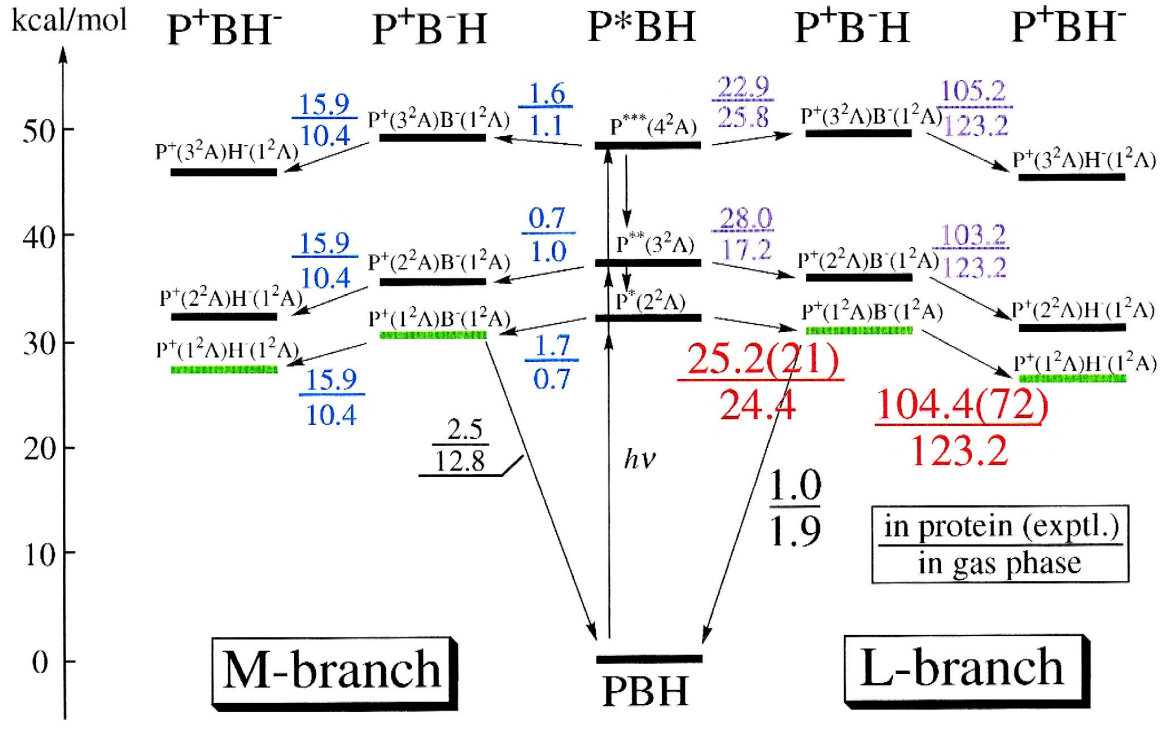

Fig. 2. Electronic factors, $|H_{IF}|^2$ ($\times 10^{-9}$ in a.u.) for the electron transfers in the PSRC of *Rps. viridis* (the upper value is in the protein model compared with the experimental value (given in parentheses [9]) and the lower one is in the gas phase). Energy levels colored green are experimentally estimated values [10] and the black ones were calculated by the SAC–CI method.

the excitation energy, oscillator strength, LD angle, and other experimental information available. In particular, the comparisons with the spectra [7] of the chemically oxidized PSRC (in which P and hemes are oxidized) and of the PSRC of *Rhodobacter* (*Rb.*) *sphaeroides* (which does not have a cytochrome c subunit) were very useful. The average discrepancy from the experimental peak positions is 0.13 eV (3 kcal/mol). The protein effects were to red-shift the peaks for most states. The present assignment of the spectrum would give a basis for future photo-experimental studies of the PSRC.

The SAC–CI wavefunctions of the chromophores were then utilized to clarify the electronic mechanism of the ET from the initial photo-excited P^* to H and the origin of its unidirectionality in the PSRC. The ET rate is expressed by Marcus and Sutin [8] as a product of the electronic and thermodynamic nuclear factors. Fig. 2 shows the electronic factors (transfer integrals), $|H_{IF}|^2$ ($\times 10^{-9}$ in a.u.), calculated in the environment of the proteins and in the gas phase. The values in parentheses are those estimated from the experimental data [9]. The energy levels of the two lower states in the L-branch colored green are the experimentally estimated values [10], but for others, the SAC–CI values were used. We assume here the sequential mechanism, since the energy levels of the intermediate states were experimentally estimated to be lower than that of P^* [10]. The calculated electronic factors (including protein

Fig. 1. Absorption and linear dichroism spectra of the PSRC. (a) Theoretical excitation spectrum calculated by the SAC–CI method. (b) Experimental absorption and linear dichroism spectra [7]. (c) Theoretical linear dichroism spectrum calculated by the SAC–CI method.

