Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications

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Supplement to chapter 22

Effects of Axial Coordination, Electronic Excitation and Oxidation on Bond Orders in the Bacteriochlorin Macrocycle, and Generation of Radical Cation on Photo-Excitation of in vitro and in vivo Bacteriochlorophyll a Aggregates: Resonance Raman Studies (Y. Koyama, Y. Kakitani, L. Limantara, R. Fujii)

Effects of Axial Coordination, Electronic Excitation and Oxidation on Bond Orders in the Bacteriochlorin Macrocycle, and Generation of Radical Cation on Photo-Excitation of in vitro and in vivo Bacteriochlorophyll *a* Aggregates: Resonance Raman Studies

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Running title: Raman Studies on Bacteriochlorin Macrocycles

Table S1. The regions of the ring-breathing frequencies (cm^{-1}) in the different electronic and coordination states of BChl *a* and in the different electronic states of BPhe *a*. Number of solvents tested are shown in parentheses.

the ring-breathing frequencies, electronic states and species		not classified	classified	
			5-coordinated	6-coordinated
ν_r	S_0 BChl *a*	1594–1611 (20)	1605–1611 (12)	1594–1599 (8)
ν_r^+	D_0 BChl *a* (radical cation)	1584–1599 (13)	1595–1599 (7)	1584–1588 (6)
ν_r''	T_1 BChl *a*	1578–1591 (13)	1585–1591 (8)	1578–1581 (5)
ν_r'	S_1 BChl *a*	1567–1568 (3)		
ν_r	S_0 BPhe *a*	1606–1610 (19)	–	
ν_r''	T_1 BPhe *a*	1586–1589 (4)	–	
ν_r'	S_1 BPhe *a*	1582–1587 (6)	–	

