

## Excitons in carbon nanotubes

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We present two-photon excitation luminescence experiments on carbon nanotubes which show the excitonic origin of the optical excitations. The two-photon allowed exciton state, which has even parity under rotation about the  $U$ -axis, is roughly 300 meV above the one-photon active, odd-parity state. This indicates exciton binding energies on the order of 400 meV for nanotubes with diameters around 8 Å. *Ab-initio* calculations of the exciton wavefunctions and energies are in good agreement with our experimental results, confirming the predictions on the symmetry of the exciton states.

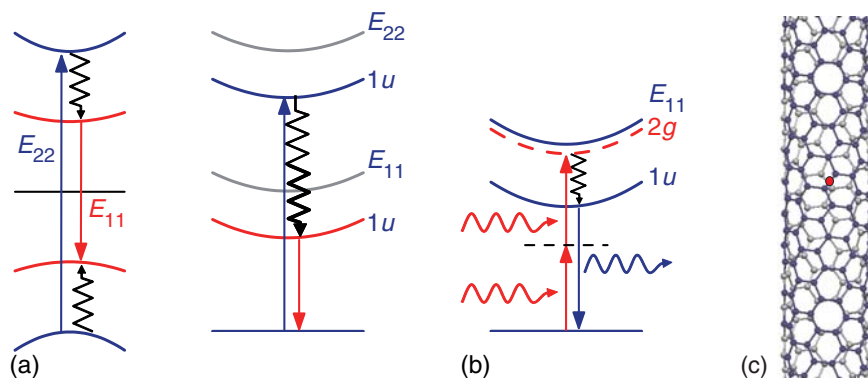
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It is by now established that the optical excitations in carbon nanotubes are due to excitons and must be described in a many-particle picture [1–4]. Direct experimental proof, however, was only recently given when the magnitude of the binding energy was determined [5, 6]. Here we present two-photon photoluminescence excitation experiments that show unambiguously the excitonic character of optical excitations in carbon nanotubes. We explain the symmetry and selection rules of the involved electronic states. *Ab-initio* calculations of the exciton wavefunctions and energies confirm our interpretation of the experiments.

One of the main difficulties in unambiguously assigning the optical spectra – such as photoluminescence excitation (PLE) or Raman resonance profiles – to excitons in carbon nanotubes is due to the fact that excitonic and band-to-band transitions are not clearly observed in the same experiment. Unlike in 3D bulk material, where at low temperature the excitonic bound states appear as sharp absorption peaks below the onset of the continuum, in quasi-1D systems the oscillator strength is almost entirely transferred from the band–band to the excitonic transition [7, 8]. Therefore, it is difficult to probe the van-Hove-like singularities of the (single-particle) joint density of states by optical experiments, in particular, if the optical spectra are broadened as in carbon nanotubes.

Therefore, to prove the excitonic nature of the optical transitions in carbon nanotubes, we addressed exciton states with different wavefunction symmetry of the series of states belonging to the same band-to-band transition [6], see Fig. 1. The one-photon optically active exciton state must have the same symmetry as the photon which is absorbed or emitted. By simultaneous absorption of two photons, on

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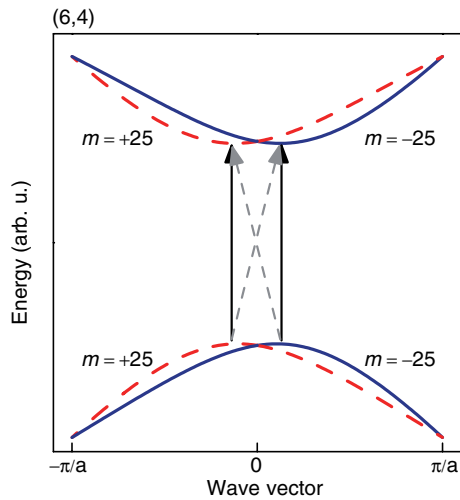


**Fig. 1** (online colour at: [www.pss-b.com](http://www.pss-b.com)) (a) Schematic picture of a photoluminescence excitation (PLE) experiment with excitation into  $E_{22}$  and emission from  $E_{11}$  in the single-particle picture (left) and in the excitonic picture (right). (b) PLE experiment with two-photon excitation into the  $2g$  state and one-photon emission from the  $1u$  state of  $E_{11}$ . (1) and (2) denote even and odd parity of the envelope with respect to  $z$  inversion. (c) (6, 4) nanotube with the  $U$ -axis indicated by the red dot between two neighboring carbon atoms. It points out of the plane of the paper.

