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The spontaneous interaction between sulfuric acid and carbon nanotubes is studied using Raman spectroscopy. We are able to determine the charge transfer without any additional parameter using the spectral signature of inner and outer walls of double-wall carbon nanotubes. While for the outer wall both the lattice contraction and the nonadiabatic effects contribute to the phonon shift, only the lattice contraction contributes for the inner nanotube. For the outer nanotube, we are able to separate these two contributions of the Raman G-band shift as a function of the charge transfer. We have carried out density functional theory calculations on graphite to see how different chemical species (HSO4−, H2SO4, H+) affect the electronic band structure and electron-phonon coupling. The Raman G-band shift for the outer nanotube, Δω, as a function of hole charge transfer per carbon atom, fc, is found to be \( \Delta \omega = (350 \pm 20) fc + (101 \pm 8) \sqrt{fc} \).

I. INTRODUCTION

Electrical properties of carbon nanotubes (CNT) are particularly attractive when incorporating them into polymers for shielding applications or making electrical wires.3 The efficient dispersion of CNTs in strong acids and the formation of a nematic phase has been used to fabricate fibers with aligned CNTs.2 Raman spectroscopy is an effective and non-invasive characterization tool to monitor true thermodynamic solutions.3 The Raman shift of the G+ band is an excellent indicator of the hole charge transfer per carbon atom fc. Sumanasekera et al. have determined a value of 320 fc (cm−1) for the Raman shift for the electrochemically doped single-wall CNTs (SW) using sulfuric acid solutions.4 However, in order to analyze the Raman shift of nanotubes in an acid solution, it is important to be able to separate the effect of lattice contraction (and hence of the strain) due to charge transfer and the effect of the electron-phonon coupling due to Fermi level shift. We use here double-wall CNTs (DW) to separate lattice contraction from electron-phonon coupling deduced G-band shifts, which is crucial for the understanding of electrochemical doping of nanotubes.3,5

Theoretically, one can take benefit of the similarity between noncovalent doping of large-diameter SW and graphene models.5 We also use graphite intercalated compounds (GICs) results for comparison. When intercalating GIC with H2SO4, the charge transfer coefficient changes by a factor 2.6 between stage 1 (a graphene monolayer surrounded on both sides with sulfuric acid) and stage 2 (a graphene bilayer surrounded by sulfuric acid), corresponding, respectively, to 460 fc and 1200 fc in cm−1.7 The absolute phonon shift for stage 1 (51 cm−1) divided by the charge transfer (fc = 1/28) yields 1430 fc in cm−1. Hydrogen is removed during the intercalation process.

Lazzeri and Mauri8 have computed electron-phonon coupling in graphene using first-principles calculations to separate out the strain contribution. A hardening of the phonons is predicted due to nonadiabaticity attributed to movement of the Fermi level near the Dirac point. The total phonon shift can be separated into a contribution due to the lattice contraction (strain) \( \Delta \omega_s \) and a contribution due to the nonadiabatic effects (dynamical) labeled \( \Delta \omega_d \) given by

\[
\Delta \omega = \Delta \omega_s + \Delta \omega_d,
\]

with

\[
\Delta \omega_s = 350 fc,
\]

obtained from Fig. 1 of Ref. 8, and by converting the Fermi level shift in hole charge transfer per carbon atom in the algebraic Eq. (13) of Ref. 8:

\[
\Delta \omega_d (\text{cm}^{-1}) = 216 \sqrt{fc} + 1.74 \ln \left( \frac{6.04 \sqrt{fc} - 0.096}{6.04 \sqrt{fc} + 0.096} \right).
\]

For large fc, the last term can be ignored (5% of modification of \( \Delta \omega_d \) for fc = 0.005). For the conversion, we use fc = −0.002 65 σ, where σ is the surface electron concentration in 10−13 cm−1.

