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Electronic Transport Properties of Carbon-Nanotube Networks: The Effect of Nitrate Doping on Intratube and Intertube Conductances

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The conductivity of carbon-nanotube (CNT) networks can be improved markedly by doping with nitric acid. In the present work, CNTs and junctions of CNTs functionalized with NO₃ molecules are investigated to understand the microscopic mechanism of nitric acid doping. According to our density-functional-theory band-structure calculations, there is charge transfer from the CNT to adsorbed molecules indicating p-type doping. The average doping efficiency of the NO₃ molecules is higher if the NO₃ molecules form complexes with water molecules. In addition to electron transport along individual CNTs, we also study electron transport between different types (metallic, semiconducting) of CNTs. Reflecting the differences in the electronic structures of semiconducting and metallic CNTs, we find that in addition to turning semiconducting CNTs metallic, doping further increases electron transport most efficiently along semiconducting CNTs as well as through the junctions between them.

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I. INTRODUCTION

Flexible carbon-nanotube (CNT) thin films are materials, where randomly oriented CNTs form a network structure [1]. The fabrication methods of CNT thin films have improved remarkably, and several applications of the CNT networks have been introduced. It may be even possible to replace the commonly used indium tin oxide films by CNT thin films. The advantages of the CNT thin films are their low absorption in a broad range of optical wavelengths [2] and a possibility to bend the films without lowering the conductivity significantly [3].

In applications, CNT thin films with high electrical conductivity and optical transparency are required. For this purpose, a significant enhancement of the conductivity of the CNT thin films has been found, for example, in the case of AuCl₃ doping [4]. Computational studies have revealed that the formation of AuCl₄ molecules or anions on semiconducting CNTs leads to a *p*-type doping effect, i.e., to electron transfer to acceptor molecules leaving behind holes in the substrate CNTs [5]. Furthermore, in our recent study, we find a significant enhancement of the electron transport through a junction of semiconducting CNTs due to the AuCl₄ doping, and the improvement is shown to be robust with respect to the molecular concentration provided that it is large enough [6]. Recently, iodine monochloride and iodine monobromide have also been used to dope CNT thin films, indicating a remarkable reduction of their electrical resistivity [7]. Another example of improving the conductivity of CNT thin films is doping them with I chains or CuCl, as presented experimentally in Ref. [8]. Moreover, previous computational studies of CNT junctions with transition-metal linker atoms have shown enhanced junction conductances [9].

A common method to improve the conductivity of CNT thin films is to dope them with nitric acid (see, for example, Refs. [10–12]). Experimentally, the nitric acid doping has been shown to reduce the junction resistances as well as increase the conductivity of individual CNTs in the network [13,14]. However, the mechanism behind the nitric acid doping of CNTs is not well known. It is assumed to be related to nitrogen oxide molecules bound to CNTs. The adsorption of various NO_x molecules on CNTs has been studied using density-functional theory (DFT) in order to understand their detection in gas-sensing applications [15]. Computationally, it has also been found that NO₂ molecules can form NO₃ molecules, and the binding energy is higher in the case of molecular pairs [16]. According to previous experimental and computational studies, the strength and type of the adsorption of nitrogen oxides are also affected by the metallicity of the CNT [17]. In addition to the chirality, recent DFT calculations of the nitric-acid-treated CNTs have shown that the charge state of the CNT also influences the adsorption process [18].

The electronic structure and transport properties of CNT junctions need to be considered in more detail to understand the effect of nitric acid on the conductivity of CNT networks. Earlier experimental studies have shown that the resistance of the CNT junction depends largely on the chiralities of the CNTs, and the resistance may be

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especially high when a metallic and a semiconducting CNT form a junction with a Schottky barrier [19]. Furthermore, CNT junctions with physisorbed O_2 and N_2 molecules have been investigated previously experimentally and theoretically [20]. According to the computational part of that work, molecules physisorbed in the vicinity of the junctions lead to an improvement of the conductance of the junction, which has been explained to result from improved tunneling probability due to hopping via molecular orbitals [20].