the other hand, an otherwise dark exciton state can be optically excited. In (chiral) carbon nanotubes, the symmetry with respect to the  $U$ -axis (two-fold rotational axis perpendicular to the tube axis [9], Fig. 1) defines the exciton series. Only absorption of light polarized parallel to the tube axis ( $z$ -polarized) is relevant. The corresponding dipole operator has odd ( $u$ ) parity under the  $U$ -axis operation and angular-momentum quantum number  $m = 0$  [9, 10]. The irreducible representation is denoted by  ${}_0A_0^-$ , where the minus sign indicates the  $U$ -axis parity. For two-photon absorption, the excited state must be compatible with  ${}_0A_0^- \otimes {}_0A_0^- = {}_0A_0^+$ , i.e., it must be even ( $g$ ) under the  $U$ -axis operation. We thus expect to excite an even ( $g$ ) state by two-photon absorption and observe emission from the one-photon active odd ( $u$ ) state, see Fig. 1(b). The energy difference between these states indicates the strength of the Coulomb interaction between electron and hole. If the Coulomb interaction is negligible, i.e., if the optical excitations were band-to-band transitions, the two-photon and the one-photon active states would have approximately the same energy.

In addition to the  $U$ -axis parity quantum numbers  $u$  and  $g$ , we can classify the envelopes of the exciton relative wavefunctions as being even or odd under  $z$  inversion, where  $z$  is the coordinate of the relative distance between electron and hole along the tube axis. As we will see below, the exciton wave function extends over several nm along the tube axis and is delocalized along the circumference. The first even envelope would be of the form  $\exp(-a|z|)$  and the first odd one of the form  $z \exp(-a|z|)$ . We denote even and odd by (1) and (2), respectively. For one-photon transitions the envelope must be even, for two-photon transitions it must be odd. As the operation  $z \rightarrow -z$  is not an exact symmetry operation of the (chiral) nanotube lattice, the resulting selection rules only weakly apply.

The lowest optical transitions in carbon nanotubes occur near the  $K$ -point in the graphene Brillouin zone. Because of the  $K - K'$  degeneracy, there are four possible configurations of how to form electron-hole pairs that would be degenerate in the absence of Coulomb interaction [11], see Fig. 2. Two of them have  $\Delta m = 0$  and are therefore optically active, while the remaining two have  $\Delta m = 2m$  and cannot be excited by a photon. With Coulomb interaction, the two  $\Delta m = 0$  states will split into an even ( $1g$ ) and an odd ( $1u$ ) state,  ${}_0A_0^+$  and  ${}_0A_0^-$ , respectively. As discussed above, the even state is forbidden for one-photon transitions. The two  $\Delta m = 2m$  states form the doubly degenerate state  $E_{\pm 2m}$ , which is optically inactive. For zig-zag nanotubes these exciton states were explicitly calculated by Perebeinos et al. [12] and Spataru et al. [13]. Perebeinos et al. [12] reported a particularly strong coupling to phonons from the  $K$ -point of graphene. We show now for a general tube that the  $E_{\pm 2m}$  states can be coupled to an optically active state by a  $K$ -point phonon. In the (6, 4) tube (Fig. 2), the lowest bands have  $m = \pm 25$  [14]; the

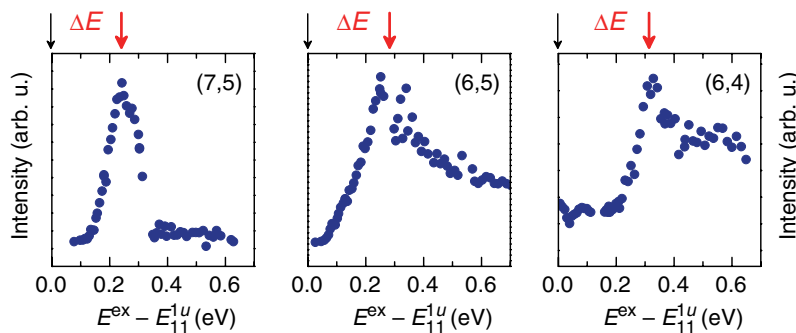


**Fig. 2** (online colour at: [www.pss-b.com](http://www.pss-b.com)) Schematic picture of the bands closest to the Fermi level in the (6, 4) tube. The angular-momentum quantum number is  $m = \pm 25$ , where  $m$  runs from  $-q/2 + 1 = -37$  to  $q/2 = +38$ .  $q$  is the number of carbon hexagons in the unit cell. The bands indicated by the blue (solid) and red (dashed) lines, respectively, are degenerate, i.e., they are transformed into each other by the  $U$ -axis operation. The black (solid) arrows indicate optically allowed transitions ( $\Delta m = 0$ ), whereas the gray (dashed) arrows show combinations with  $\Delta m = \pm 2$  ( $m = \pm 50 \equiv \mp 26$ ), which are not optically active.

