LETTERS

Near-Infrared Absorbance of Single-Walled Carbon Nanotubes Dispersed in Dimethylformamide

Ralph Krupke,*,† F. Hennrich,† Oliver Hampe,† and Manfred M. Kappes†,‡

Institut für Nanotechnologie, Forschungszentrum Karlsruhe, D-76021 Karlsruhe, Germany, and
Institut für Physikalische Chemie II, Universität Karlsruhe, D-76128 Karlsruhe, Germany

Received: January 13, 2003; In Final Form: May 7, 2003

Absorption spectra of single-walled carbon nanotubes (SWNT) dispersed in dimethylformamide (DMF) have been recorded in the visible to near-infrared range. Besides broad absorption bands, the spectra show a sharp peak at 5187 cm^{-1}, which has been attributed in the literature to the absorption of semiconducting nanotubes with a band gap of 0.64 eV [Ausman et al. *J. Phys. Chem. B* **2000**, *104*, 8911]. On the basis of absorbance measurements for samples that show the sharp absorbance peak but do not contain SWNTs, we conclude that the origin of the peak at 5187 cm^{-1} is not due to semiconducting nanotubes but due to water present in the SWNT/DMF suspension. A comparative study of D_2O in DMF reproduces a similar peak that is isotope-shifted into the near-infrared.

Single-walled carbon nanotubes (SWNT)[2] are unique 1-D nanostructures in terms of structural and electronic properties. Band structure calculations show that the electronic density of states (DOS) consists of a series of van Hove singularities.[3–5] The position of the singularities depends on diameter and helicity and is considerably different for metallic and semiconducting SWNTs. Visible to near-infrared absorption spectroscopy (vis–NIR) measures transitions between van Hove singularities and is therefore an important analytical tool for the characterization of SWNTs.[6–11] In general, nanotubes are produced with a certain variation of diameter and helicity. SWNTs also tend to form heterogeneous bundles. As a result, ensemble measurements show absorption peaks corresponding to the response of individual SWNTs of different chiral indices or of different diameter or both. Typically for liquid suspensions of SWNTs, the absorption responses of isolated tubes and tubes in bundles are superposed and form broad, often asymmetric bands. Usually three broad bands, M1, S1, and S2, are observed in the vis–NIR range, and it is widely accepted that M1 is due to the first intraband transition of metallic SWNTs and that S1 and S2 are due to the first and second interband transition of semiconducting SWNTs, respectively.

Ausman and co-workers[1] recently published UV/vis–NIR absorption spectra of SWNTs suspended in organic solvents. The authors observed a sharp peak at 5190 cm^{-1} and attributed the peak to the absorption of semiconducting SWNTs with a band gap of 0.64 eV. The authors have also pointed out the unexplained sharpness of the peak. Recently, sharp absorption peaks, albeit at different energies, have indeed been observed in an aqueous suspension of small diameter SWNTs stabilized with surfactant.[12,13] The sharp peaks were associated with isolated SWNTs, which were separated from bundles by ultra centrifugation. Hence, sharp absorption peaks could be an indicator for individual SWNTs being present in a suspension. This prompted us to investigate in some more detail SWNTs suspended in DMF. Similar to Ausman and co-workers, we have

---

* To whom correspondence should be addressed. E-mail: ralph.krupke@int.fzk.de.
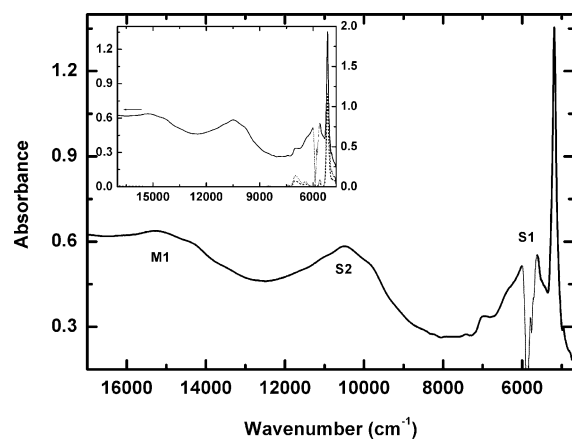† Forschungszentrum Karlsruhe.
‡ Universität Karlsruhe.

Figure 1. Visible and near-infrared absorption spectra of SWNTs dispersed in DMF (full line). The thin line marks the data in a region of strong absorbance of the solvent. The inset shows the data of Figure 2 over an extended spectral range.