In this work, we consider the influence of nitric acid on CNT networks by studying CNTs with adsorbed NO₃ molecules and junctions of NO₃-doped CNTs. On the basis of simple electron counting, NO₃ molecules are expected to work as acceptors (or anions). More specifically, optimal geometries, band structures, and electronic transmission functions for NO3-doped CNTs are determined using DFT. The DFT calculations reveal that the physisorbed NO₃ molecules receive electrons from the CNT resulting in a down-shift of the CNT Fermi level and ensuing p-type doping of the CNT. According to our electronic transport calculations, intratube as well as intertube conductances achieved in doping depend on the chiralities of the CNTs. Semiconducting CNTs become conductive in NO₃ doping, and the electron transport can be further efficiently increased by lowering the Fermi level below van Hove singularities increasing the number of open conductance channels. Moreover, junctions of two NO3-doped semiconducting CNTs with a large number of molecules show a clearly improved conductance so that the improvement, which is associated with van Hove singularity crossings, can be a factor of 10 or even more. The doping of metallic CNTs decreases the intratube conductances due to increased electron scattering a little depending on the molecular concentration. However, the doping does not lower the Fermi level as efficiently toward the van Hove singularities of the CNT electronic structure as in the case of semiconducting CNTs. This difference diminishes the positive effect of doping on the intratube and intertube conductances. The clearly dissimilar electronic structures of semiconducting and metallic CNTs hinder to enhance the conductance of their junctions by doping. Similar to the predictions for complex molecular systems [21], we find that water molecules coordinated to NO3 molecules enhance the doping effect both in semiconducting and in metallic CNTs.

The structure of this article is as follows. The main aspects of the methods and investigated systems are presented in Sec. II. Then, the geometries and band structures with the ensuing doping efficiencies are discussed at the beginning of Sec. III. The essential topics at the end of this section are electron transport in NO₃-doped CNTs and CNT junctions. A brief summary of the results is given in Sec. IV.

II. METHODOLOGY AND SYSTEMS

The calculations presented are carried out using two different electronic structure codes, FHI-aims [22–24] and

GPAW [25,26]. We use the FHI-aims code to perform most of the calculations apart from calculations including the Perdew-Zunger self-interaction correction (SIC) [27]. The latter calculations are carried out with the GPAW electronic structure code package. The FHI-aims code package is based on numeric atom-centered orbitals and also provides tools for studying the transport properties of materials. Two exchange-correlation functionals are used, namely, the generalized-gradient approximation functional PBE [28] and the hybrid functional HSE06 [29]. Since van der Waals interactions can be significant in nanocarbon systems, the Tkatchenko-Scheffler-van der Waals correction is applied together with PBE in all atomic structure optimizations in this work [30]. Charge transfer in NO₃-doped CNT systems is investigated also with GPAW by applying the Perdew-Zunger SIC to the DFT calculations [27,31]. In this case, the exchange-correlation functional is chosen to be PW91 [32]. The PW91 energy functional is corrected by subtracting a SIC term that is scaled by a factor of 1/2 (for details, see Ref. [31]).

The effect of nitric acid doping is considered in infinitely long NO₃-doped semiconducting (10,0) and metallic (8,8) CNTs by computing band structures for the computational unit cells depicted in Figs. 1(a)–1(c). Computational unit cells with several NO₃ molecules [Figs. 1(a) and 1(b)] or NO₃-H₂O complexes [Fig. 1(c)] are shown. In Fig. 1(c), each NO₃ molecule lying on the CNT is coordinated to three H₂O molecules.

The geometries of the primitive unit cells of (10,0) and (8,8) CNTs are first optimized with the FHI-aims code. The initial positions of the carbon atoms are computed by using the TubeGen 3.4 nanotube generator [33], and all primitive unit cells including the lattice vectors are relaxed. In addition, the structures of the molecules added on the CNTs are relaxed separately. Thereafter, NO₃-doped CNT



FIG. 1. Computational unit cells of (a) a semiconducting (10,0) zigzag CNT with eight NO₃ molecules, (b) a metallic (8,8) armchair CNT with eight NO₃ molecules, and (c) an (8,8) CNT with three NO₃ molecules each coordinated to three H₂O molecules. The computational (10,0) and (8,8) unit cells comprise four and seven primitive unit cells and 160 and 224 C atoms, respectively. The structures of the unit cells are presented using both side and axis views.

systems are constructed with the help of the relaxed molecules and primitive CNT unit cells. The lengths of the computational unit cells of the (8,8) and (10,0) systems are 17.3 and 17.1 Å, respectively. When the lengths of the (8,8) and (10,0) systems are almost equal, placing the same number of molecules in the computational unit cell results in nearly equal dopant concentrations per unit length, as can be seen by comparing the concentrations in Tables I and II. Periodic boundary conditions are used, and the distance between the axes of the CNTs in the neighboring unit cells is 30.0 Å. The relaxation is performed with PBE and stopped when all the force components have decreased below 10^{-2} eV/Å. A 1 × 1 × 27 k-point grid is used when the computational unit cells of the doped systems are relaxed. The calculations of semiconducting (10,0) CNTs with NO₃ molecules can include spin since in some cases it gives a ground state with a lower energy than a non-spinpolarized system.

