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Nanotechnologies — Characterization of single-wall carbon nanotubes using near infrared photoluminescence spectroscopy

Nanotechnologies — Caractérisation de nanotubes de carbone monofeuillet en utilisant la spectroscopie de photoluminescence dans le proche infra-rouge

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Introduction

Discovery of band gap photoluminescence (PL) of single-wall carbon nanotubes (SWCNTs) has provided a new way to characterize their unique electronic properties induced by their low dimensionality. The method can provide the chiral indices of the semi-conducting SWCNTs in a sample and their relative integrated PL intensities. With the knowledge of their PL cross-sections, the relative mass concentrations of semi-conducting SWCNTs in a sample can be estimated.

Nanotechnologies — Characterization of single-wall carbon nanotubes using near infrared photoluminescence spectroscopy

1 Scope

This Technical Specification provides guidelines for the characterization of single-wall carbon nanotubes (SWCNTs) using near infrared (NIR) photoluminescence (PL) spectroscopy.

This Technical Specification provides a measurement method for the determination of the chiral indices of the semi-conducting SWCNT in a sample and their relative integrated PL intensities.

The method can be expanded to estimate relative mass concentrations of semi-conducting SWCNTs in a sample from measured integrated PL intensities and knowledge of their PL cross-sections.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/TS 80004-3, *Nanotechnologies — Vocabulary — Part 3: Carbon nano-objects*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 80004-3 and the following apply.

3.1
chiral vector of SWCNT
vector notation used to describe the helical structure of a single-wall carbon nanotube

[ISO/TS 80004-3:2010, definition 4.5]

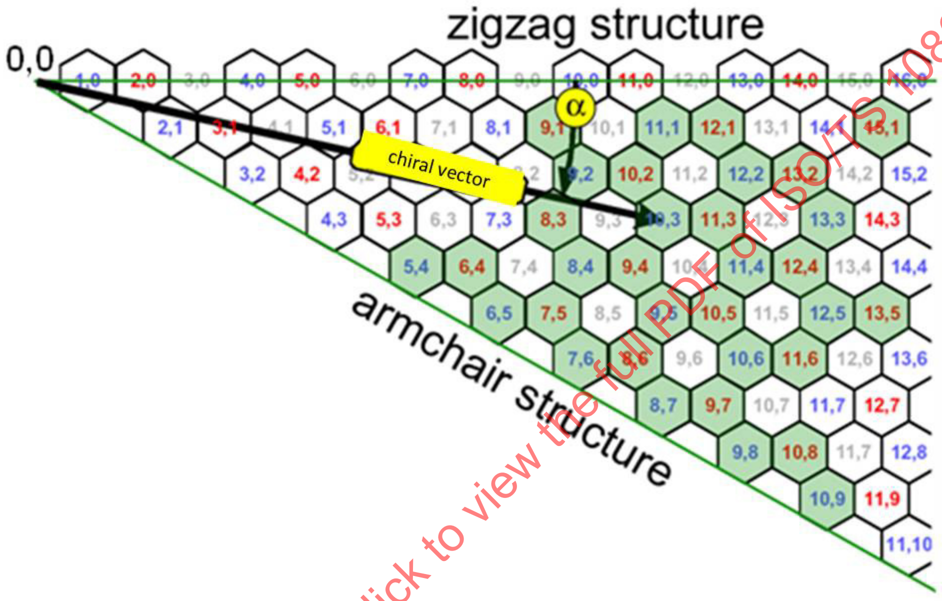
3.2
chiral indices
two integers that define the chiral vector of a single-wall carbon nanotube

3.3
relative mass concentration
mass concentration of nanotube species relative to that of the most common nanotube species

4 Principles of band gap photoluminescence of SWCNTs

4.1 Structure of SWCNTs

An SWCNT consists of a single cylindrical graphene layer. The specific geometry of SWCNTs is defined in terms of a *chiral vector* containing a length (the tube's circumference) and a *chiral angle* α (ranging from 0 to 30°). Alternatively, the structure of SWCNTs is unambiguously defined by the two integers, so-called chiral indices (n, m). Figure 1 shows the indexed graphene sheet with chiral vector for designating nanotube structure, and how the vector starting at point (0,0) to (n, m) determines the nanotube designation [1]. The chiral angle is measured between the *zigzag structure* (α = 0°) and the chiral vector. When the chiral angle is between 0 and 30°, a *chiral structure* arises. The SWCNT having the maximum chiral angle, 30°, is called the *armchair* SWCNT.