Figure 2. Near-infrared absorbance of (—) SWNTs dispersed in DMF, (— — —) the supernatant of an aged suspension, and (•••) water at a concentration of 0.1 mol/L in DMF. The thin lines mark the data in a region of strong absorbance of the solvent. The inset shows the same data in a narrower spectral range and, in addition, D_2O at a concentration of 3.8 mol/L in DMF (○). Note that the D_2O measurement is plotted against the isotope-shifted ordinate shown at the top of the inset.

observed an additional sharp absorption peak as well, at 5187 cm^{-1}. However, we will show that in our samples the sharp peak is not due to absorption of semiconducting nanotubes but due to water present in the SWNT/DMF suspension.

SWNTs were grown in a laser ablation system.[14] The as-grown material was treated with nitric acid, which removes amorphous carbon and catalyst particles in the sample to a large degree.[15] Thermographic analysis and transmission electron microscopy yield a 99% sample purity. The tubes were finally suspended in *N,N*-dimethylformamide (DMF) at a typical concentration of a few micrograms per milliliter and sonicated for 30 min in a closed vessel with a 120 W bath sonicator.

Absorption spectra were recorded with a Varian Scan 500 UV−vis−NIR spectrometer using Quartz Suprasil cells with 10 mm light path. The spectrometer is a dual beam system, which allows measuring simultaneously a reference spectrum of the solvent. We recorded instead the reference spectra in successive measurements using the same cell and beam. We found this to give better results when subtracting the absorption spectra of the solvent because it eliminates any errors caused by differences in the optical path length using two cells.

For further characterization of the suspended SWNTs, the tubes were transferred onto a surface in three different ways: (1) a drop of suspension was deposited onto a silicon substrate and subsequently dried, (2) a silicon surface terminated with an (aminopropyl)triethoxysilane (APTES) self-assembled mono-layer (SAM) was immersed into the suspension,[16] or (3) SWNTs were trapped onto lithographically patterned metallic electrodes by dielectrophoresis.[17] The samples with adsorbed SWNTs were then investigated with a scanning electron microscope (SEM) or an atomic force microscope (AFM).

Figure 1 shows the absorbance of SWNTs dispersed in DMF as a function of wavenumbers. The data show three broad bands centered at ~15 000, 10 500, and 5800 cm^{-1}. The peaks are located on top of a roughly linearly decreasing background and have an observable fine structure. In particular, there is a sharp peak at 5187 cm^{-1}. Ausman and co-workers have recorded very similar data of SWNTs dispersed in DMF and in *N*-methylpyr-rolidone (NMP).[1]

Our suspensions of SWNTs in DMF are stable on a time scale of days. After some weeks, SWNTs start to precipitate. After such precipitation, we have carefully extracted the supernatant and measured the absorption (Figure 2). The spectra again show a sharp peak at 5187 cm^{-1} and some of the fine structure observed before; however, broad absorption bands are
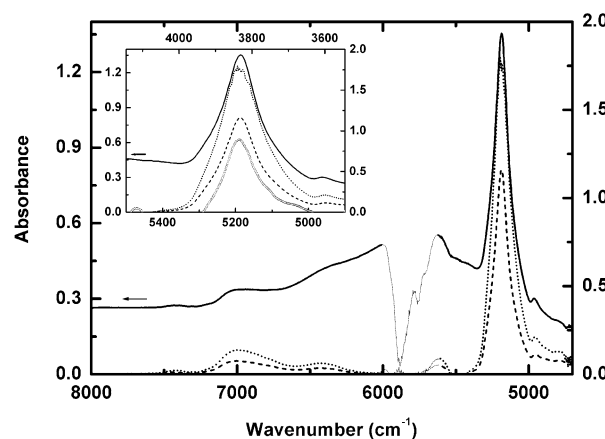
no longer found. The procedures described above to transfer SWNTs onto a surface were applied to this supernatant. However, SWNTs could be found neither with SEM nor with AFM. Also dielectrophoretic trapping of SWNTs was not possible. We therefore deduce that the supernatant of the aged suspension does not contain measurable amounts of SWNTs.