The binding energy E_b for a NO₃ molecule on a CNT can be expressed as

$$E_b = E_T[\text{CNT-NO}_3] - E_T[\text{CNT}] - E_T[\text{NO}_3], \quad (1)$$

where E_T [CNT-NO₃], E_T [CNT], and E_T [NO₃] are the computational unit-cell total energies of the CNT with one NO₃ molecule, the pristine CNT, and the isolated NO₃ molecule, respectively. If the binding energy is determined for a doped system with water molecules, the total energy of the NO₃ molecule in Eq. (1) has to be replaced by that of the molecular complex.

Electron transport in infinitely long homogeneously doped CNTs and in junctions of CNTs at the zero-bias limit is investigated using the transport module of the FHI-aims code based on the DFT nonequilibrium Green's function method [34]. Two- or four-terminal transport systems are divided into the central scattering region and semi-infinite leads (see Fig. 2). First, the electronic structure of the transport system relaxed with PBE and including the van der Waals correction has to be determined. Then, one computes the electronic transmission function by solving the Green's function G^r consistent with the PBE exchange-correlation potential for the CNT system from the equation [34,35]

$$\left\{E - \hat{H}_0 - \sum_i \Sigma_i^r(E)\right\} G^r(\mathbf{r}, \mathbf{r}'; E) = \delta(\mathbf{r} - \mathbf{r}'), \quad (2)$$

where \hat{H}_0 represents the Hamiltonian of the junction region, and Σ_i^r (i = 1, 2, 3, 4) are the self-energies of the semi-infinite leads. Nonreflecting open-boundary conditions are assumed in the calculations. After computing the Green's function G^r , the transmission function between leads i and j is given by [35]





FIG. 2. A junction of two perpendicular NO_3 -doped (10,0) CNTs. The junction is constructed using the doped computational unit cells with eight NO_3 molecules.

$$T(E)_{i-j} = \int_{\partial\Omega_i} \int_{\partial\Omega_i} \int_{\partial\Omega_j} \int_{\partial\Omega_j} d\mathbf{r}_i d\mathbf{r}'_i d\mathbf{r}_j d\mathbf{r}'_j \times \Gamma_i(\mathbf{r}_i, \mathbf{r}'_i) G^r(\mathbf{r}'_i, \mathbf{r}_j) \Gamma_j(\mathbf{r}_j, \mathbf{r}'_j) G^a(\mathbf{r}'_j, \mathbf{r}_i), \qquad (3)$$

where the function Γ_i is $\Gamma_i = i(\Sigma_i^r - \Sigma_i^a)$. In the previous expressions, Σ_i^a and G^a are the Hermitian conjugates of Σ_i^r and G^r , respectively. A significant challenge is aligning the energy levels of the semi-infinite leads and their counterparts in the computational transport unit cell. This alignment is discussed in Refs. [6,35]. The *k*-point grid used for finding the electronic structure in the transport calculations is $1 \times 1 \times 27$ for individual metallic (8,8) CNTs. A sparser grid is used for the transport calculations of semiconducting CNTs, but the calculations are converged despite the different grid. In the case of a CNT junction, the *k*-point mesh is $1 \times 3 \times 3$.

III. RESULTS AND DISCUSSION

A. Semiconducting CNTs with NO₃ molecules

Relaxation of the computational unit cell of a semiconducting (10,0) CNT with one NO₃ molecule is carried out first with spin. After the relaxation, the center of the NO₃ molecule (the N atom) lies above a carbon atom. Our results are consistent with those of Peng *et al.* [15]. In a more recent study by Kroes *et al.* [36], the optimal geometry is different so that the NO₃ molecule has moved a bit from the top configuration.

The distance between the CNT and the NO₃ molecule $d_{\text{CNT-NO}_3}$ is defined as a distance between the nitrogen atom and the carbon atom to which the NO₃ molecule binds. With the van der Waals correction, the distance between the NO₃ molecule and the (10,0) CNT is 3.09 Å, in agreement with Kroes *et al.* [36]. This value is significantly larger than the distance 2.87 Å calculated with a local spindensity approximation (LSDA) [15]. The overbinding of



FIG. 3. Band structures of (a) a pristine (10,0) CNT. (b),(c) (10,0) CNTs doped with six and eight NO₃ molecules per computational unit cell, respectively. The DOSs for the systems studied are also shown in (a) and (c). The DOS peaks in (a) are van Hove singularities, and the additional high-DOS peaks in (c) are due to localized molecular states. The red dashed line represents the valence-band maximum E_v of the pristine (10,0) CNT or the Fermi level of the NO₃-doped (10,0) CNT.

the LSDA is a known issue and is largely due to the rapid (exponential) decay of the LSDA potential. The binding energy for one NO₃ molecule on a (10,0) CNT calculated using Eq. (1) is -0.80 eV, in good agreement with the value found in Ref. [36].