NOTE The chiral angle α and chiral vector are shown. The gray indices are for nanotubes that are not photoluminescent.

Figure 1 — Indexed graphene sheet with chiral vector for designating nanotube structure [2]

The length of the chiral vector is the circumference of the tube, or π × the tube diameter d_t. The tube diameter d_t is given in terms of (n, m) by

$$d_{\mathrm{t}} = L/\pi = \frac{\sqrt{3}\,a_{\mathrm{C-C}}\sqrt{m^2 + mn + n^2}}{\pi}$$

where

d_{t} is the diameter of the SWCNT;

L is the length of the chiral vector;

$a_{\mathrm{C-C}}$ is the nearest-neighbour distance (0,144 nm) between pairs of carbon atoms;

m is one of the chiral indices;

n is the other chiral index.

The chiral angle α in terms of (n, m) is defined by the equation

$$\alpha = \tan^{-1}\left[\sqrt{3}m/(2n+m)\right]$$

where

α is the chiral angle;

m is one of the chiral indices;

n is the other chiral index.

4.2 Band structure and PL peaks

Quasi-one-dimensional SWCNTs have an electronic density of states roughly as shown in Figure 2, with sharp van Hove peaks such as v_1 and v_2 (in the valence band) and c_1 and c_2 (in the conduction band).

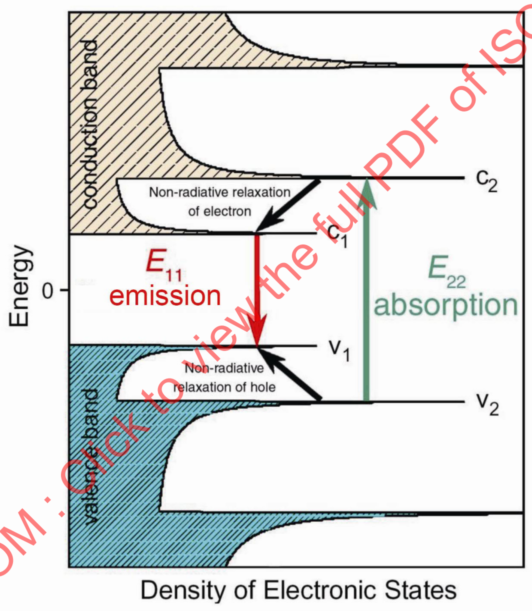


Figure 2 — Qualitative description of the electronic density of states for SWCNTs [2]

Just as the positions of the van Hove peaks depend on the structure (and chiral vector) of the particular SWCNTs, so will the absorption energy E_{22} and fluorescent emission energy E_{11}. Therefore, the positions of the spectral peaks corresponding to E_{22} and E_{11} are characteristic of the structure of each SWCNT, and can be used as a measurement method to determine the component SWCNTs of an unknown mixture. The following equation relates peak wavelength to transition energy

$$E = hc/\lambda = hc\bar{\nu}$$

where

E is energy of the transition;

c is the speed of light;

h is Planck's constant;

$\bar{\nu}$ is the peak position, expressed in wavenumber units (cm^{-1});

λ is the wavelength of the photon absorbed or emitted.

Those structures where the difference ($n - m$) is divisible by three [e.g., (3,0), (4,1), or (6,3)], and those structures where $n = m$, do not fluoresce because SWCNTs with ($n - m$) = a multiple of 3 are semi-metals, with a band gap in the meV range, and those with $n = m$ are metals (no band gap). The remaining structures are semi-conductors with a band gap of about 0,5 eV to 1 eV (1 eV = 1,602 176 53 (14) × 10^{-19} J), and can fluoresce under specific sample preparation conditions.

NOTE As-prepared SWCNTs samples contain left- and right-handed helical structures. The peak positions of the PL signals are basically the same for these enantiomers.

4.3 Exciton effects

Electron-hole pair excitations giving rise to PL are better described in terms of excitons. Excitons are the result of Coulomb interaction, which for SWCNTs is very important and significantly affects the energy spectrum, for example with phonon sidebands and excitonic manifolds of excited states, and the strength of optical transitions. The exciton binding energy was estimated to be 0,420 eV for SWCNTs with the diameter of 0,8 nm in a polymer matrix and a surfactant solution [3]. This value substantially depends on the nanotube environment.