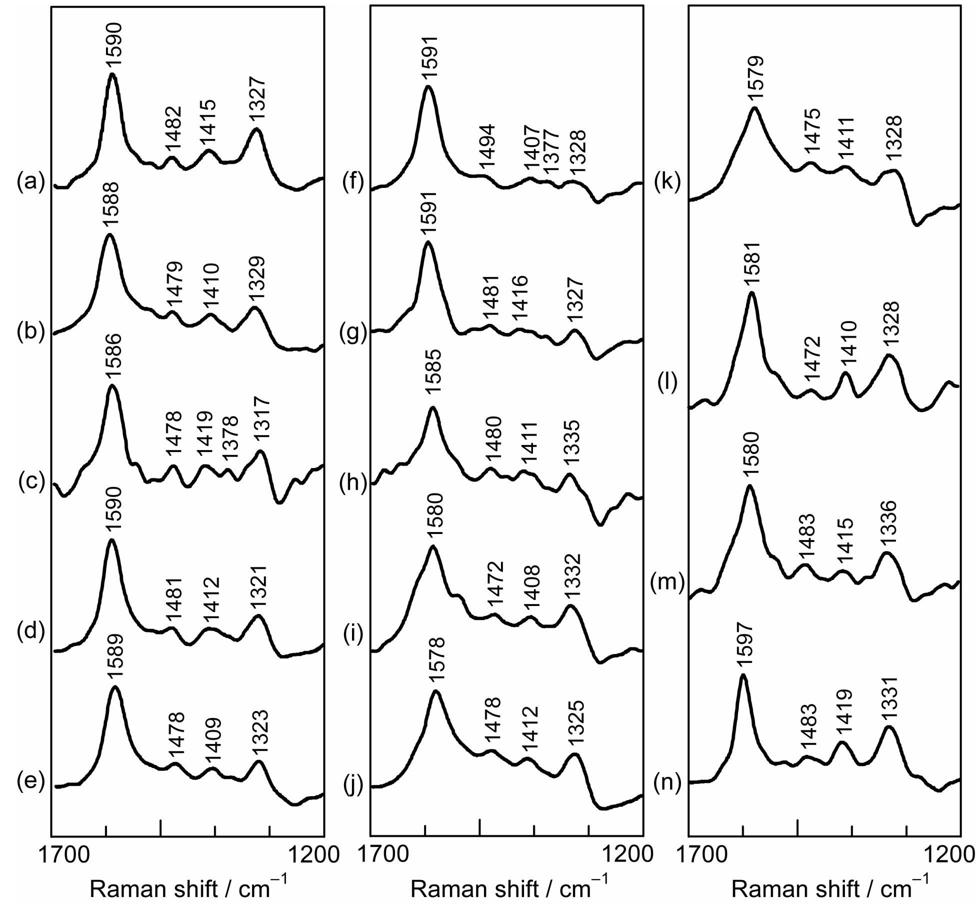

Fig. S1. The Raman spectra of BChl *a* in the T_1 state in (a) acetonitrile, (b) acetone, (c) 2-butanone, (d) 3-pentanone, (e) 2-octanone, (f) diethyl ether, (g) propyl ether, (h) 2-propanol, (i) 1-butanol, (j) 1-hexanol, (k) 1-decanol, (l) pyridine and (m) THF. (n) The Raman spectrum of BChl *a* in the D_0 (radical-cation) state generated by photo-excitation of BChl *a* aggregates in methylene chloride. The Raman spectra were obtained by a one-color, pump-and-probe method using the 420 nm, 5 ns pulses; each transient Raman spectrum was obtained as a difference spectrum of high power minus low power.

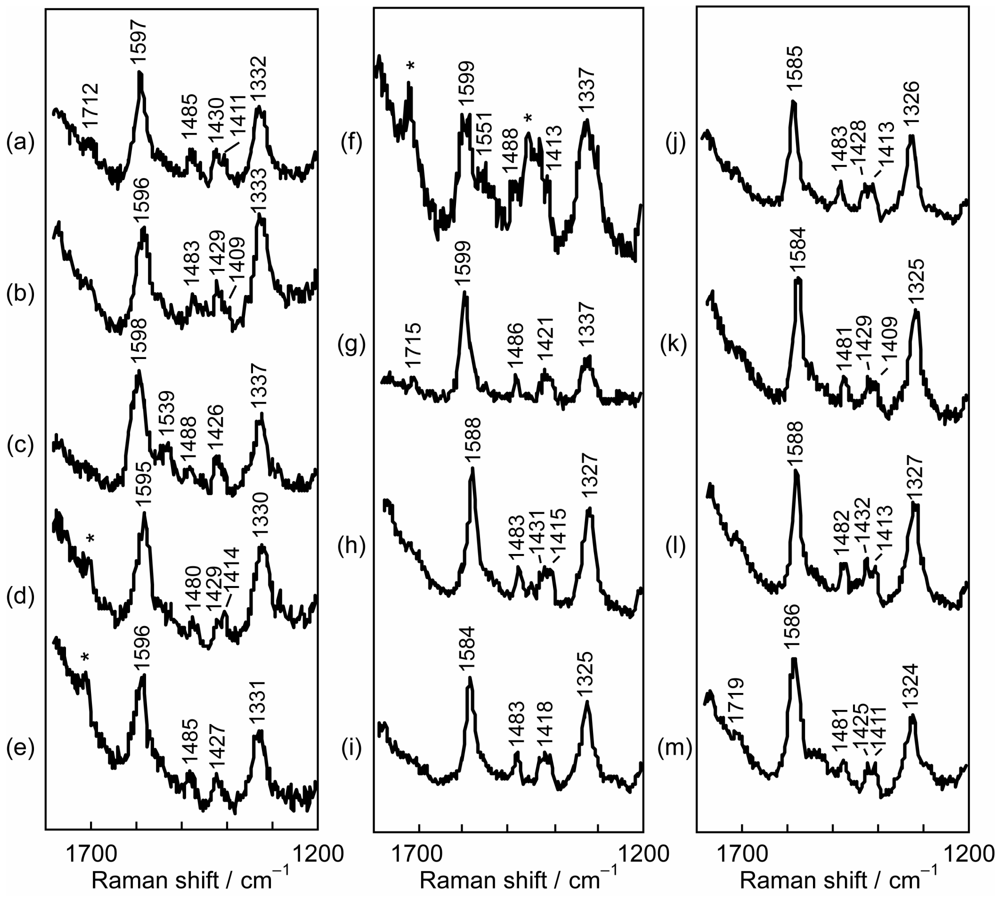

Fig. S2. The Raman spectra of radical cation (the D_0 state) electrochemically generated by one-electron oxidation of BChl *a* in (a) propionitrile (b) 1-butyronitrile, (c) acetone, (d) 2-butanone, (e) 3-pentanone, (f) 2-octanone, (g) methylene chloride, (h) 2-propanol, (i) methanol, (j) ethanol, (k) 1-propanol, (l) 1-butanol, and (m) THF. (Asterisks indicate Raman lines due to the solvents.) A thin-layer Raman cell was built, and the 418.5 nm pulses were used for Raman measurements.