The results are similar if we filter a fresh suspension of SWNTs in DMF using a 0.2 μm polytetrafluoroethylene (PTFE) filter (Phenomenex). The filtrate shows the sharp absorption peak at 5187 cm^{-1}, as well as the described fine structure, but no broad absorption bands are observable and no SWNTs are detectable. An additional important observation is that the sharp absorption peak at 5187 cm^{-1} and some of the fine structures become stronger with time whereas the broad bands do not (not shown). This is a hint toward an extrinsic factor.

Finally, we have prepared a solution of 5 μL of H_2O dissolved in 3 mL of DMF (water concentration ≈ 0.1 mol/L). The absorption spectra are shown in Figure 2. The spectra are very similar to the spectra of the supernatant from the aged suspension and clearly reproduce the sharp peak at 5187 cm^{-1}, as well as the fine structure at 7000, 6430, and 5600 cm^{-1}. By comparison of the data with the absorption spectra of the suspended SWNTs in DMF, it is clear that most of the fine structure between 4800 and 7500 cm^{-1}, including the sharp peak at 5187 cm^{-1}, is due to H_2O present in the SWNT/DMF suspension. Only the broad absorption band centered between 5800 and 6200 cm^{-1} can be attributed to SWNTs. The inset of Figure 1 shows that H_2O in DMF does not absorb at wave-numbers larger than 7500 cm^{-1}; hence, the structure on top of the broad absorption bands at 15 000 and 10 500 cm^{-1} is due to intrinsic absorption of SWNTs. We are convinced that our analysis also applies to the data of Ausman and co-workers.[1] It would explain why their peak at 5190 cm^{-1} disappears upon heating because this is a procedure for drying DMF or NMP.

The sharp peak at 5187 cm^{-1} remains to be explained. The strongest NIR absorption for water, the overtone of the $\nu_2 + \nu_3$ combination band of the asymmetric stretch (ν_2) and the bending vibration (ν_3), is around 5200 cm^{-1}. In liquid water the absorption becomes a broad band extending from 4600 to 5400 cm^{-1}, due to a large configuration space for hydrogen bonding between water molecules, perturbing the bond strength within a molecule. However for small amounts of water dispersed in

TABLE 1: Fitting Parameters of the Sharp NIR Absorption Peak for Various Solutions/Suspensions

	peak position (cm^{-1})	Lorentzian width (cm^{-1})
SWNTs dispersed in DMF	5187.1 ± 0.2	97 ± 3
supernatant of aged suspension	5187.1 ± 0.1	98.3 ± 0.6
0.1 mol/L H$_2$O in DMF	5187.2 ± 0.3	133 ± 7
3.9 mol/L D$_2$O in DMF	3833.4 ± 0.2	114 ± 10

a solvent, the absorption becomes a sharp peak, the position depending on the specific solvent used.[18−21] For instance, small concentrations of water in *N*-methyl pyrrolidinone (NMP) give rise to a sharp NIR absorption peak at 5175 cm^{-1}.[21] It has also been shown that for small concentrations of water the integral of the absorption peak scales linearly with the water concentration suggesting that isolated H$_2$O molecules or small H$_2$O clusters are the carriers of the absorption. On this basis, we estimate the amount of water in our SWNT/DMF suspension to be on the order of 50 mmol/L. The Lorentzian width of the sharp NIR peak at 5187 cm^{-1} for the SWNT/DMF suspension, as well as for the supernatant of the aged suspension, is about 100 cm^{-1} (Table 1). The values are in agreement with measurements of similar water concentrations, albeit in different solvents.[21] For comparison, we have measured in addition the absorption of 250 μL of D$_2$O in 3 mL of DMF (D$_2$O concentration ≈ 3.8 mol/L). The absorption peak is now shifted into the NIR because of the isotope shift (inset Figure 2, Table 1). The wavenumber ratio of the H$_2$O and D$_2$O absorption peaks is 1.353 ± 0.005 and reproduces the value of 1.349 ± 0.002 from gas-phase data[22] within the experimental error. We add to our analysis that the weak absorption band at ∼7000 cm^{-1}, observed in Figure 2, could be the first overtone of the symmetric stretch (ν_2) of the H$_2$O molecule, which in liquid water is observed around 7140 cm^{-1}. Concerning the origin of the water observed in the SWNT/DMF suspensions, we can only speculate whether it is released from the acid-treated SWNT bundles or it is absorbed from air during sonication in a closed vessel.