The band structures and densities of states (DOSs) of pristine and NO₃-doped (10,0) CNTs are shown in Figs. 3(a)-3(c). The systems with either six or eight NO₃ molecules in the computational unit cell are investigated without relaxing the atomic structure, except for the CNT-NO₃ distance because the molecules do not affect the CNT structure remarkably, and the interaction between the molecules is small. The pristine (10,0) CNT has a direct band gap of 0.77 eV at the Γ point in the case of PBE as shown in Fig. 3(a).

A down-shift of the Fermi level in the band structures of NO_3 -doped (10,0) CNTs in Figs. 3(b) and 3(c) is observed. In addition, there is a dispersionless molecular state just below the Fermi level in the band structures shown in Figs. 3(b) and 3(c). A previous study of graphene doped with nitric acid has proposed that the work function of the half-filled orbital of the NO_3 molecule is greater than that of the pristine graphene, and, therefore, the molecular state lies below the Fermi energy [37]. Furthermore, the Fermi level in the highly doped system in Fig. 3(c) is pinned to a van Hove singularity and the flat molecular state. This is similar to our previous observation in the case of $AuCl_4$ doping, and it is an important ingredient for establishing a robust enhanced intertube conduction [6].

We estimate the charge transfer in the NO₃-doped systems by using the method described in Ref. [6] based on the direct inspection of the one-dimensional band structures. In this method, the crossing points of the Fermi level and the valence bands are first searched for. These points divide the bands into occupied and unoccupied parts. Thereafter, by measuring the widths of the unoccupied regions and dividing these values by the maximum k_z wave vector, contributions due to the different bands to the charge transfer can be obtained. The total charge transfer is calculated by summing them up so that the orbital and spin degeneracies are taken into account. In the case of the (10,0) CNT, only one fourfold degenerate band is partly occupied.

The doping efficiency for one NO3 molecule in the computational unit cell, i.e., the electron transfer from the CNT to NO₃ molecules, is 0.6 electrons per molecule when the band structure is computed with PBE. Band structures for computational unit cells consisting of (10,0) CNTs with two NO₃ molecules are shown in the Appendix, and the charge transfer per one molecule in this system is 0.5 electrons. The band structures for highly doped (10,0) CNTs in Figs. 3(b) and 3(c) show significant down-shifts of the Fermi level, but the average doping efficiencies of the NO₃ molecules are smaller than those determined for the two-molecule system (see Table I). Therefore, the doping efficiency decreases as the dopant density increases. In the case of two molecules in the computational unit cell, the total energy of the system is 0.15 eV lower when spin is included in the calculation. No significant differences between the band structures of the NO₃-doped CNTs with and without spin polarization are found, but a clear (spin) splitting of the molecular state close to the Fermi level occurs in the spin-polarized case [see Fig. 11(b) in the Appendix]. Otherwise, almost all of the bands in the -2.0to 2.0 eV range, relative to the Fermi level, overlap with

TABLE I. Doping efficiency in NO₃-doped (10,0) CNTs per one molecule. The values are given per molecule as a function of the number of NO₃ molecules (N_{NO_3}) in the computational unit cell, i.e., as a function of the NO₃ concentration per unit CNT length. The results are computed with PBE.

$N_{\rm NO_3}$	NO ₃ concentration (molecules/Å)	Includes spin	Doping efficiency per NO ₃ molecule (e)
1	0.06	No	0.6
2	0.12	No	0.5
2	0.12	Yes	0.4
6	0.35	No	0.4
8	0.47	No	0.3



FIG. 4. Band structures of (a) a pristine (8,8) CNT. (b),(c) (8,8) CNTs doped with four and eight NO_3 molecules per computational unit cell, respectively. The DOSs for the systems studied are also shown in (a) and (c). The red dashed lines denote the Fermi level. The origin of the DOS peaks is the same as in Fig. 3.

each other in the spin-polarized band structure presented in Fig. 11(b). The doping efficiency determined for a computational unit cell with two NO_3 molecules taking the spin into account is approximately 0.4 electrons per one molecule.