It is important to keep in mind that there is a fundamental difference between chemical doping, where new electronic states are introduced, and a gate-induced doping in a solid-state device, where the position of the Fermi level is modified by the gate voltage while the electronic band structure is left intact. A nonadiabatic effect can change the phonon energy by up to 30% in GIC, which can be considered as a limiting case of doped graphene with intercalants.9 However, the nonadiabatic effect can be removed by the modification of the electronic band structure. GIC with sulfuric acid is more complicated to calculate because the dissociation of the species has to be fully taken into account. While bulk graphite is inert in sulfuric acid, a spontaneous interaction occurs when CNTs are exposed to sulfuric acid.4 Protonation and formation of layers around the nanotubes has been experimentally observed.10–14 So far the Raman shift due to charge transfer has been deduced through electrochemical measurements using 320 fc in cm−1 (Ref. 4). This conversion factor for charge transfer value is not in accord
with the phonon shifts observed in GIC. While the variation of the wave-number shift in the electrochemical measurements is linear with $f_c$, Lazzeri and Mauri\(^1\) shows that apart of the linear strain dependence, an additional nonadiabatic term exists which is proportional to $\sqrt{f_c}$. The interaction of charged species with the nanotubes is complex and so far no attempt has been made to independently link the observed phonon wave-number shift with charge transfer taking into account the strain-induced effects. The modification of the electron-phonon coupling by perturbing the band structure near the Fermi level needs to be taken into account. The accurate value of the spontaneous wave-number shift due to this effect is important when optimizing processes when working with large amounts of nanocarbons.

The Raman spectrum of pristine SW is composed of a $G^+$ mode (1592 cm\(^{-1}\)) and a less intense $G^-$ mode. The position of the $G^-$ mode is diameter dependent and also depends on whether the nanotube is metallic or semiconducting.\(^{15}\) For DW, there are two main contributions attributed to the two $G^+$ modes that are located at 1592 cm\(^{-1}\) for the outer nanotube and 1581 cm\(^{-1}\) for the inner nanotube. The $G^+$ modes are weaker in intensity and are located at lower wave numbers.\(^{16}\) The $G^+$ band has a complex behavior.\(^{17}\) The $G^-$ bands overlap at normal pressure and split with increasing pressure.\(^{18}\)

Using SW, the phonon shift induced by doping is due to both lattice contraction and electron-phonon coupling. Hence, a calibration is necessary to determine the contribution of both effects. DWs are ideal for this purpose. Their inner nanotube can be taken as a strain indicator while their outer nanotube is affected by charge transfer that contracts bonds and modifies electron-phonon coupling. As the strain is linear with the charge transfer,\(^{8,19}\) we can determine from the inner nanotube the strain of the outer nanotube and subsequently the intrinsic charge transfer. We use temperature- and pressure-dependent measurements as a function of sulfuric acid concentration to verify our assessments. With GIC, HSO\(^4^-\) is the main species in interaction with the graphenesheet.\(^1\) Undissociated H\(_2\)SO\(_4\) has been proposed as dopant.\(^{20}\) Moreover, for CNTs, protonation has been observed experimentally\(^{10-12}\). To understand which species is really a dopant and thus what is the associated modification of the electronic band structure, we have conducted density functional theory (DFT) calculations with periodic boundary conditions using H\(_2\)SO\(_4\), H\(_2\), and HSO\(_4^–\). These are the three major molecular species in pure sulfuric acid. We compare our results to the literature and explain why, for CNTs, the wave-number shift versus the charge transfer is composed of a part due to lattice contraction and a part due to nonadiabatic effects.