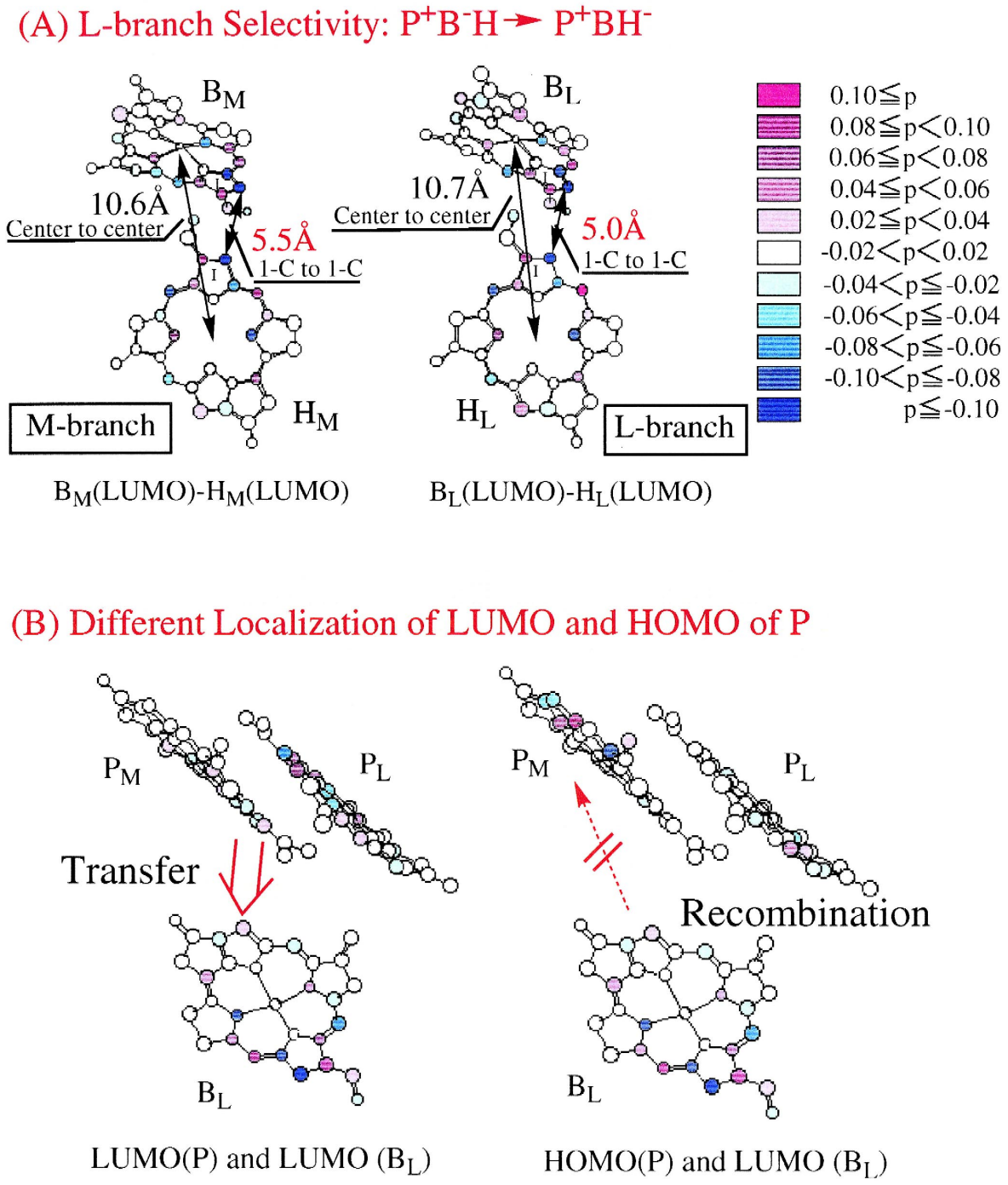

Fig. 3. Geometries of the chromophores and the MO populations for (A) the LUMOs of B and H in M- and L-branches and (B) the LUMO(P)–LUMO(B_L) pair and the HOMO(P)–LUMO(B_L) pair which are the MO pairs responsible for the ET and CR processes, respectively. The sign of the population indicates the phase of the orbital.

