Picosecond time-resolved near-IR spectra of C_{60} excited states by pump-probe measurements using a probe beam based on broad-band optical parametric generation

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Picosecond time-resolved absorption spectra of C_{60} singlet and triplet excited states are observed in the near-IR region in the region 700–1300 nm by the pump-probe technique using a probe beam based on broad-band optical parametric generation (OPG) in β-barium borate (BBO) pumped by a picosecond laser pulse at 532 nm and using an InGaAs multichannel detector.

Transient intermediates during photochemical reactions show characteristic absorption bands in the near-IR region. For example, the triplet state and radical anion of C_{60} show absorption maxima at 740 and 1060 nm, respectively.[1–3] In previous papers,[4–6] we studied the photochemical behaviour of the C_{60} triplet state and electron transfer with electron donors by time-resolved near-IR spectroscopy using a Ge avalanche photodiode (Ge-APD) as detector over nanosecond timescales. The observation of the growth of the C_{60} radical anion and donor radical cation with decreasing C_{60} triplet ($^3C_{60}{}^*$) by time-resolved near-IR spectra in the region 600–1600 nm gives direct information about the electron transfer from electron donors to $^3C_{60}{}^*$.[4,5] Time-resolved near-IR spectroscopy is also effective in determining the transition energies of fullerene excited states. The triplet–triplet (T–T) absorption band of C_{70} in the region 800–1200 nm was first observed by laser flash photolysis using a Ge-APD detector.[6] However, the time resolution is limited to the nanosecond domain due to the response of the Ge-APD, for which the cut-off frequency is < 1 GHz. Picosecond time-resolved absorption spectra of fullerenes have been observed by the pump-probe technique.[7–10] In the pump-probe measurements, the white continuum picosecond probe pulse was generated by self-phase modulation by passing the laser beam through a liquid cell, containing D_2O–H_2O, and a Si-multichannel photodiode array is usually used as the detector. By using the pump-probe technique in the range 400–960 nm, the intersystem crossing process from C_{60} singlet ($^1C_{60}{}^*$) to $^3C_{60}{}^*$ has been demonstrated clearly for C_{60} dispersed in poly(methyl methacrylate) film.[8] The absorption maximum of $^1C_{60}{}^*$ was observed at 920 nm, but neither the absorption edge nor the lowest $S_1 \rightarrow S_n$ transition energy of $^1C_{60}{}^*$ was determined. There are two difficulties in the measurements of picosecond time-resolved absorption spectra in the near-IR and IR region by the pump-probe technique. The first problem is the limitation of the sensitivity of multichannel detector for the probe beam. However, this problem has recently been overcome by a recent development of an InGaAs multichannel detector which is sensitive in the wavelength range 700–1700 nm. The second problem is the limitation of the spectral wavelength range and the intensity of the probe beam in the near-IR region. The probe beam generated by self-phase modulation in a liquid such as a D_2O–H_2O is unstable in the near-IR region due to absorption by the solution itself and its thermal fluctuation as a result of the IR beam. Recent advances of optical parametric oscillators (OPO) have opened up many possibilities in spectroscopic studies; however, the narrow linewidth of the OPO is not convenient for time-resolved absorption spectroscopy by pump-probe meas-

urements using a multichannel detector system. In this study, therefore, we used broad-band optical parametric generation (OPG) based on a β-barium borate (BBO) crystal pumped by a 532-nm pulse of a picosecond mode-locked Nd:YAG laser, where the focused pump beam passed through the BBO crystal at various phase-matching angles. Our intention was to establish a picosecond time-resolved near-IR spectroscopic study by the pump-probe technique using a probe beam based on broad-band OPG and an InGaAs multichannel detector and to measure fullerene excited states in the near IR region.

The block diagram of the picosecond time-resolved near-IR spectroscopic apparatus is shown in Fig. 1. The second harmonic generation (SHG, 2ω, 532 nm) and the third harmonic generation (THG, 3ω, 355 nm) of an active/passive mode-locked Nd:YAG laser (Continuum, PY61C-10, 30 ps fwhm) were used for OPG and a pump beam to excite a sample solution, respectively, after the separation of the SHG beam from the THG beam by a dichroic mirror. After passing an optical delay line, the SHG beam (2–3 mJ) was focused by a 10 cm lens on the BBO crystal (4 × 7 mm², 7 mm thickness), which was set within the focusing length (10 cm) to avoid damage. The OPG based on the BBO pumped by 532 nm laser pulse shows a narrow tuning angle for phase matching.[11] The tuning angle for the idler wave is quite narrow in the near-IR and IR regions. Therefore, it is expected that the distribution of the incident angle of the SHG beam causes OPG over a wide wavelength range. The broad-band OPG beam was split into probe and reference beams, which were focused on optical fibre heads and detected by two coupled sets of a polychromator and an InGaAs multichannel detector with a 128-element linear
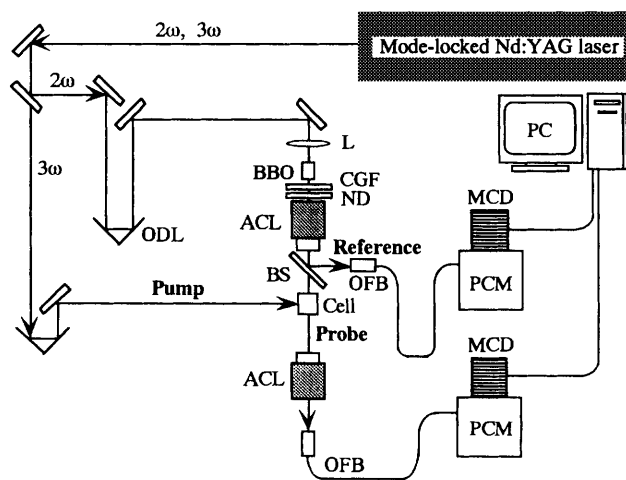