5 NIR-PL apparatus

5.1 NIR-PL spectrometer

For SWCNTs produced by the chemical vapor deposition (CVD) method with typical diameter distribution of 0,6 nm to 1,3 nm, a NIR detector covering the spectral range from 800 nm to 1 600 nm is sufficient to detect their PL. However, to detect the PL signal of the larger diameter SWCNT produced by the laser vaporization and electric arc techniques, a spectral range of 1 200 nm – 2 000 nm is usually required.

NOTE 1 Examples of detector materials are InGaAs and InP/InGaAs.

NOTE 2 The spectral resolution, which in a scanning monochrometer is a complex function of the bandpass of the monochromators, the stepping increment and slit width, needs to be adjusted to resolve the SWCNT peaks of interest in the sample. In general, bandpass values approaching 10 nm have been shown to be sufficient for most surfactant suspensions of SWCNTs. With multi-channel NIR detection systems, a resolution of 5 nm is recommended.

5.2 Light source

Excitation sources are available such as monochromated Xenon or tungsten lamps, continuous Titan-Sapphire lasers or fixed wavelength diode lasers.

NOTE Suitable wavelengths of diode lasers can be selected to suit the diameter distribution of the SWCNT sample (see Figure A.2 and Figure A.4).

6 Sample preparation methods

6.1 Preparation of D_2O dispersion for measurement

For the preparation of a liquid dispersion of SWCNTs, the following procedure shall be used.

a) Use D_2O as the dispersing medium, which transmits light in the broad range from UV-Vis to 1 800 nm.

NOTE H_2O is unsuitable because it strongly absorbs light at 1 400nm and longer wavelengths.

b) Use water-soluble surfactants, preferably anionic ones such as sodium dodecyl sulfate (SDS) (purity > 95 %), sodium dodecylbenzene sulfonate (SDBS) (purity > 95 %) or sodium cholate (SC) (purity > 98 %) as dispersants.

NOTE Recent work suggests sodium deoxycholate over other dispersants [4].

c) Prepare a D_2O solution of a dispersant, approximately at a concentration of 1 % mass fraction.

d) Add a small amount (approximately 1 mg) of the sample containing SWCNTs into the dispersant solution, approximately 20 mL.

e) To facilitate the process and to obtain homogeneous SWCNT dispersion, sonicate the mixture using an ultrasonic homogenizer.

NOTE 1 An example of sonication conditions is given in Annex A.

NOTE 2 Even after the sonication steps, there can be a significant amount of bundled SWCNTs in the micelle solution.

f) To separate the bundled SWCNTs from the isolated SWCNTs, ultracentrifuge the dispersion and use the supernatant for the PL measurements.

NOTE 1 An example of ultracentrifugation conditions is given in Annex A.

NOTE 2 Insufficient centrifugation leaves a large amount of the bundled SWCNTs unseparated in the sample. On the other hand, excess centrifugation causes a severe reduction in the concentration of SWCNTs in the solution.

g) If the optical density (O.D.) of the probed volume is above 0,5 after sonication and centrifugation, dilute with the surfactant solution to lower the O.D. below 0,5.

h) Adjust pH of the solution to be approximately 8 by adding an appropriate amount of NaOH [5].

6.2 Preparation of solid film dispersion for measurement

When the PL signals beyond 1 800 nm are required, for example, in the case of the SWCNTs produced by electric arc technique which have a size larger than about 1,4 nm in diameter, prepare the sample by the following method.

a) Use H_2O as the dispersing medium, following the same procedures as described in 6.1, including sonication and ultracentrifugation, to obtain the supernatant.

b) Mix the supernatant with the same volume of an H_2O solution of gelatine from alkali-processed bovine bone with a concentration of 10 % mass fraction. Here gelatin is used as a film forming agent [6].

c) Cast the mixed solution on to a quartz substrate and let it dry (ten hours or longer). This results in the formation of an optically uniform film in which SWCNTs are homogenously dispersed.

7 Measurement procedures

The PL spectra of SWCNTs shall be measured as follows (see Figure A.1 and Figure A.3):

a) Turn on the light source, the spectrometer and the detector, and wait until they stabilize.

b) Calibrate the wavelength-dependent instrumental factors and excitation intensities. For the calibration of the PL system, a light source providing wavelength values traceable to the International System of Units (SI) shall be used for correcting the instrument’s emission detector signal and a calibrated detector shall be used for correcting the instrument’s excitation reference detector signal.

c) Set the SWCNT sample in the correct position according to the spectrometer manual. For this method to work well, pre-existing knowledge is needed of SWCNT diameter ranges. The excitation wavelengths must be matched to the sample under study.