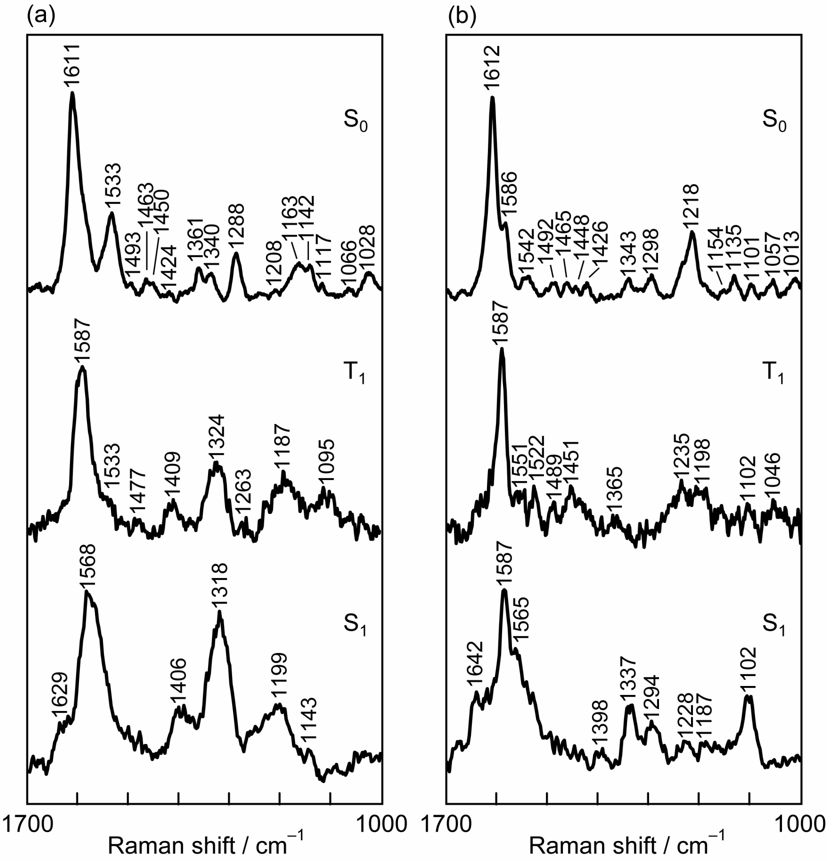

Fig. S3. The Raman spectra of unlabeled (a) BChl *a* and (b) BPhe *a* in the S_0, T_1 and S_1 states. The stationary-state S_0 Raman spectra were recorded by a conventional method using the CW 457.9 nm line (by which only the ground, S_0 state can be probed). The T_1 Raman spectra were recorded by a one-color, pump-and-probe method using the 420 nm, 5 ns pulses; and the S_1 Raman spectra were recorded by another one-color, pump-and-probe method using the 351 nm, ~50 ps pulses. Both the T_1 and S_1 Raman spectra were obtained as difference spectra of high power minus low power. [The $S_1(Q_y)$ lifetime in the range 2.3–3.6 ns and the quantum yield of intersystem crossing in the range of 0.7–0.9 (Connolly JS, Samuel EB and Janzen AF (1982) Effects of solvent on the fluorescence properties of bacteriochlorophyll *a*. Photochem Photobiol 36: 565–574) lead to a time constant of intersystem crossing in the range of 2.6–5.1 ns. Thus, the S_1 and T_1 Raman spectra can be time-resolved by the above pump-and-probe pulses with different duration.]