Fig. 1 Block diagram of the picosecond time-resolved near-IR spectroscopy apparatus: ODL, optical delay line; L, lens; BBO, BBO crystal; CGF, colour glass filter; ND neutral-density filter; ACL, aberration-corrected camera lens; BS, beam splitter; OFB optical fibre; PCM, polychromator; MCD, InGaAs multichannel detector; PC, personal microcomputer
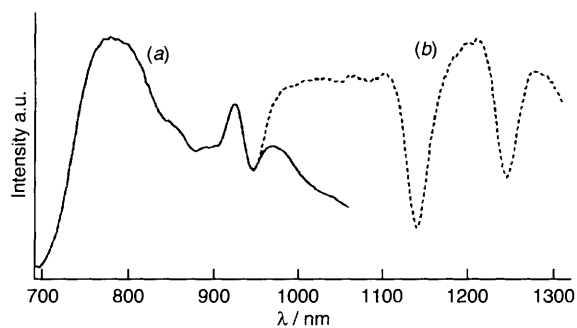
Fig. 2 Spectral profiles of white continuum by the broad-bandwidth OPG based on a BBO crystal pumped by a 532 nm pulse of picosecond mode-locked Nd : YAG laser; (a) tuning centred at 880 nm and (b) tuning centred at 1130 nm

image sensor. The pump beam (THG) was focused on a cell containing 0.1 mmol dm^{-3} C$_{60}$ in deoxygenated benzene using a cylindrical lens. The spectra were obtained by averaging 100–200 pulses of the probe and reference beams on a microcomputer.

The spectral profiles of the probe beam after passing through a 0.1 mmol dm^{-3} C$_{60}$ benzene solution without THG-excitation are shown in Fig.2. The probe beam by OPG at an appropriate tuning angle shows a broad continuum in the wavelength range 700–1320 nm, which is suitable for a multichannel detector system. By changing the BBO tuning angle, we observed extension of the continuum to 1700 nm, which is at the high-wavelength limit for the InGaAs multichannel detector. The spectral properties of the white continuum depend significantly on the divergence of laser beam and the focusing length on the BBO crystal. In Fig. 2, two sharp absorptions are seen at 1140 and 1240 nm which are attributed as due to the solution and the optical fibre.

The time-resolved near-IR spectra obtained by pump-probe measurements for 0.1 mmol dm^{-3} C$_{60}$ are shown in Fig. 3. The C$_{60}$ was excited by a 355 nm laser pulse of the Nd : YAG laser and the transient absorption bands of the C$_{60}$ excited states were monitored using the probe beam based on the broad-band OPG. Fig. 3(a) shows absorption maxima at 750 and 960 nm, which are assigned to ^{3}C$_{60}$* and ^{1}C$_{60}$*, respectively. The intersystem crossing process from ^{1}C$_{60}$* to ^{3}C$_{60}$* is demonstrated by the decay of 960 nm band (^{1}C$_{60}$*) and the growth of 750 nm band (^{3}C$_{60}$*). Fig. 3(b) shows time-resolved absorption spectra of ^{1}C$_{60}$* in the range 940–1320 nm, which show an absorption shoulder at 1100 nm and an absorption edge at 1200 nm (1.03 eV). This is the first observation of the lowest S$_1$ → S$_n$ transition band and the absorption edge of ^{1}C$_{60}$*.
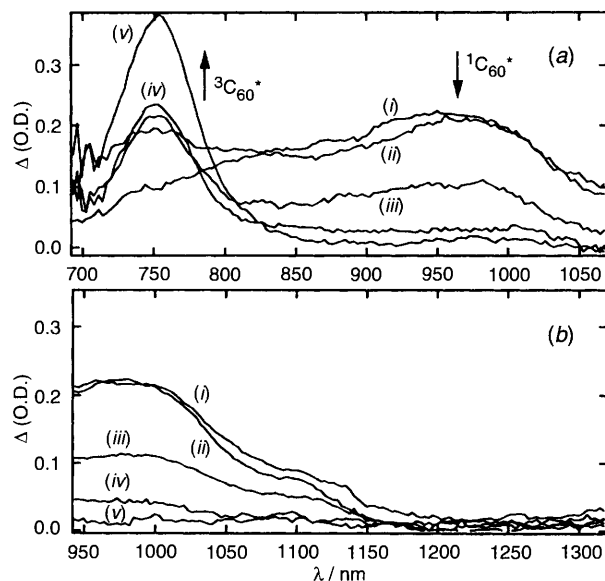

Fig. 3 Picosecond time-resolved near-IR spectra obtained by pump-probe measurements for 0.1 mmol dm^{-3} C$_{60}$ in deoxygenated benzene; (i) 0, (ii) 200 (iii) 730, (iv) 1270 and (v) 2330 ps. Excitation wavelength 355 nm.

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