Electronic and Mechanical Coupling of Carbon Nanotubes: A Tunable Resonant Raman Study of Systems with Known Structures

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We report on the first tunable resonant Raman scattering study performed on suspended isolated and coupled single-wall carbon nanotubes, unambiguously identified by electron diffraction. Besides the confirmation of the relation between the structural properties, the radial breathing frequency and the optical resonances for isolated metallic nanotubes, we evidence that interacting nanotubes experience drastic modifications of their resonance fingerprints. We first demonstrate a degeneracy lifting of an electronic level in a bundle of identical zigzag nanotubes. We then show the existence of a strong energy transfer mediated by a mechanical coupling between two nonidentical bundled nanotubes.

The importance of single-wall carbon nanotubes (SWNTs) for the understanding of the electronic and optical properties of 1D systems is not to be demonstrated anymore. The optical properties of SWNTs are determined by the one-dimensional quantum confinement of the electrons, which leads to sharp transitions at energies \( E_{ii} \), strongly dependent on the structural parameters \((n, m)\) of the nanotubes. Many optical experiments have been reported on macroscopic samples (fluorescence spectroscopy or resonant Raman scattering (RRS) [1,2]) and the excitonic character of the involved optical transitions is well documented [3]. Surface-enhanced raman scattering [4], RRS [5–7] and Rayleigh scattering [8] have been obtained, at the single nanotube level.

Only a few of these studies [6–8] have been performed together with an independent determination of the structural parameters of the nanotube, a mandatory condition to determine the accuracy of the theoretical models. Combining electron diffraction (ED) with RRS at given laser excitations on the same isolated SWNT, Meyer et al. [6] have clearly confirmed the \( \omega_0 = A/D + B \) relationship between the RBM frequency \( \omega_0 \) and the inverse diameter \( 1/D \) of nanotubes (with \( A = 204 \text{ cm}^{-1} \cdot \text{nm} \) and \( B = 27 \text{ cm}^{-1} \)), but with only an approximate determination of \( E_{ii} \). Seif et al. [8] have used ED in combination with Rayleigh spectroscopy to determine the chiral indices and to access the energies of the optical transitions \( E_{ii} \) of several isolated SWNTs.

However, the problem of the effect of coupling between nanotubes [9–11], which is likely to happen in real applications, has never been studied experimentally with an independent structural characterization.

In this Letter, we investigate the optical properties of SWNTs, by recording both the resonant Raman excitation profile (REP) and the electron diffraction pattern (ED) on the same suspended isolated or interacting SWNTs. We first make use of the correlations between REP and ED data on individual SWNTs to validate the state-of-the-art modeling of the SWNTs’ optical properties. We then report on two different signatures of interactions between identified SWNTs. First, the electronic coupling is shown to lift the electronic level degeneracy in a small rope of identical SWNTs. Second, the mechanical coupling in a pair of identified SWNTs is shown to produce an unexpectedly efficient energy transfer mechanism.

The ED and REP measurements on the same individual SWNTs or small sets of SWNTs have been performed as follows: we optimized the production of sparsely distributed individual SWNTs or small ropes of SWNTs by making them grow on holey Si\(_3\)N\(_4\) membranes by hot filament CCVD [12]. The same SWNT(s) could thus be studied both by ED and RRS. RRS experiments were performed with a homemade confocal tunable micro Raman setup in a backscattering configuration, enabling having a diffraction limited spot weakly dependent on the used wavelength. Spectra were acquired in a double additive spectrometer equipped with a liquid-N\(_2\)-cooled CCD camera in the range 700–900 nm, with a tunable Ti:sapphire laser and without any Notch filter. The excitation power was kept from below 100 \( \mu \text{W} \) to below 150 \( \mu \text{W} \). An accurate location of the probed holes was obtained with additional optical confocal imaging [13]. Resonant SWNTs were found by scanning a set of holes at a fixed excitation wavelength while recording Stokes spectra in the range of 120–280 cm\(^{-1}\). The REP of the relevant SWNTs were then retrieved. The holes exhibiting RRS signal were located in a transmission electron microscope, and the diffraction patterns acquired in a nanodiffraction [14] configuration on a high sensitivity CCD camera.
For the interpretations, we used a non-orthogonal tight-binding (NO TB) model [15]. Neglecting electron-hole interactions, the dependance of the $E_{ij}$ on the chiral indices and on the mod-type family behavior of the nanotubes can be retrieved by this method. We took into account the many-body and excitonic effects by rigidly shifting by 0.32 eV the NO TB values, as it turned out to be sufficient for the interpretation of earlier experimental results for $E_{11}$ of metallic and semiconducting (SC) NTs and for $E_{22}$ of SC NTs [7,8]. Here, such rigidly-shifted NO TB $E_{ij}$ will be referred to as the corrected NO (cNO) TB $E_{ij}$.