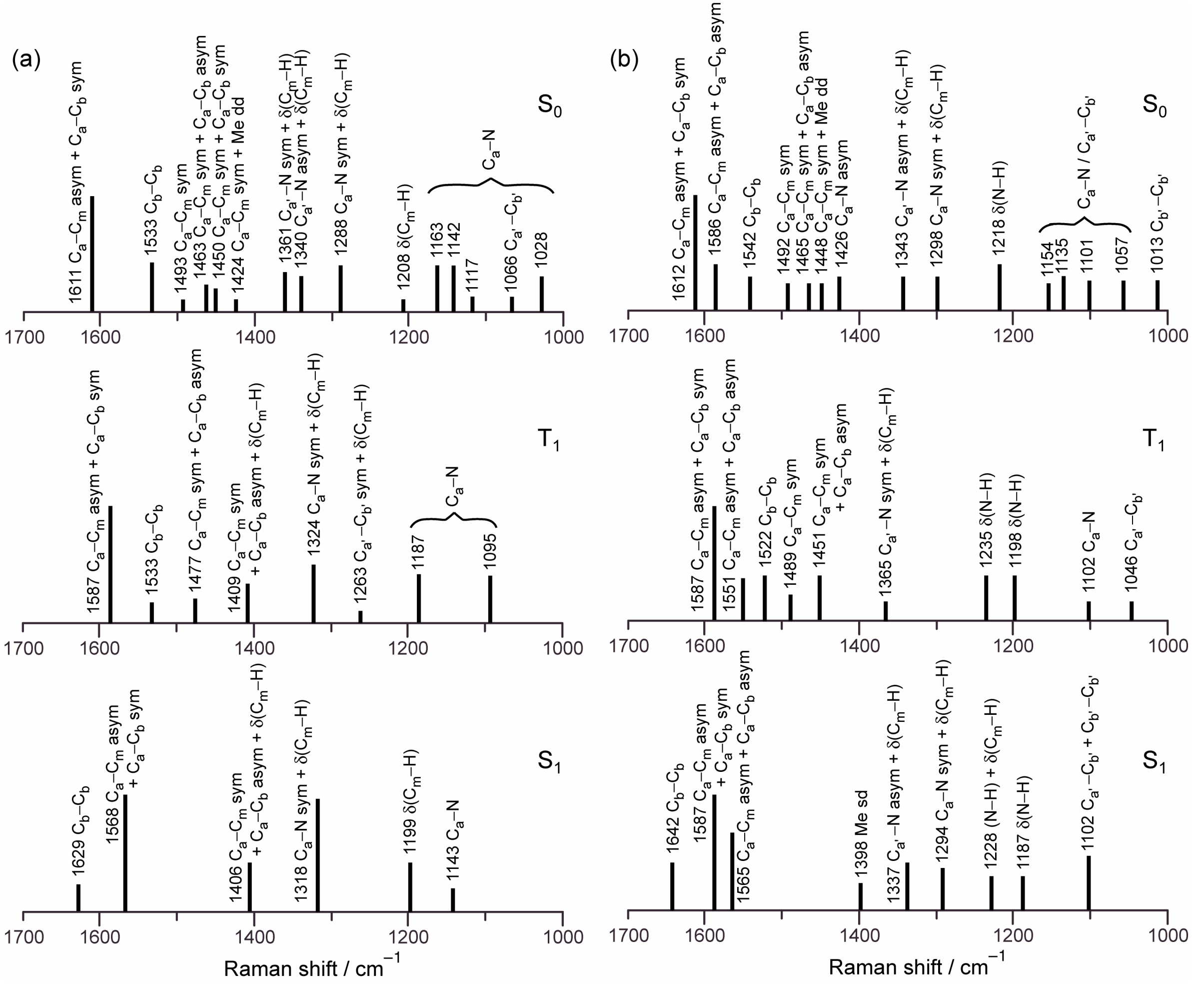

Fig. S4. Assignment of Raman lines of (a) BChl *a* and (b) BPhe *a* in the S_0, T_1 and S_1 states. Symbols 'asym' and 'sym' indicate asymmetric and symmetric stretching, respectively. 'Me sd (dd)' indicates the methyl symmetric (degenerate) deformation, and 'δ(C_m–H)' indicates the in-phase deformation of the methine C_m–H.