II. EXPERIMENTAL AND COMPUTATIONAL INFORMATION

A. Samples and experiments

Purified SW material was purchased from Nanocarlab (electric arc method, diameter range: 1.2–1.6 nm). DWs were synthesized using catalytical chemical vapor deposition.\(^{21}\) The outer diameter ranges from 1.3 to 2.2 nm. One milligram of each material was immersed in 1 mL of sulfuric acid at 98% (or 120%) purchased from Aldrich Company. The high-pressure Raman measurements were performed in a diamond anvil cell (DAC) using a Renishaw spectrometer. The hydrostatic pressure was measured using the $R$-line emission of a small chip of ruby placed in the DAC. This allowed calibration\(^{22}\) of the pressure to within ±0.1 GPa. We observed a clear double peak from the ruby emission at all pressures. The solution with nanotubes has been injected in a hole which was drilled in the steel gasket. After closing the cell, a visual checking ensured that the material was present and the phonon spectrum was used to detect doping level. Sulfuric acid reacts to some degree with steel and absorbs water humidity, leading to a reduction of the overall doping. To reduce this effect we have dried the gasket before loading. The laser power incident on the sample was estimated to be 12 mW (spot size around 3 µm with an objective ×20). The wavelength used was 632.8 nm.

Temperature-dependent measurements were conducted on a droplet of sulfuric acid with nanotubes between two glass slides using a T64000 Jobin-Yvon Horiba spectrometer. As the partial pressure is low and the temperature of vaporization (dissociation) high (340 °C), we dried the cryostat by heating it and used nitrogen atmosphere to avoid water adsorption during the experiment. A red (647 nm) and a blue (476 nm) excitation wavelengths were used. The solution was sensitive to laser power. The spectra changed above 0.5 mW with an objective lens ×50 and a new mode appeared at around 1570 cm\(^{-1}\), which made accurate fitting difficult.

To estimate the uncertainties, we considered both the standard deviation and the inherent error of all reported values.\(^{23}\)

B. Calculations

DFT calculations were performed on a (7 × 7) primitive cell of graphene, containing 98 C atoms, using the Vienna \textit{ab initio} simulation package \textsc{vasp}.\(^{24-27}\) A coverage value of one molecule per 98 carbon atoms was used to study doping effects. The code uses the full-potential projector augmented wave (PAW) framework.\(^{28,29}\) Exchange-correlation effects have been approximated using the PBE functional\(^30\) and applied in spin-polarized calculations. In addition, we have tested the so-called vdW-DF\(^{31}\) as implemented in \textsc{vasp}.\(^{32}\) A kinetic energy cutoff of 400 eV was found to be sufficient to achieve a total-energy convergence within several meV considering a $k$-point sampling with a $(3 \times 3 \times 1)$ grid. Charge analysis was performed using Bader formalism.\(^{33-35}\)

III. RESULTS

When CNTs are immersed in superacids, a spontaneous interaction takes place.\(^3\) Before considering the measured Raman shift in greater detail, we discuss the spontaneous interaction of sulfuric acid with nanotubes as a function of temperature and pressure.

A. Temperature effect: SW and DW

Figure 1 shows the Raman spectra of SW and DW in concentrated solution at room temperature and by increasing the temperature from 0 °C to 50 °C by steps of 10 °C using excitation wavelength of 647 nm for SW and 478 nm for DW.
For SW, the Fano shaped \( G^- \) mode is not present while the \( G^+ \) mode is upshifted from 1591.5 ± 0.2 to 1603.7 ± 0.4 cm\(^{-1}\). The doping effect is constant within the temperature range explored. For DW, the \( G^+ \) mode associated with the outer nanotube is upshifted by 18 ± 0.4 cm\(^{-1}\) due to doping, while the \( G^+ \) mode associated to the inner nanotube is upshifted by only 3.2 ± 0.8 cm\(^{-1}\). The Raman spectra have been fitted using two Lorentzian line shapes. The differences observed for inner and outer nanotubes gives a direct measure of the strain-induced shifts experienced by the inner nanotube and dynamical effects and strain-induced shift on the outer nanotube. A slight decrease in wave number of the \( G^+ \) bands is observed when increasing the temperature, which can be explained by anharmonic effects.

### B. High pressure: DW

The relation between the tangential strain due to pressure of inner and outer nanotubes has been established earlier and

![Graph showing Raman spectra of SW and DW](image1)

**FIG. 1.** (Color online) Raman spectra of SW and DW in concentrated sulfuric acid as a function of temperature. Each spectra has been recorded by increasing the temperature by 10 K. Wavelengths of the laser are 647 nm for SW and 478 nm for DW.