Figure 1 shows the diffraction pattern (a) together with the resonant Raman data (b) of the same carbon nanotube. The analysis of the so-called layer-lines (parallel intensity lines) shows that a single nanotube chirality is observed [14,16], while the oscillation of the central line intensity (hereafter called the equatorial line) unambiguously proves the presence of an individual SWNT. From the analysis of the positions of the layer-lines and of the oscillations of the equatorial line according to [14,16], we determine the indices of the observed tube to be (16,4).

Figure 1(b) shows a reconstructed 3D map of the Stokes-Raman cross section as a function of the excitation wavelength and Raman shift, exhibiting a clear resonant feature. A Raman spectrum featuring the RBM at 169 cm$^{-1}$ together with the Stokes (S) and anti-Stokes (AS) REP of the RBM mode are also displayed. The S curve is satisfactorily fitted with the RRP formula [17] for a single transition, which gives, among other parameters, the $E_{ij}$ value. Using the temperature-dependent ratio ($K$) [18] between S and AS spectra for normalization, the AS REP is satisfactorily retrieved without further fitting [see Fig. 1(b)]. With a diameter $D = 1.44$ nm extracted from the experimental $\omega_0$ [6], and an experimental value of $E_{ij} = 1.707$ eV, the comparison with the cNO TB simulations [15,19] gives three different possibilities: $E_{11} = 1.72$ eV, for a (16,4) tube ($\omega_0 = 169$ cm$^{-1}$ predicted by the $\omega_0(D)$ relation) [6], $E_{11} = 1.71$ eV for a (15,6) tube ($\omega_0 = 165$ cm$^{-1}$) and $E_{11} = 1.73$ eV for a (17,2) tube ($\omega_0 = 170$ cm$^{-1}$). The two latter possibilities are unambiguously ruled out on the basis of the ED data.

Another SWNT, identified as (13,10) by ED, has been studied, leading to a close to perfect agreement between ED, RRS, and cNO TB. The RBM frequency is 158 cm$^{-1}$ (157 cm$^{-1}$ predicted by [6]). The $E_{11}$ value deduced from the REP analysis is 1.668 eV, which almost perfectly matches the cNO TB value of 1.68 eV for a (13,10).

As a first conclusion from the REP and ED measurements on isolated metallic SWNTs, we confirm the $\omega_0 = A/D + B$ relationship [6] within 1 cm$^{-1}$ for isolated metallic SWNTs. Second, our experimental $E_{11}$ values for the identified individual metallic SWNTs (16,4) and (13,10) confirm the approximate 0.32 eV many-body correction to be added to NO TB or DFT electronic calculations [8,19].

We now turn to two different situations which illustrate the physical consequences of the coupling between nanotubes. Figure 2 shows the diffraction pattern (a) and both S and AS REPs of the same individual set of SWNTs (b). In the Raman spectrum, a single RBM peak at 150 cm$^{-1}$ is observed (not shown). From the layer-line position, one can conclude that a single helicity is present, corresponding to a zigzag nanotube. However, the modulation of the equatorial line intensity (red) and of other layer-lines (blue) clearly indicates that the diffracted object is a rope of SWNTs (and not a multiwalled nanotube), as already observed in CCVD samples [20]. From the layer-line patterns and from the $\omega_0$, we deduce that the rope is homogeneously made up of (21,0) nanotubes.