A recent DFT study has revealed that the NO₃ molecule on a (10,0) CNT obtains a charge of 0.5–0.6 e according to a Bader charge analysis [36]. The charge transfer found in the present work is rather close to that result. For comparison, we determine the Hirshfeld charge for a single NO₃ molecule and obtain a value 0.4 e. This value is also in agreement with the Bader charge although slightly smaller than that given by the band-structure analysis.

B. Metallic CNTs with NO₃ molecules

The number of NO₃ molecules in the computational unit cell of a metallic (8,8) CNT is varied, and the atomic structure of each doped system is optimized separately. After the relaxation, the nitrogen atom of the NO₃ molecule resides, as in the case of the semiconducting (10,0) CNT, on top of a carbon atom, and the oxygen atoms are located near the centers of the carbon hexagons. The CNT-NO₃ distance in a NO₃-doped (8,8) CNT shown in Fig. 1(b) is 3.06 Å. The binding energy given by Eq. (1) for a NO₃ molecule on an (8,8) CNT is -1.31 eV, indicating a more stable structure than the (10,0) CNT, which has a binding energy of -0.80 eV. The trend that the binding energy is higher for metallic CNTs is in accordance with experimental findings for semiconducting and metallic CNTs [17]. It is due to the stronger polarization of the electron gas in metallic CNTs. The CNT-molecule distance does not change significantly when the number of NO₃ molecules in the computational unit cell of the CNT is increased from one to eight. It is discussed in the Appendix.

The band structures of a pristine (8,8) CNT and NO₃-doped (8,8) CNTs are displayed in Figs. 4(a)–4(c). An (8,8) CNT without doping has a band structure of a metallic system, and the Fermi level is located at a point where two bands cross each other. Placing NO₃ molecules on top of an (8,8) CNT results in a relative down-shift of the

Fermi level, as can be seen from Fig. 4(b). This down-shift can be regarded as a *p*-type doping effect since there is charge transfer from the CNT states to the molecular ones. In addition, similar to the case of the NO₃-doped semiconducting (10,0) CNTs, there is a flatband very close to the Fermi level that is a molecular state. A similar state has been observed in another study [38], but it was found lower below the Fermi level compared with this work. The downshift of the Fermi level can be enhanced by increasing the number of molecules in the computational unit cell. The Fermi level, however, does not reach the first van Hove singularity, although the molecular concentration is increased to the same level as that of the highly doped semiconducting (10,0) CNT. Thus, obtaining a stable doping effect via the Fermi-level pinning at the van Hove singularity can be challenging [6].

The values for the charge transfer in NO₃-doped (8,8) CNTs are given in Table II. They are obtained similarly to those for the (10,0) CNT taking into account that now two spin-degenerate bands cross the Fermi level. The doping efficiency of one NO₃ molecule on an (8,8) CNT per computational unit cell is close to 0.7 electrons. A significant finding is also that the doping efficiency of NO₃ molecules decreases when the molecular concentration on the CNT is increased. If the number of NO₃

TABLE II. Doping efficiency in NO₃-doped (8,8) CNTs. The values are given per molecule as a function of the number of NO₃ molecules (N_{NO_3}) in the computational unit cell, i.e., as a function of the NO₃ concentration per unit CNT length. The results are computed with PBE.

$N_{\rm NO_3}$	NO ₃ concentration (molecules/Å)	Doping efficiency per NO ₃ molecule (<i>e</i>)
1	0.06	0.7
2	0.12	0.6
3	0.17	0.6
4	0.23	0.5
5	0.29	0.5
8	0.46	0.4

molecules around the (8,8) CNT is doubled, the doping efficiency decreases approximately by 0.1 electrons per molecule. In the case of a computational unit cell with eight NO₃ molecules, the value of the charge transfer has decreased to 0.4 electrons per molecule.

C. Doping efficiencies determined with HSE06 and SIC

The spurious self-interaction error inherent to practical implementations of DFT, particularly at the generalizedgradient-approximation level of theory, makes chargetransfer systems notoriously difficult to describe [39]. This error is due to incomplete cancellation of the self-Coulomb term (i.e., an electron feels its own Coulomb repulsion) in the exchange-correlation potential. Electrons tend to delocalize in space in order to minimize the selfrepulsion and, as a result, the observed charge transfer, or effective doping, is lowered. This delocalization can be remedied by including (partial) exact exchange-as in hybrid exchange-correlation functionals-or by explicitly subtracting the self-Coulomb term from the total energy functional. An example of the latter method is the Perdew-Zunger SIC used in the present work. Perdew-Zunger SIC calculations have been successful in describing challenging systems where the commonly used exchange-correlation functionals of DFT are in error. These systems include a localized defect state in a crystal [31] and charged localized states of a molecule [40].