For SW, the value found for both inner (\( i \)) and outer (\( o \)) nanotubes are \( \Delta \omega_{G+i} = 1601.2 \pm 0.8\) cm\(^{-1}\), \( \Delta \omega_{G+o} = 7.8 \pm 0.6\) cm\(^{-1}\), \( \Delta \omega_{G+i} = 1582.4 \pm 0.4\) cm\(^{-1}\), and \( \Delta \omega_{G+o}/dP = 5.2 \pm 0.3\) cm\(^{-1}\). The ratio \( \Delta \omega_{G+o}/\Delta \omega_{G+i} \) is 1.5 ± 0.2. The Table 1 lists the measured values. As the values come from different sample batches, a small change of the DW mean diameter is probably at the origin of the observed differences.

The quasilinearity of the Raman shift for both \( G \) bands as a function of pressure has been established experimentally. The band position is deduced using the fit with two Lorentzians. The ratio of the \( G^- \)-band shift of the inner nanotube is 1.7 times larger than the \( G^+ \)-band shift of the inner nanotube. We have used highly concentrated sulfuric acid earlier and found the zero-pressure values for the phonon wave number. In Fig. 2, the value found for both inner (\( i \)) and outer (\( o \)) nanotubes are \( \omega_{G+i} = 1601.2 \pm 0.8\) cm\(^{-1}\), \( \omega_{G+o} = 1582.4 \pm 0.4\) cm\(^{-1}\), and \( \Delta \omega_{G+o}/dP = 5.2 \pm 0.3\) cm\(^{-1}\). The ratio \( \Delta \omega_{G+o}/\Delta \omega_{G+i} \) is 1.5 ± 0.2. The Table 1 lists the measured values. As the values come from different sample batches, a small change of the DW mean diameter is probably at the origin of the observed differences.

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**IV. INTERACTION OF SPECIES ON GRAPHENE LAYER USING DFT CALCULATIONS**

To explore the effect of chemical doping on the electronic structure, we have carried out DFT calculations. To reduce the complexity due to numerous nanotube chiralities, we have focused our attention on a single graphene layer. These calculations are important first for interpreting GIC-H\(_2\)SO\(_4\) systems but also for estimating the effect on nanotubes, neglecting curvature effects, as a first approximation.

DFT calculations have been performed to see how each species in sulfuric acid solution interacts with graphene and how the electronic band structures is modified. Modifications in the electronic band structures change the Fermi velocity \( v_F \) and the electron momentum relaxation time \( \tau \). The latter results from all possible momentum exchange scattering mechanisms of the electrons near the Fermi surface. A nonadiabatic effect will be present when the two following conditions are satisfied: \( |q \cdot v_F| \ll \omega_0 \) and \( \hbar \omega_0 \gg \sigma \), with \( \hbar \omega_0 \) the G phonon energy, \( q \) the wave vector, and \( \sigma = h/\tau \). From the work of Saitta et al., on giant nonadiabatic effects in GIC, we know that a large relaxation time of the electrons near the Fermi surface is a good indicator of nonadiabaticity. Figure 3 shows the electronic band structures of pristine

**TABLE I. Raman shifts at zero pressure as a function of doping for DW. Argon as the pressure-transmitting medium is used as a reference. The DW samples used in the two experiments come from different sample batches.**