   NOTE The sample cell should be transparent to the excitation and the emission wavelengths.

d) Measure the PL spectrum. Excitation wavelengths should be selected to give excitation of the range of SWCNT species to be analyzed in the sample. A dense set of excitation wavelengths may be used to generate a full two-dimensional excitation-emission map, or alternatively a sparse set of excitation wavelengths may be used to generate emission spectra that can be analyzed using knowledge of SWCNT peak positions [2,5,7,8].

e) An approximately 1/10 concentration solution sample should also be measured to ensure linearity.

f) Compile the data to obtain a corrected excitation-emission map or a corrected set of emission spectra correlated with the excitation wavelength.

8 Data analysis and results interpretation

8.1 Empirical rules for structural assignment

To analyze spectra from numerous SWCNTs in aqueous SDS suspension, the following empirical rules for relating peak position to (*n*, *m*) SWCNT structure apply [2,5,7].

$$\overline{\nu_{11}} = \frac{1 \times 10^7}{157{,}5 + 1066{,}9 d_\mathrm{t}} + \frac{A_1 \cos 3\alpha}{{d_\mathrm{t}}^2}$$

where

$\overline{\nu_{11}}$ is the emission peak position, expressed in wavenumber units (cm^{-1});

d_t is the diameter of SWCNTs, expressed in nanometer units (nm);

A_1 is -710 cm^{-1} and 369 cm^{-1} for ($n - m$) mod 3 = 1 and 2, respectively;

α is the chiral angle (°).

And

$$\overline{\nu_{22}} = \frac{1 \times 10^7}{145{,}6 + 575{,}7 d_t} + \frac{A_2 \cos 3\alpha}{{d_t}^2}$$

where

$\overline{\nu_{22}}$ is the absorption peak position, expressed in wavenumber units (cm^{-1});

d_t is the diameter of SWCNTs, expressed in nanometer units (nm);

A_2 is 1375 cm^{-1} and -1475 cm^{-1} for ($n - m$) mod 3 = 1 and 2, respectively;

α is the chiral angle (°).

Errors using these formulae are low, less than 65 cm^{-1} in all cases, which is far below the spectral line widths of 150 cm^{-1} – 200 cm^{-1} [2,5,7].

NOTE 1 A_1 and A_2 are parameters to predict the experimental values based on the theoretical model [2]. These values depend on the type of SWCNTs [2].

NOTE 2 Spectral peak positions are very similar when SDBS is used as a dispersant and somewhat shifted in SC dispersant. In all cases, changes in sample preparation procedures may lead to minor systematic spectral shifts [9].

8.2 Determination of the chiral indices of the semi-conducting SWCNTs in a sample

The PL signals from (*n*, *m*) nanotubes are obtained by starting with emission spectra that have been corrected for the wavelength-dependent sensitivity of the detection system and the wavelength-dependent excitation intensity at the sample. For each species, the E_{11} emission intensity at its E_{22} excitation maximum shall be integrated across the spectral peaks. If there are overlapping emission features, the magnitudes of the separate components shall be obtained by simulating the experimental emission curve as a sum of peaks, each of which is a Voigt function with appropriate width and shape parameters.

Each experimental (*n*, *m*) PL signal, expressed as an area in the PL mapping, is the product of the relative mass concentration of the (*n*, *m*) SWCNT species multiplied by the PL cross-section for that (*n*, *m*) species. PL cross-sections are the product of E_{22} absorption cross-sections and PL quantum yields. Relative mass concentrations of (*n*, *m*) species can thus be deduced by dividing the experimental (*n*, *m*) signals by the corresponding PL cross-sections. The diameter distribution is obtained from the relative mass concentrations of each (*n*, *m*) SWCNT.

NOTE Accurate values of the PL cross-section for all (*n*, *m*) SWCNTs have not been determined yet. Experimental and theoretical results are available for some SWCNTs [8,10,11].

9 Uncertainties

Currently, the NIR-PL characterization of SWCNTs is accompanied by the risk of uncertainties that come from:

a) Mis-assigning a sideband to an (*n*, *m*) species.

b) Bundles of SWCNTs contained in the sample.

c) Double-wall carbon nanotubes contained in the sample.