To assess the validity of PBE in our study, we compare our PBE results shown above with those obtained by using the HSE06 functional [29] and the Perdew-Zunger SIC approach [27,31]. The doping efficiencies of NO₃-doped semiconducting (10,0) CNTs are given for different methods in Table III. The results of this table come from calculations that are carried out in practice using a computational unit cell which is half of that used to obtain the results of the other sections of the present paper. This choice is due to the high computational costs of the Perdew-Zunger SIC, which can, in practice, be applied only to relatively short CNT systems. Thus, the results discussed in this section correspond to the NO₃ concentration of 0.12 molecules/Å, i.e., two molecules per computational unit cell used in the other parts of this paper. The results are also

TABLE III. Doping efficiency determined with PBE, HSE06, and the Perdew-Zunger SIC in a (10,0) CNT doped with two NO₃ molecules or NO₃-H₂O complexes per computational unit cell, i.e., the NO₃ concentration per unit CNT length is 0.12 molecules/Å.

Functional	Doping efficiency per NO ₃ molecule without $H_2O(e)$	Doping efficiency per NO ₃ -H ₂ O complex (<i>e</i>)
PBE	0.5	0.8
HSE06	0.6	0.9
PW91 (SIC)	0.9	1.1

shown for systems with NO₃-H₂O complexes which are studied in more detail in Sec. III D. The doping efficiencies are determined, as described above, using the band structures when the calculations are performed with the PBE and HSE06 functionals. In the case of the Perdew-Zunger SIC method, our calculations are restricted to the Γ point of the first Brillouin zone, and we carry out a Bader charge analysis [41] and determine the partial charges of the NO₃ molecule or the NO₃-H₂O complex.

As we discuss in Sec. III A (see Table I), the doping efficiency of one NO₃ molecule without water is 0.5 electrons when the NO₃ concentration is 0.12 molecules/ Å. The doping efficiency increases to 0.6 electrons per molecule when using the HSE06 hybrid functional. The Perdew-Zunger SIC gives a value of 0.9 electrons per adsorbed NO₃ molecule. Therefore, the SIC method results in clearly higher doping efficiency for the NO₃ molecule than the PBE or HSE06 calculations. The charge transfer enhances a lot when the NO₃ molecule coordinates to three H₂O molecules, and the doping efficiency is close to one electron per complex if the calculation is performed with the HSE06 functional or the Perdew-Zunger SIC.

In conclusion, HSE06 gives results closer to the selfinteraction-free ones, especially in the case of NO_3 -H₂O complexes. Therefore, we use the HSE06 functional in the more systematic study of the effects of H₂O on the doping efficiency reported below. However, the functional in our transport calculations is PBE due to the computational costs of the HSE06 transport calculations. The comparison between the PBE and HSE06 band structures indicates that our transport calculations give qualitative results. However, they predict phenomena taking place with doping and, thereby, they give insight into the electron-transport mechanisms along individual CNTs and across CNT junctions in particular.

D. Carbon nanotubes with NO₃-H₂O complexes

The charge transfer (or doping efficiency) can be enhanced by water molecules which coordinate to anionic species in molecular systems [21]. Because of strong dielectric screening, water molecules stabilize charged atoms or molecules, facilitating a more chemically robust charge transfer, in the sense that a unit, or near unit, of charge is transferred between the donor and acceptor. Inspired by this observation, we study NO_3 -H₂O complexes on metallic (8,8) CNTs. After structure optimizations with the PBE functional and the van der Waals correction, the band structures are calculated using the HSE06 functional.

In the case of the metallic (8,8) CNT, we examine systems of several NO₃-H₂O complexes per computational unit cell [see Fig. 1(c)]. The HSE06 band structures for one, two, and three NO₃ molecules each coordinated to three H₂O molecules in the computational unit cell are presented in Fig. 5. The remarkable qualitative effect of H₂O



FIG. 5. Band structures computed with HSE06 for (8,8) CNTs with NO₃-H₂O molecular complexes. The number of molecular complexes on the CNT is (a) one, (b) two, or (c) three per computational unit cell. The Fermi level is marked with a red dashed line.

molecules is the pushing of molecular states clearly below the Fermi level, as can be seen by comparing the panels with each other. As a result, the calculated doping efficiencies indicate in all the cases studied a complete charge transfer of one electron per NO₃-H₂O complex. It is distinguishably more than a doping efficiency of 0.9 electrons per one bare NO₃ molecule calculated by HSE06. The band structure and doping efficiency computed with HSE06 for a NO₃-doped (8,8) CNT system are presented in the Appendix. More clearly, it is in contrast to the clear decreasing trend in the doping efficiency as a function of increasing concentration of doping molecules seen in Tables I and II. Figure 5 shows also the increase of dispersionless molecular states in number due to coordinated H₂O molecules. Moreover, when the concentration of the molecular complexes increases, the splitting of the molecular states originating from the interactions between the large complexes enhances. At the same time, also part of the dispersive CNT states are split indicating some hybridization between the states of the CNT and the