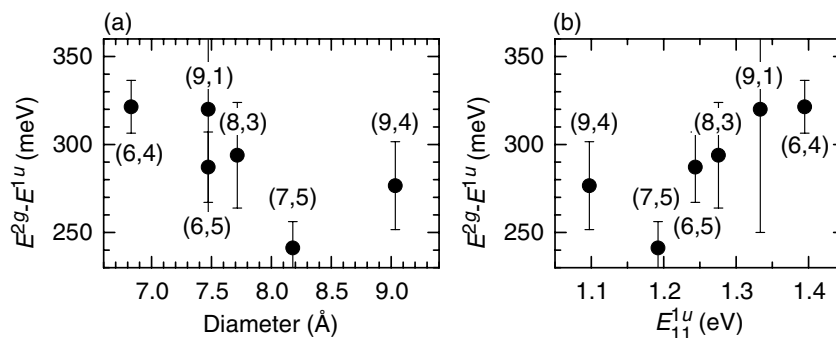
maximum angular-momentum quantum number for this tube is  $m = 38$ . For any tube, the maximum  $m$  is given by  $m = q/2$ , where  $q$  is the number of carbon hexagons per unit cell [9, 10, 15]. In general, in semiconducting tubes with  $\mathcal{R} = 1$  [9], the states closest to the  $K$ -point have  $m = q/3 + \nu/3$ , where  $\nu = (n_1 - n_2) \bmod 3 = \pm 1$  and  $(n_1, n_2)$  is the chiral index. Therefore, the angular-momentum quantum number of the degenerate exciton state  $E_{\pm 2m}^{2g}$ ,  $\Delta m = 2m$ , is equal to  $2m = 2q/3 + 2\nu/3 \equiv 2q/3 + 2\nu/3 - q = -q/3 + 2\nu/3 = -m \pm 1$ . This is again a state close to the  $K$ -point in graphene; it can thus be excited by coupling an optically active state and a phonon from close to the  $K$ -point.

Our samples are HiPCO produced nanotubes dispersed in  $D_2O$  and wrapped by SDS [16]. We excited the sample by 150 fs pulses of an optical parametric oscillator with wavelengths ranging from 1150 to 2000 nm. The emitted light was collected in  $90^\circ$  scattering geometry and recorded between 850 and 1070 nm [6]. In Fig. 3 we show the (one-photon) luminescence intensity at the wavelength of maximum emission as a function of (two-photon) excitation energy for three nanotubes  $(n_1, n_2)$ . The two-photon absorption maximum is approximately 240–325 meV above the emission energy. We identify this absorption maximum with the two-photon allowed  $E_{11}^{2g}$  exciton state as predicted [6]. The measured energy difference indicates an exciton binding energy on the order of 300–400 meV for the tubes with diameters between 6.8 and 9 Å.

The exciton binding energy was predicted to increase with decreasing diameter [4, 11]. In Fig. 4 we observe that indeed the energy difference  $\Delta E = E_{11}^{2g} - E_{11}^{1u}$  roughly increases for smaller diameter. The



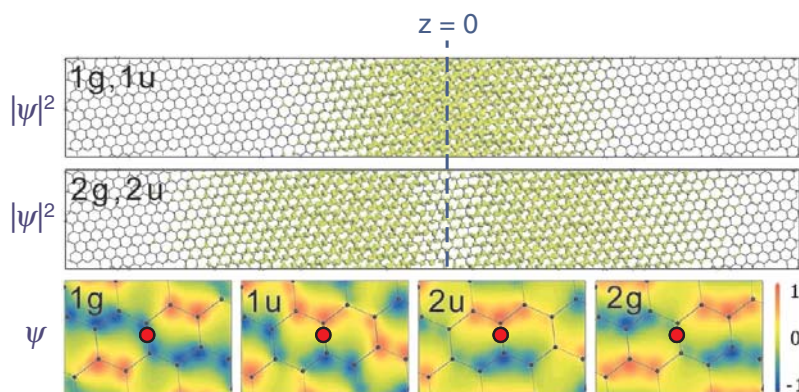
**Fig. 3** (online colour at: [www.pss-b.com](http://www.pss-b.com)) Emission intensity as function of two-photon excitation energy for the (7, 5), (6, 5), and (6, 4) tube. The black (thin) arrow indicates the emission energy  $E_{11}^{1u}$ , the red (thick) arrow the two-photon absorption maximum identified with the  $E_{11}^{2g}$  state.