<table>
<thead>
<tr>
<th>Medium</th>
<th>( \Delta \omega_i ) (cm(^{-1}))</th>
<th>( \Delta \omega_o ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)SO(_4) from Ref. 17</td>
<td>6 ± 0.5</td>
<td>26 ± 0.5</td>
</tr>
<tr>
<td>H(_2)SO(_4)</td>
<td>1.4 ± 0.5</td>
<td>9.3 ± 0.5</td>
</tr>
</tbody>
</table>
graphene and graphene in interaction with H$_2$SO$_4$, H, and HSO$_4$. For pristine graphene, the conduction and valence bands meet at the Fermi level (the Fermi level is indicated with a dashed line). When a single H$_2$SO$_4$ molecule is approaching the graphene surface, it is only physisorbed and thus no charge transfer occurs. This observation is in contradiction with a previous study. However, this difference can be explained by the use of a simple local density approximation of exchange correlation functional in the work of Cordero and Alonso. This approximation is well known to exaggerate artificially the electron density delocalization, leading to a too-large charge transfer between the two. Results from GIC with C$_p$+HSO$_4$−, C$_p$+H$_2$SO$_4$, and reversible protonation of SW reported in literature show that species H and HSO$_4$ need to be considered.

It is important to keep in mind that pure H$_2$SO$_4$ is more complex as it contains HSO$_4$−, H$_2$SO$_4$+−, H$_3$O+, HS$_2$O$_7$−, H$_2$S$_2$O$_7$, and traces of H$_2$O (Ref. 40). When hydrogen atoms are positioned in the vicinity of the surface, they move closer to the surface forming a quasi-covalent C-H bond. As a consequence, the electronic band structure is strongly affected and a large gap is opening up. The Fermi level is positioned in the middle of the band gap and close to the localized states induced by the presence of hydrogen. In the presence of a positive charge on H, the electronic band structure remains the same and only the position of the Fermi level is modified. The presence of HSO$_4$ on graphene creates localized electronic states which are far from the Dirac point. Thus, the electronic properties in the latter case are similar to the ones induced by a gate voltage. We have also observed that the charge transfer leads to charge configuration close to the one of HSO$_4$− and C$_p$+. The Fermi level is consequently shifted to the valence band and indicates a strong p doping. When placing a single H adatom and an HSO$_4$ molecule close to a graphene layer, we find that they spontaneously reform the H$_2$SO$_4$ molecule. Additionally, no spontaneous dissociation of H$_2$SO$_4$ was found on a pristine surface. This implies that only a limited number of ions are in contact with the surface.

In summary, we have explored several molecular species interacting with graphene. We find some of them modify the Fermi level without significant modification of the electronic band structure at the Fermi level and hence contribute to the change of the phonon energy via nonadiabatic effects. This is the case for HSO$_4$−. Other molecules like H$_3$O+ lead to a charge transfer and modify the electronic band structure of pristine graphene. In this case, a full calculation is needed to know how the phonon energy is modified, which is challenging for acid solutions. We expect fewer nonadiabatic effects due to electronic band structure distortion in the presence of H$_3$O+. Finally, we find that some molecules such as H$_2$SO$_4$ do not participate in transfer of holes or electrons and do not contribute to the dynamical effect.

V. DISCUSSION

A. GIC-H$_2$SO$_4$

In Fig. 4(a), the experimental values of the G-band wave number of the GIC-H$_2$SO$_4$ stage one and two compounds are plotted as a function of charge transfer per carbon atom. The function which fits the two points consists of a linear and a square-root term. The linear term due to strain $\Delta \omega_C$ (cm$^{-1}$) = 350 $f_C$ is consistent with neutron measurements and DFT calculation and has been kept fixed. It is assumed that the doping effect is isotropic. When fitting, we only varied the prefactor of the square-root term. The prefactor for $\sqrt{f_C}$ is 204 ± 8, which is close to the value found from first-principles calculations using a gate voltage. The linear strain shift is deduced using the lattice parameter variation as determined from Raman spectroscopy.

![FIG. 3. (Color online) Electronic band structure for a single graphene layer (a) pristine, (b) in contact with H$_2$SO$_4$, (c) in contact with a H adatom with a new state close to the Fermi level, and (d) in contact with HSO$_4$ with a new state below the Fermi level.](image)
by neutron diffraction \((da/a = 0.0025)\)\(^1\) and the G-band shift as a function of pressure of graphite \((da/a = 2.1 \times 10^{-4} da/\nu)\).\(^2\) We note that there is a difference of \(-20\, \text{cm}^{-1}\) in the slope between the DFT calculations and the experimental strain-induced shifts. This small error in the slope demonstrates that the bond contractions due to charge transfer are consistent with the bond contractions measured by applying a hydrostatic pressure.