Using the same fit function as in the case of a SWNT, we find within 1% the same value of $E_{11} = 1.69$ eV (733.6 nm) for both S and AS profile analysis. This value corresponds to the cNO TB data within 10 meV. Nevertheless, contrary to the previous cases, this analysis does not give the good $K$ ratio between the AS and S intensities. Moreover, as seen in Fig. 2(b), the fit function does not reproduce correctly the shape of the REPs. This narrow REP, observed in other set of nanotubes not studied by ED, suggests an interference effect and the participation of more than one excited set of nanotubes, leading to a close to perfect agreement between ED, RRS, and cNO TB. The RBM frequency is 158 cm$^{-1}$ (157 cm$^{-1}$ predicted by [6]). The $E_{11}$ value deduced from the REP analysis is 1.668 eV, which almost perfectly matches the cNO TB value of 1.68 eV for a (13,10).

FIG. 1 (color online). Electron diffraction pattern and resonant Raman scattering data from the same SWNT. (a) Top: Electron diffraction pattern, and bottom: Corresponding equatorial line with its fit (dotted line). (b) Left: Stokes-Raman map of the same nanotube. Right, top: Raman spectrum taken under excitation of 727.3 nm (1.705 eV). Middle, bottom: Stokes and anti-Stokes resonant excitation profile. Dotted lines: fitted data for the Stokes signal and calculated spectra for the anti-Stokes signal with the same parameters normalized by $K$ (see text). Acquisition time per Raman spectrum: 120 s, laser power: 100 $\mu$W.
predicted by a valence force field model [24] to upshift the RBM values to respectively between the two nanotubes, only separated by 3.15 Å, for which the strong mechanical interaction between the two nanotubes is expected to be particularly efficient for ropes of identical nanotubes. Moreover, the efficiency of the process is measured by the ratio of the RBM intensities: roughly a factor 2 in favor of the (8,6) resonant tube. There are at least two processes that could be at the origin of such an energy transfer (ET) from the optically resonant (8,6) tube to the nonresonant (18,4) one. It is also underlined by the striking similarity between the shapes of the REPs of the nanotubes. The first mechanism involves a fast migration of photoexcited carriers from a SC SWNT of a given band-gap to another of a smaller band-gap, as recently observed by Rayleigh scattering in nanotube ropes [10] and attributed to a screening of Coulomb interaction inside the tube due to its surrounding.

On the other hand, surprisingly, the RBM of the (18,4) is rather efficiently excited even if no electronic transitions are predicted at this energy (cNO TB $E_{22} = 1.29$ eV and $E_{33} = 2.37$ eV). The observation of the resonant (18,4) RBM peak can thus only result from an efficient energy transfer (ET) from the optically resonant (8,6) tube to the nonresonant (18,4) one. It is also underlined by the striking similarity between the shapes of the REPs of the nanotubes. Moreover, the efficiency of the process is measured by the ratio of the RBM intensities: roughly a factor 2 in favor of the (8,6) resonant tube. There are at least two processes that could be at the origin of such an energy transfer. The first mechanism involves a fast migration of photoexcited carriers from a SC SWNT of a given band-gap to another of a smaller band-gap, as recently observed [11]. However, the large difference between the optical transition energies of the two SWNTs should weaken the

in the resonant energy can be explained by an electronic coupling between the nanotubes in the rope [22]. Such coupling is expected to be particularly efficient for ropes of identical nanotubes.

Figure 3(a) displays the diffraction pattern of a set of nanotubes exhibiting two different helicities. The equatorial line is characteristic of two individual aligned nanotubes of different diameters, corresponding to either a (8,6) and (18,4) tube. The analysis gives (8,6) and (18,4) as chiral indices. The RRS spectra show two RBM lines at 245 cm$^{-1}$ and 274 cm$^{-1}$ which are predicted at this energy (cNO TB $E_{22} = 1.29$ eV and $E_{33} = 2.37$ eV). The observation of the resonant (18,4) RBM peak can thus only result from an efficient energy transfer (ET) from the optically resonant (8,6) tube to the nonresonant (18,4) one. It is also underlined by the striking similarity between the shapes of the REPs of the nanotubes. Moreover, the efficiency of the process is measured by the ratio of the RBM intensities: roughly a factor 2 in favor of the (8,6) resonant tube. There are at least two processes that could be at the origin of such an energy transfer. The first mechanism involves a fast migration of photoexcited carriers from a SC SWNT of a given band-gap to another of a smaller band-gap, as recently observed [11]. However, the large difference between the optical transition energies of the two SWNTs should weaken the

not nested, interacting SWNTs [25]. This is a strong confirmation that the two nanotubes are bundled rather than nested.