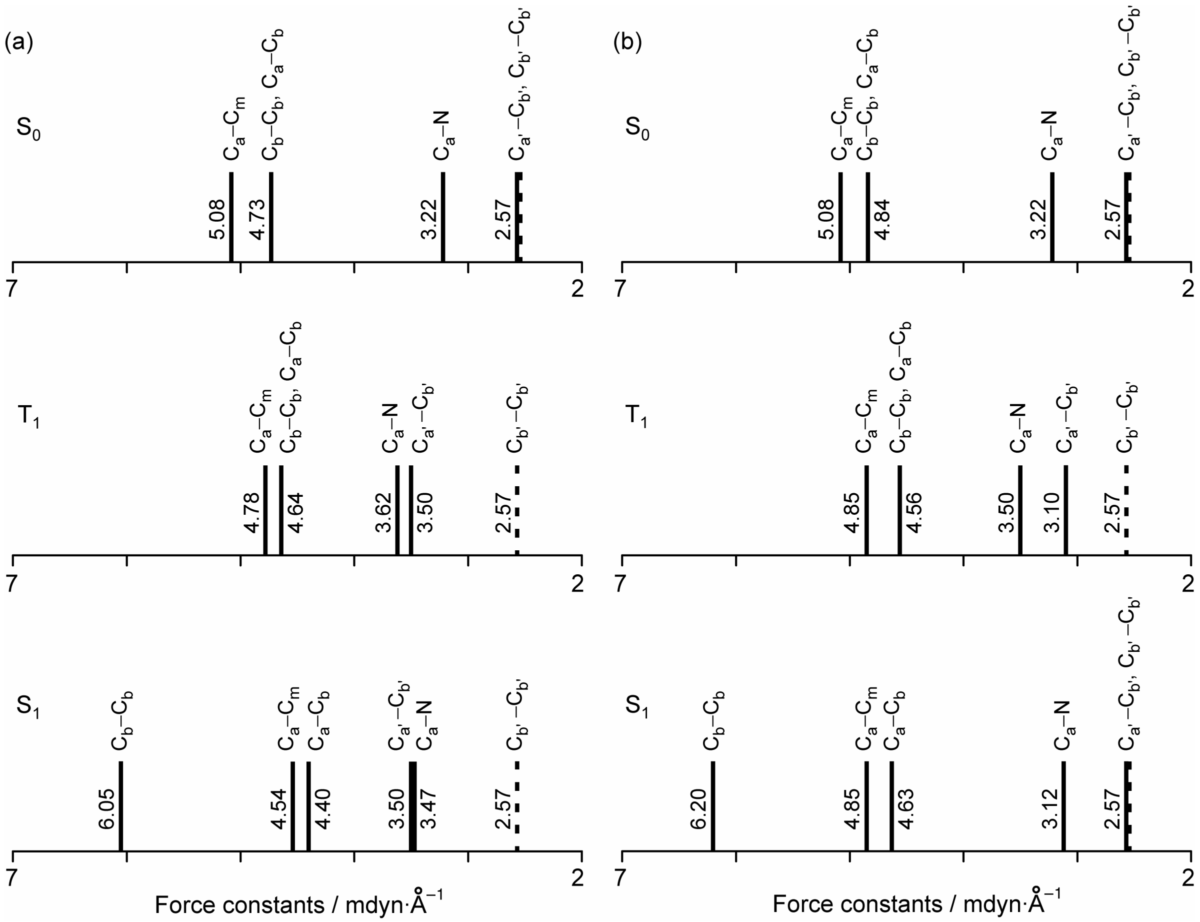

Fig. S5. Carbon-carbon and carbon-nitrogen stretching force constants determined for the macrocycles of (a) BChl *a* and (b) BPhe *a* in the S_0, T_1 and S_1 states. Here, 'C_a–C_m' collectively include both C_a–C_m and $C_{a'}$–C_m, whereas 'C_a–N' collectively include both C_a–N and $C_{a'}$–N.

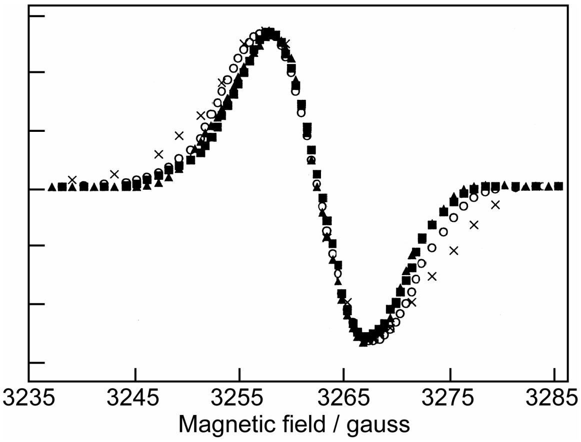

Fig. S6. Normalized EPR signals for radical cation (the D_0 state) generated by photo-excitation (using the 532 nm, 5 ns pulses) of BChl *a* aggregates in carbon tetrachloride (×), and those in the carotenoid-less LH1 (■) and LH2 (▲) complexes from *Rba. sphaeroides* R26 and R26.1. Those generated by photo-excitation of the carotenoidless RC (○) is also shown for comparison.