 NO_3 - H_2O molecular complexes. In conclusion, the adsorption of H_2O molecules to NO_3 molecules enhances the doping efficiency, which has a positive effect on the intratube and intertube conductances. However, the increased interactions between the molecular and CNT states increase the electron scattering and are harmful to the intratube electron transport.

E. Electron transport in doped individual (10,0) and (8,8) CNTs

Studying the conductivity of single NO₃-doped CNTs is done by constructing a two-terminal transport system by using the computational unit cells depicted in Fig. 1. Then, the system contains three similar computational unit cells of which the first and third ones belong to the leads that are also doped. The middle cell forms the scattering region. The electronic transmission functions for individual pristine and NO₃-doped semiconducting (10,0) and metallic (8,8) CNTs are shown in Fig. 6.

In the case of a pristine (10,0) CNT, the transmission function possesses several steps and has a gap indicating semiconducting behavior. In contrast, there is no gap in the transmission function for the pristine (8,8) CNT. Therefore, this system is metallic. Corresponding to the changes in the band structures, in the case of both CNTs the transmission curves are shifted upward in energy when the number of NO₃ molecules on the CNT is increased. Importantly, in the case of the doped semiconducting CNT, the transmission at the Fermi level is remarkable; i.e., the doped CNT is metallic. Interestingly, a significant dip appears near the Fermi level in the transmission function for the NO₃-doped (8,8) CNT. The position of the dip corresponds to the energy of the molecular state in Figs. 4(b) and 4(c). The decrease in the electronic transmission function at the Fermi energy can be attributed to Fano antiresonances in nanostructures [42], effects found also, e.g., in graphene nanoribbon systems [43]. A decrease in the conductance has been observed in a computational study where a metallic (8,8) CNT with a NO₂ molecule has been placed

> FIG. 6. Electronic transmission functions for individual pristine (black solid lines) and NO₃-doped (red dashed lines) CNTs. The systems in the left panel are a pristine semiconducting (10,0) CNT and a (10,0) CNT with eight NO₃ molecules in the computational unit cell. The right panel presents the transmission functions for a pristine metallic (8,8) CNT and for a metallic (8,8) CNT doped with eight NO₃ molecules in the computational unit cell. The energy zero denotes the top of the valence band of the pristine semiconducting (10,0) CNT or the Fermi level of the metallic systems.

between two Au(111) electrodes [44] so that our finding of the lowering of the transport in the NO₃-doping process is in agreement with the previous work.

F. Junctions of doped CNTs

The computational unit cells of doped CNTs investigated in the previous sections can also be used to form CNT junctions. In particular, we consider junctions of two perpendicular doped semiconducting (10,0) or metallic (8,8) CNTs (see Fig. 2). These junctions consist of CNTs with eight NO₃ molecules in the computational unit cell. Further, another junction between a NO₃-doped metallic (8,8) and a NO₃-doped semiconducting (10,0) CNT is investigated. In this junction, the numbers of NO₃ molecules in the computational unit cells of (8,8) and (10,0) CNTs are eight and six, respectively.

The distances between the doped CNTs are optimized before performing the transport calculations. When the van der Waals correction is taken into account, the distance between the (10,0) CNTs with NO₃ molecules is 3.21 Å. Thus, the distance is larger than 2.5-2.6 Å obtained in similar calculations for a junction of (8,8) CNTs without doping [9,35], reflecting the effect of electron charge transfer from the CNTs to the molecules leaving the CNTs slightly electron deficient and resulting in Coulomb repulsion between the CNTs. In the junction between two NO₃-doped (8,8) CNTs, the CNT-CNT distance is 3.16 Å. The distance in the third junction between a metallic (8,8) and a semiconducting (10,0) CNT is 3.11 Å. Thus, the doping increases the CNT-CNT distance, but the distances do not vary significantly when changing the chiralities of the CNTs.