The REPs give a similar resonant energy of 1.670 eV for both RBM. The cNO TB results predict a $E_{22}$ of 1.75 eV for the (8,6) nanotube (experimental values are 1.72 eV [8] for an isolated SWNT and 1.73 eV for nanotubes in suspension [23]). The difference with the present value (50 meV) can be compared to redshifts of 20 to 56 meV, observed by Rayleigh scattering in nanotube ropes [10] and attributed to a screening of Coulomb interaction inside the tube due to its surrounding.

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FIG. 2 (color online). Electron diffraction pattern and resonant Raman scattering data from the same zigzag rope of nanotubes. (a) Electron diffraction pattern of a rope (top) and corresponding equatorial layer-line (red) and (01) layer-line (blue) (bottom). The hexagon emphasizes the zigzag quality of the nanotubes, while the equatorial line and the (01) line demonstrates the crystallinity of the rope. (b) Top: Experimental Stokes profile (green triangles) with its fit (red dotted line) and the experimental anti-Stokes profile (pink triangles) with a generated anti-Stokes profile (blue dotted line) deduced from the Stokes fit and the theoretical $K$-ratio in a model where only one optical transition exists. Middle: Stokes profile (triangles) and corresponding fit (dotted line) in a two-level model (see text). Bottom: anti-Stokes profile (triangles) together with its two-level model curve (dotted line) calculated with the parameters given from the Stokes fit, normalized by $K$ (see text).

FIG. 3 (color online). Electron diffraction pattern and resonant Raman scattering data from the same two-nanotubes rope. (a) Top: Electron diffraction pattern. The arrows on the left (right) indicate the positions of the layers of the first (second) nanotube constituting the rope, and the bold arrow indicates the equatorial line. Bottom: corresponding equatorial line (red) and (01) layer-line (blue) (bottom). (b) Left, Stokes-Raman maps of the same rope with extracted resonant diffused signal profile (middle) and resonant Raman excitation profiles corresponding to the two modes (top and bottom). (c) Phonon mode of a (11,2)–(12,12) pair of nanotubes (see text).
efficiency of the process. The second mechanism relies on a mechanical energy transfer between the two SWNTs. Because the efficiency of this mechanism is not obvious, we performed simulations in the framework of a valence field approximation [25] to model the mechanical coupling between two commensurate nanotubes [(11,2)–(12,12)] with diameters close to those of the (8,6)–(18,4) pair. We illustrate the mechanical coupling between the nanotubes in Fig. 3(c) for the low frequency RBM mode of the (11,2)–(12,12) pair of nanotubes. The RBM of the large SWNT is seen to be efficiently coupled with the three-fold symmetry E3 mode of the narrow tube. The strength of the mechanical coupling alone is high enough to reasonably account for our experimental findings. We note that both RBM and E3 modes are diameter-dependent and that our conclusions should remain valid irrespective of the tube chirality [we obtained similar results for the (12,0)-(20,0) pair of equivalent diameters]. This result points out clearly that the van der Waals coupling is sufficiently strong to be responsible for a mixing of the normal mode of vibration of the two SWNTs, which, in turn, leads to a very efficient ET mechanism.

In conclusion, we have presented a combined REP and ED analyses on individual and on interacting SWNTs. Beyond the confirmation of previous findings on individual SWNTs of known atomic structure, we have evidenced unambiguous signatures of the interaction of identified nanotubes. Our results demonstrate that electronic and mechanical coupling can efficiently modify the optical properties of the system of nanotubes. This result is important for the understanding of interactions between two nanometer-scale objects, and for the future control and development of nanotube-based devices.

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[18] $K = \frac{n_{ph}}{n_{ph}+1}\left(\frac{E_i + \omega_{un}}{E_i - \omega_{un}}\right)^2$, with $n_{ph}$ the temperature-dependent population of the vibrational levels, and $E_i$ the laser energy.