We conclude that the broad absorption bands at ∼15 000, 10 500, and 5800 cm^{-1} in our absorbance data of SWNTs dispersed in DMF are the well-established M1, S2, and S1 absorption peaks of SWNTs, respectively. The fine structure on top of S1, including the sharp peak at 5187 cm^{-1}, is caused by small amounts of water present in the SWNT/DMF suspen-

sion. A comparative study of D$_2$O in DMF reproduces a similarly sharp peak that is isotope-shifted into the NIR.

References and Notes

(1) Ausman, K. D.; Piner, R.; Lourie, O.; Ruoff, R. S.; Korobov, M. *J. Phys. Chem. B* **2000**, *104*, 8911−8915.
(2) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603−605.
(3) Mintmire, J. W.; Dunlap, B. I.; White, C. T. *Phys. Rev. Lett.* **1992**, *68*, 631−634.
(4) Hamada, N.; Sawada, S.-I.; Oshiyama, A. *Phys. Rev. Lett.* **1992**, *68*, 1579−1581.
(5) Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Phys. Rev. B* **1992**, *46*, 1804−1811.
(6) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95−98.
(7) Kataura, H.; Kumazawa, Y.; Maniwa, Y.; Umezu, I.; Suzuki, S.; Ohtsuka, Y.; Achiba, Y. *Synth. Met.* **1999**, *103*, 2555−2558.
(8) Petit, P.; Mathis, C.; Journet, C.; Bernier, P. *Chem. Phys. Lett.* **1999**, *305*, 370−374.
(9) Jost, O.; Gorbunov, A. A.; Pompe, W.; Pichler, T.; Friedlein, R.; Knupfer, M.; Reibold, M.; Bauer, H.-D.; Dunsch, L.; Golden, M. S.; Fink, J. *Appl. Phys. Lett.* **1999**, *75*, 2217−2219.
(10) Itkis, M. E.; Niyogi, S.; Meng, M. E.; Hamon, M. A.; Hu, H.; Haddon, R. C. *Nano Lett.* **2002**, *2*, 155−159.
(11) Hennrich, F.; Lebedkin, S.; Malik, S.; Tracy, J.; Barczewski, M.; Rösner, H.; Kappes, M. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2273−2277.
(12) O'Connell, M. J.; Bachilo, S. M.; Huffman, C. B.; Moore, V. C.; Strano, M. S.; Haroz, E. H.; Rialon, K. L.; Boul, P. J.; Noon, W. H.; Kittrell, C.; Ma, J.; Hauge, R. H.; Weisman, R. B.; Smalley, R. E. *Science* **2002**, *297*, 593−596.
(13) Lebedkin, S.; Hennrich, F.; Skipa, T.; Kappes, M. M. *J. Phys. Chem. B* **2003**, *107*, 1949−1956.
(14) Lebedkin, S.; Schweiss, P.; Renker, B.; Malik, S.; Hennrich, F.; Neumaier, M.; Stoermer, C.; Kappes, M. M. *Carbon* **2002**, *40*, 417−423.
(15) SWNTs were refluxed in 3 M HNO$_3$ for 48 h, subjected to centrifugation, followed by dispersion/suspension with Triton X-100 in water, ultrafiltration, membrane filtering, and washing with H$_2$O and acetone, and dried in a vacuum (1×10^{-3} mbar) for 12 h and resuspended in DMF.
(16) Krupke, R.; Malik, S.; Weber, H. B.; Hampe, O.; Kappes, M. M.; v. Löhneysen, H. *Nano Lett.* **2002**, *2*, 1161−1164.
(17) Krupke, R.; Hennrich, F.; Weber, H. B.; Beckmann, D.; Hampe, O.; Malik, S.; Kappes, M. M.; v. Löhneysen, H. *Appl. Phys. A* **2003**, *76*, 397−400.
(18) Keyworth, D. A. *Talanta* **1961**, *8*, 461−469.
(19) Cordes, H. F.; Tait, C. W. *Anal. Chem.* **1957**, *29*, 485−487.
(20) Meeker, R. L.; Critchfield, F. E.; Bishop, E. T. *Anal. Chem.* **1962**, *34*, 1510−1511.
(21) Dickens, B.; Dickens, S. H. *J. Res. Natl. Inst. Stand. Technol.* **1999**, *104*, 173−183.
(22) *NIST Chemistry Webbook*, July 2001 release; NIST Standard Reference Database Number 69; National Institute of Standards and Technology: Washington, DC, 2001.