effect) for the ETs from P^* to B and from B to H in the L-branch are 25.2 and 104.4, respectively, which are in good agreement with the experimentally estimated values of 21 and 72, respectively, and are much larger than the corresponding values for the M-branch of 1.7 and 15.9, respectively. The calculated branching ratio, $|H_L|^2/|H_M|^2 \approx 15$ in proteins ($|H_L|^2/|H_M|^2 \approx 35$ in the gas phase), is large enough to explain the experimental branching ratio $k_L/k_M > 5$ [11]. These ETs occur mainly through the lowest unoccupied molecular orbitals (LUMOs) of P, B, and H.

A competitive reaction to the ET from B to H is the charge recombination (CR) reaction from P^+B^-H to the ground state of PBH. This CR is essentially a transfer of an electron from the LUMO of B_L to the highest unoccupied molecular orbitals (HOMO) of P. The electronic factor calculated for the CR is 1.0 which is much smaller than that for the charge transfer (CT), 104.4, so that CR is much less preferable to ET: the branching ratio here to the CR is 1.0/105.4, $\sim$1% of that of the ET, which corresponds well with the so-called efficiency (quantum yield) of the photosynthesis.

The L-branch selectivity is explained by the asymmetry of the electronic factors. Namely, the L-side route is much wider than the M-side one. Therefore, we have analyzed the electronic factors in some detail and found that this asymmetry originates mainly from a small structural asymmetry of the PSRC: the L-side chromophores are closer locally than the M-side ones, though the average separations are almost the same. Fig. 3A shows the geometries of B and H and the populations of the LUMOs of the B–H pairs in the M- and L-branches. The analysis of the transfer integrals has revealed that the transfer between ring I of B and ring I of H is dominant in both branches, but since the inter-ring distance is closer by 0.5 Å in the L-branch than in the M-branch, the ET occurs more easily in the L-branch. Note that the B–H center-to-center distance is almost the same between both branches. A similar argument also holds for the ET from P^* to B.

The smallness of the CR rate, on the other hand, is attributed to the difference in the electron localization between the LUMO and HOMO of the special pair. In Fig. 3B, the populations of the LUMO and HOMO of P and the LUMO of B are shown. The populations of P_M and P_L are different in the HOMO and LUMO [12]. In P_M, which is closer to B_L, the LUMO population is localized in the lower area, while the HOMO population is localized in the upper area, so that the effective distance between P and L is much less in the LUMO(P)–LUMO(B_L) pair than in the HOMO(P)–LUMO(B_L) pair. Therefore, although the ET occurs easily, it is difficult for CR to take place.

The role of the proteins is decisive as the three-dimensional arrangement of the chromophores in the L- and M-branches is supported by them. However, the protein effects accounted for by the electrostatic point-charge model were found to be very small.

Nature offered a duality in the electron path, but now only one is utilized. Since we could attribute the primary origin of the L-branch selectivity of the ET to a bio-structural factor – the local closeness of the chromophores in the L-region relative to the M-region – we propose a mutation experiment which would make the M-side chromophores locally closer than the L-side ones, since this should result in an occurrence of the M-side ET. This would certainly be an exciting experiment, and would lead to the clarification of many other facts. More details of the present study will be published in the near future [13,14].

2. Method

All calculations were carried out using the geometries of the chromophores and proteins as determined by X-ray crystallography [15,16]. Huzinaga et al.'s basis sets [17] plus some anion and polarization functions [18] were commonly used in the calculations of all the chromophores. The proteins and waters were replaced by the point charge model using the published charges [19]. The polarization effect of proteins was considered only for P. In the SAC–CI calculations, the active MOs were selected such that at least p-orbitals of C, N, and O and the valence orbitals of the other atoms should be included. For the hemes in the cytochrome subunit, only the inner 1s orbitals were frozen, so that the accuracy is better for the hemes. The dimensions of the SAC–CI calculations were reduced by doing perturbation selections for double linked operators:

the thresholds are similar to the previous ones [20]. The calculations were done using the HONDO8 program [21] for the self-consistent field (SCF)–MO calculations and SAC–CI 96 program [22] for the SAC–CI calculations. Other details of the calculations are described in Refs. [13,14].

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