In GIC, \(H_2\) is partially removed during electrochemical intercalation and the main interacting species with graphene is HSO\(^4^-\). From Fig. 3, it is seen that the additional state introduced with HSO\(^4^-\) is far from the Fermi level and the charge transfer is similar to what has been found when using a gate voltage. The electronic band structure is assumed to be affected only to a minor degree, leading to a large nonadiabatic effect. Our DFT calculation shows that HSO\(^4^-\) is a dopant which does not alter the electronic band structure in an important way.

B. Nanotubes with H\(_2\)SO\(_4\)

The spontaneous interaction of sulfuric acid with nanotubes is different, however. H\(^+\) ions are still present and not removed, as in the case of intercalating. In Fig. 4(b) we have plotted the linear shift \(\Delta \omega (\text{cm}^{-1}) = 320 f_C\) of Sumanasekera et al.\(^3\) obtained by charging SW after a first spontaneous interaction. The slope is very close to what has been found for the experimental strain shift found in Fig. 4(a). So far it is not clear why nonadiabatic effects are not observed here.

Figure 4(b) shows the effect of chemical doping on DW. The shift of the inner nanotube is taken as a reference for strain. The strain on the inner nanotube is reduced due to the presence of the outer nanotube and one can obtain the strain on the outer nanotube by multiplying the measured strain of the inner nanotube by 1.7. This value has been observed experimentally\(^4\) and also determined by model calculations.\(^5\)

We can convert the strain shift to charge transfer using the conversion factor as deduced from DFT calculations:

\[
\text{number of carbon atoms} = \text{number of sulfuric acid molecules} \times \text{conversion factor}.
\]

The results are compared with intercalating graphite. In order to separate strain and nonadiabatic effects due to charge transfer on the phonon energy, we have used DW. The inner nanotube is used as a strain indicator. This allowed us to identify two effects to the observed Raman G-band shift associated to the outer nanotube. The total shift is found to be \(\Delta \omega (\text{cm}^{-1}) = (350 \pm 20) f_C + (101 \pm 8) \sqrt{f_C}\) when using sulfuric acid solutions. By using the relation from Sumanasekera et al.,\(^3\) we are overestimating the nanotube charging. DFT calculations exploring the interaction of ions on the band structure of graphene showed that HSO\(^4^-\) keeps the electronic band structure intact but leads to a large nonadiabatic effect, while H\(^+\) modifies the electronic band structure and leads to only a small nonadiabatic effect. While doping of CNT is always associated with protonation, we have shown that HSO\(^4^-\) plays an important role and needs to be fully taken into account to explain the observed phonon shifts to detect accurately charge transfer on CNT.

VI. CONCLUSION

We considered the spontaneous interaction of sulfuric acid as a function of concentration and temperature with CNTs using the Raman G band. The results are compared with intercalated graphite. In order to separate strain and nonadiabatic effects due to charge transfer on the phonon energy, we have used DW. The inner nanotube is used as a strain indicator. This allowed us to identify two effects to the observed Raman G-band shift associated to the outer nanotube. The total shift is found to be \(\Delta \omega (\text{cm}^{-1}) = (350 \pm 20) f_C + (101 \pm 8) \sqrt{f_C}\) when using sulfuric acid solutions. By using the relation from Sumanasekera et al.,\(^3\) we are overestimating the nanotube charging. DFT calculations exploring the interaction of ions on the band structure of graphene showed that HSO\(^4^-\) keeps the electronic band structure intact but leads to a large nonadiabatic effect, while H\(^+\) modifies the electronic band structure and leads to only a small nonadiabatic effect. While doping of CNT is always associated with protonation, we have shown that HSO\(^4^-\) plays an important role and needs to be fully taken into account to explain the observed phonon shifts to detect accurately charge transfer on CNT.