**Fig. 4** (online colour at: [www.pss-b.com](http://www.pss-b.com)) (a) Diameter dependence of the measured energy difference  $\Delta E = E_{11}^{2g} - E_{11}^{1u}$ .  $\Delta E$  tends to increase for smaller diameter. The (9, 1) and the (6, 5) tubes have the same diameter but belong to families  $\nu = -1$  and  $\nu = +1$ , respectively, where  $\nu = (n_1 - n_2) \bmod 3$ . (b) Same as in (a) but with the emission energy as abscissa.

same behavior has been recently reported on a larger set of data [17]. Because of the dependence on the electron and hole effective mass, the exciton binding energy is expected to depend on the nanotube family  $\nu = \pm 1$ . ( $\nu = -1$  corresponds to  $\nu = 2$  as sometimes used in the literature.) The exciton binding energy is larger in  $\nu = -1$  tubes for the  $E_{11}$  transitions and in  $\nu = +1$  tubes for the  $E_{22}$  transitions [4, 11]. Our data on the (9, 1) and (6, 5) tubes with same diameter but different family index  $\nu$  appear to confirm this prediction, see Fig. 1; however, a larger number of different tubes is required for a definite conclusion from experiment.

We performed *ab-initio* calculations of the one-photon and two-photon active exciton states for the (6, 4) nanotube. The single-particle wavefunctions are calculated within density functional theory, and the self-energy operator is obtained in the *GW* approximation. Finally, the Bethe–Salpeter equation for the two-particle excitations is solved [2, 6]. The four lowest bound exciton states with  $\Delta m = 0$  are  $1g$ ,  $1u$ ,  $2u$ , and  $2g$  with binding energies of 0.54, 0.50, 0.16, and 0.16 eV, respectively. One-photon absorption is strongest for the  $1u$  state, whereas the largest contribution to two-photon absorption is from the  $2g$  state, as predicted from the symmetry considerations. The calculated energy difference  $\Delta E = E^{2g} - E^{1u} = 340$  meV is in excellent agreement with our experimental results. If we do not include



**Fig. 5** (online colour at: [www.pss-b.com](http://www.pss-b.com)) Exciton states from *ab-initio* calculations of the (6, 4) nanotube. The probability of finding the electron is shown when the hole is fixed in the middle (upper two panels). The tube axis is in horizontal direction; the length is 15.9 nm (approximately eight translational unit cells). In the lower four panels, the amplitude of the wavefunction is given, where different colors indicate different sign. The  $U$ -axis is shown by the red dot between two carbon atoms.

electron–hole interaction in the calculations, the one-photon and the two-photon absorption peaks are at approximately the same energy.

In Fig. 5 we show the calculated exciton wavefunctions of the (6, 4) tube. The tube axis is along the horizontal direction, the circumference of the unrolled tube along the vertical direction. The upper two panels show the probability of finding the electron when the hole is fixed in the middle ( $z = 0$ ). In the first panel, the envelope is approximately even (1) under  $z$  inversion with the maximum at  $z = 0$ . The envelope in the second panel is approximately odd (2) and has a nodal plane at  $z = 0$ . In the four lowest panels the amplitude of the wavefunction is shown at a few carbon atoms with the hole again fixed in the middle. Now the parity quantum numbers  $g$  and  $u$  with respect to the  $U$ -axis (indicated by the red circle) are clearly visible as the wavefunction changes sign under  $\pi$  rotation about the  $U$ -axis for the odd ( $u$ ) states.

In conclusion, we showed that the optical spectra from carbon nanotubes originate from excitonic transitions. By two-photon absorption we excited exciton states with  $2g$  symmetry and observed emission from the one-photon active  $1u$  state. The energy difference between these two states is 240–320 meV for nanotubes with diameters between 9 Å and 6.8 Å, indicating strong Coulomb correlation. Optical excitation of carbon nanotubes, e.g., in photoluminescence or Raman experiments, thus always probes excitonic states, which for tubes with diameters around 8 Å lie several hundred meV below the band-to-band transition energy.

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