NOTE Emission from double-wall carbon nanotubes is controversial at the present time [12].

d) Absorption of PL by the suspending medium.

e) Self-absorption of PL by SWCNTs.

f) Surfactant and solvent can alter PL intensities.

g) Fluorescent impurities.

h) The relationship between the SWCNT mass fraction, length, O.D., and PL intensity is still under investigation [13]

10 Test report

The test report shall contain the following information (see annex A):

a) all information necessary for sonication and ultracentrifugation processes;

b) the type of apparatus used;

c) the emission and the absorption peak positions of each (n, m) type of semi-conducting SWCNTs in the sample;

d) the integrated PL intensities of each (n, m) type of semi-conducting SWCNTs in the sample;

e) Uncertainty discussion.

Annex A
(informative)

Case studies

A.1 General

The determination of the (*n*, *m*) types of semi-conducting SWCNTs in several SWCNT samples and their relative integrated PL intensities are derived based on PL analyses. The examined SWCNTs were produced by Direct Injection Pyrolytic Synthesis (DIPS) that was one of chemical vapor deposition (CVD) methods [14] and the pulsed-laser vaporization (PLV) method [15]. Detailed experimental procedures are described for each production method of SWCNTs.

A.2 SWCNTs synthesized by the direct inject pyrolytic synthesis (DIPS) method

A.2.1 Sample preparation

As-grown DIPS-SWCNTs (about 1 mg) were dispersed in about 15 ml of D_2O containing 1 % (mass fraction) of SDBS using an ultrasonic homogenizer equipped with a titanium alloy tip (13 mm in diameter). Pulsed ultrasound was applied (on: 1 sec, off: 2 sec) with a power of 200 W for 30 min. A 20 ml vial was used as a sample container. Each solution was then centrifuged at 127 600 *g* for 2,5 h with a swing rotor, and the supernatant was used.

A.2.2 PL measurements

The PL was measured with a spectrofluorometer equipped with a Xenon lamp and a near infrared photomultiplier module (see Figure A.1). The bandpass of light throughput and the scan steps were 5 nm and 10 nm, respectively, where these parameters were applied to both excitation and emission.

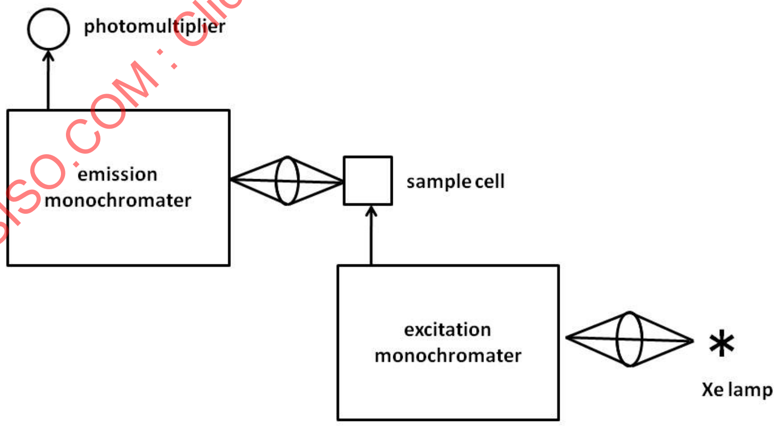


Figure A.1 — Schematic illustration of experimental set-up

Each PL peak in the two-dimensional PL excitation/emission map can be assigned to the individual chiral indices (*n, m*) according to the equation in clause 8.1. For example, Figure A.2 shows a typical two-dimensional contour plot of the NIR-PL mappings of DIPS-SWCNTs/SDBS/D_2O. The PL peak positions measured experimentally are compared to those that have been empirically determined to correspond to a given (*n, m*) [7]. An identification of the (*n, m*) represented by a PL peak can be made when the difference between the experimental peak and the empirical peak positions is less than 65 cm^{-1} as shown in Figure A.2.

NOTE The data of emission and absorption peaks for 220 (*n*, *m*) SWCNTs in SDS micelle solution are listed in the reference [7].