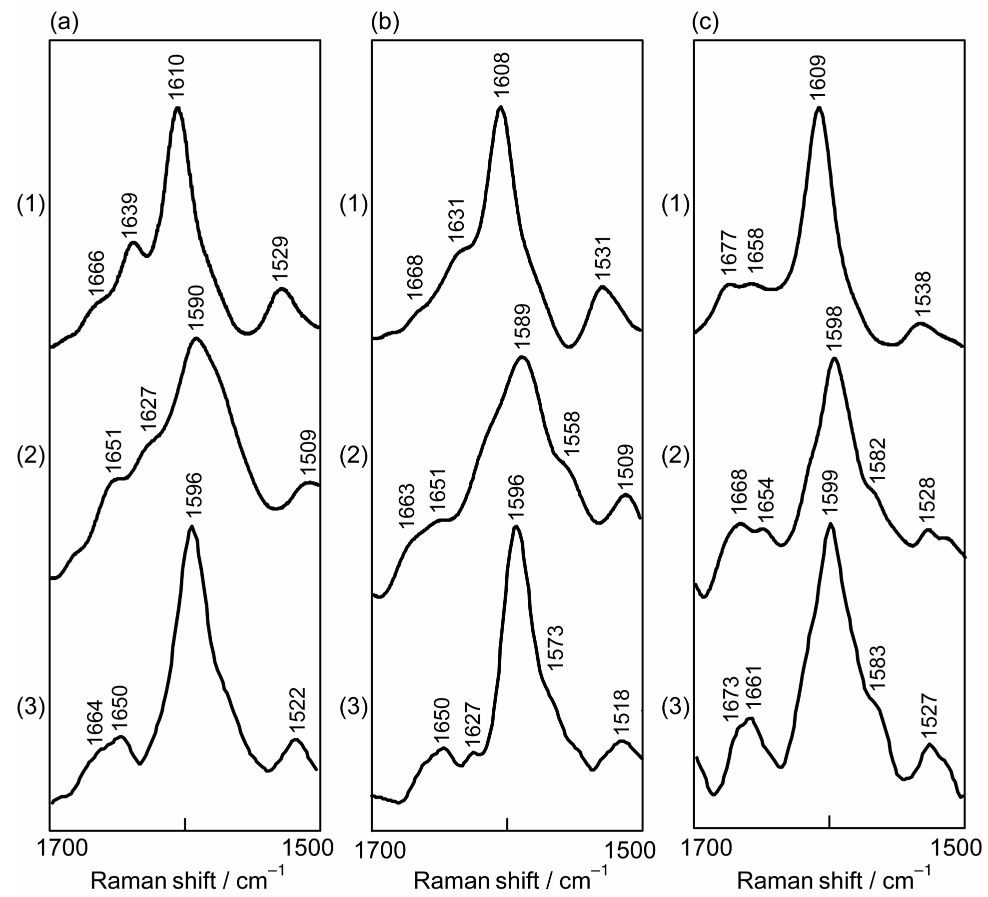

Fig. S7. (1) The S_0 Raman spectra, (2) the picosecond transient-Raman spectra, and (3) the nanosecond transient-Raman spectra for the carotenoid-less (a) LH1, (b) LH2 and (c) RC complexes from *Rba. sphaeroides* R26, R26.1 and R26, respectively. The S_0 Raman spectra and the picosecond transient-Raman spectra were obtained by a one-color pump-and-probe method using the 351 nm, ~50 ps pulses. The low-power spectra were regarded as the S_0 Raman spectra, whereas difference spectra of high power minus low power were regarded as Raman spectra of transient species generated within ~50 ps. The nanosecond transient-Raman spectra were obtained by a one-color pump-and-probe method using the 355 nm, 12 ns pulses. Difference spectra of high power minus low power were regarded as Raman spectra of transient species generated within 12 ns.