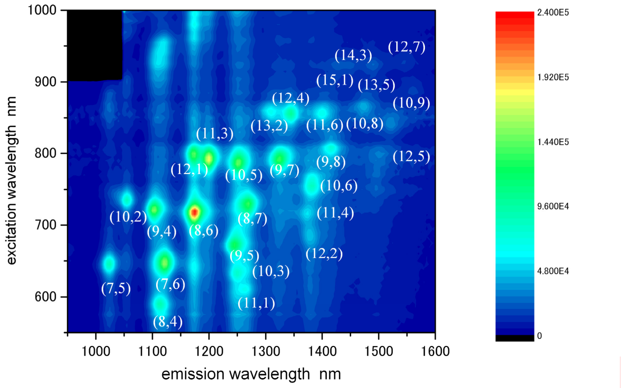
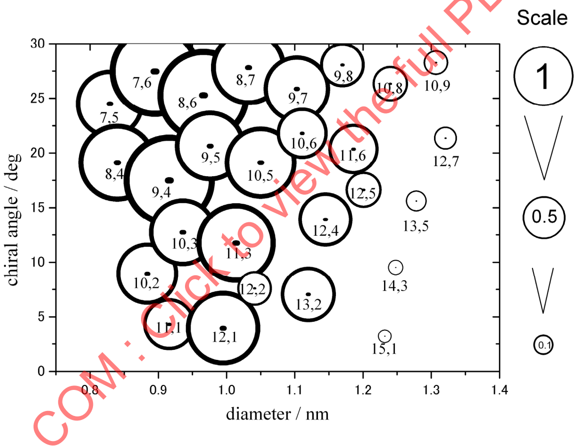


Figure A.2 — Two-dimensional contour plot of the NIR-PL mappings of DIPS-SWCNTs/SDBS/D_2O [16]

A.2.3 Integrated PL intensities of each (*n*, *m*) type of semi-conducting SWCNTs

Figure A.3 shows the relative integrated PL intensities of each (*n*, *m*) type of semi-conducting SWCNTs in DIPS-SWCNTs (Figure A.2) plotted as functions of diameter and chiral angle of the tubes, where the size of each circle denotes the relative integrated PL intensity. The obtained relative integrated PL intensities of all (*n*, *m*) types of semi-conducting SWCNTs are listed in Table A.1.



NOTE The areas of circles are proportional to the relative integrated PL intensities of the (*n, m*) type of semi-conducting SWCNTs.

Figure A.3 — Relative integrated PL intensities of each (*n*, *m*) type of semi-conducting SWCNTs in DIPS-SWCNTs/SDBS/D_2O [16]

Table A.1 —The relative integrated PL intensities of each (*n*, *m*) type of semi-conducting SWCNTs in DIPS-SWCNTs [16]

(*n*, *m*)	**Diameter** nm	**Chiral angle** degree	**Emission peak position** nm	**Absorption peak position** nm	**Integrated PL intensity relative to the most common species**
(7, 5)	0,829	24,50	1 024	645	0,55 ± 0,03
(8, 4)	0,840	19,11	1 114	589	0,71 ± 0,04
(10, 2)	0,884	8,95	1 055	735	0,46 ± 0,03
(7, 6)	0,895	27,46	1 121	647	0,96 ± 0,08
(11, 1)	0,916	4,31	1 264	611	0,32 ± 0,03
(9, 4)	0,916	17,48	1 104	721	0,98 ± 0,08
(10, 3)	0,936	12,73	1 251	633	0,54 ± 0,06
(8, 6)	0,966	25,28	1 175	717	1,00 ± 0,06
(9, 5)	0,976	20,63	1 246	672	0,58 ± 0,07
(12, 1)	0,995	3,96	1 173	797	0,66 ± 0,06
(11, 3)	1,014	11,74	1 199	795	0,75 ± 0,05
(8, 7)	1,032	27,80	1 267	728	0,66 ± 0,05
(12, 2)	1,041	7,59	1 379	687	0,14 ± 0,02
(10, 5)	1,050	19,11	1 252	787	0,61 ± 0,03
(9, 7)	1,103	25,87	1 324	791	0,51 ± 0,03
(10, 6)	1,111	21,79	1 382	756	0,31 ± 0,02
(13, 2)	1,120	7,05	1 310	857	0,36 ± 0,05
(12, 4)	1,145	13,90	1 343	855	0,34 ± 0,04
(9, 8)	1,170	28,05	1 414	806	0,24 ± 0,03
(11, 6)	1,186	20,36	1 399	855	0,30 ± 0,02
(12, 5)	1,201	16,63	1 501	797	0,15 ± 0,01
(15, 1)	1,232	3,20	1 427	923	0,022 ± 0,003
(10, 8)	1,240	26,33	1 474	865	0,15 ± 0,01
(14, 3)	1,248	9,52	1 448	923	0,026 ± 0,007
(13, 5)	1,278	15,61	1 489	923	0,052 ± 0,009
(10, 9)	1,307	28,26	1 558	886	0,072 ± 0,007
(12, 7)	1,321	21,36	1 544	927	0,064 ± 0,011