The intratube and intertube transmission functions for a junction of NO₃-doped (10,0) CNTs are presented in Fig. 7. The intratube transport in Fig. 7 is rather good, although the CNTs are doped with a large number of molecules. There are, however, small dips near the energy zero that are related to Fano antiresonances due to localized molecular states. The logarithmic plot in the bottom panel of Fig. 7 shows an increase of about one decade in transmission when crossing a single van Hove singularity below the Fermi level. A similar increase can be seen in the transmission between two pristine (10,0) CNTs over the same singularity (published in Fig. 6 in our previous work [6]). This increase is clearly larger than the corresponding increase in DOS reflecting the fact that also changes in the wave functions and not only the number of states available affect the intertube transmission.

In addition to the change in the average transmission over the Fermi level, the intertube transmission function in Fig. 7 increases strongly just at the Fermi level, where there is a van Hove singularity and a molecular state. Thus, the increased DOS of the CNTs enhances the electron tunneling between the CNTs. Moreover, when comparing the intertube transmission with that between two pristine (10,0) CNTs (Fig. 6 in Ref. [6]), we notice a clear broadening of the van Hove singularity-derived peak just below the Fermi level. It means that the CNT and molecular levels are hybridized increasing the extent of the wave functions and the ensuing electron transmission. Because the Fermi level can be pinned to regions of high DOS and because the electric current is determined by integrating the transmission function over a Fermi-level-centered bias window, the total current through the junction will increase. We should also note that for this reason, the total current will increase due to doping, although the intertube distance increases.

The results from the four-terminal transport calculations for a junction of NO₃-doped (8,8) CNTs are displayed in Fig. 8. In this case, electron transport along individual CNTs (see the upper plot in Fig. 8) remains almost as good as in pristine metallic (8,8) CNTs. The values of the intertube transmission function increase over the van Hove singularity nearly by one decade, and the singularity causes a sharp peak. There is also a sharp and high peak close to the Fermi energy. This peak, which is due to tunneling through localized molecular states, is higher than a similar one found in the intertube function in Fig. 7. When we compare the intertube transmission in Fig. 8 with that between two pristine (8,8) CNTs [see Fig. 3(b) in our



FIG. 7. Intratube (upper plot) and intertube (middle and lower plots) electronic transmission functions for a junction of two (10,0) CNTs with eight NO_3 molecules in the computational unit cell. The energy zero is at the Fermi level.



FIG. 8. Intratube (upper plot) and intertube (middle and lower plots) electronic transmission functions for a junction of two (8,8) CNTs with eight NO₃ molecules in the computational unit cell. The energy zero is at the Fermi level.

previous article [9]], we notice that the transmission peaks corresponding to van Hove singularities below the Fermi level have similar widths. These observations about the peak shapes mean that the hybridization between the CNT and molecular states is minimal, the extents of the wave functions do not increase, and a doping-induced increase in the total intertube current is expected to remain lower than for the junction of two doped semiconducting (10,0) CNTs.

The enhancement of the electron transport through the junction of NO₃-doped (10,0) CNTs relative to that of NO₃-doped (8,8) CNTs follows from enhanced hybridization of the CNT and molecular states, as shown by the charge densities of the highest occupied eigenstates of the CNT-NO₃ systems [see Figs. 9(a) and 9(b)]. The spreading of the wave functions and the hybridization between the CNT and molecular orbitals is remarkably larger in the NO₃-doped (10,0) CNTs than in the NO₃-doped (8,8) CNTs. This result is also consistent with the trend that the doping efficiencies are, in general, smaller for the molecules on the (10,0) than on the (8,8) CNTs (compare the corresponding values in Tables I and II). The increased hybridization leads to spreading of the eigenstates in energy and an ensuing increase in the intertube transmission over wide energy regions between broadened transmission peaks at van Hove singularities.



FIG. 9. Charge density of the highest occupied eigenstate of (a) a (10,0) CNT and (b) an (8,8) CNT with one NO_3 molecule in the computational unit cell. The value of the electron density of the isosurface is the same for both systems.

Performing a four-terminal transport calculation for a junction consisting of a doped metallic (8,8) and a doped semiconducting (10,0) CNT shows that the intratube transmission curves (see the upper panel of Fig. 10) of this junction are similar to those presented in Figs. 7 and 8. The intertube transmission function in the two lowest plots of Fig. 10 indicates that the transmission through the junction below the band gap of the (10,0) CNT is rather high in comparison with the symmetric junctions discussed above. Moreover, the molecular state at the Fermi level causes a



FIG. 10. Intratube (upper plot) and intertube (middle and lower plots) electronic transmission functions for a junction of a NO_3 -doped (8,8) and a NO_3 -doped (10,0) CNT. The numbers of NO_3 molecules in the computational unit cells of the (8,8) and (10,0) CNTs are eight and six, respectively. The energy zero is located at the Fermi level.

very narrow transmission peak. However, clear steps and wider regions of higher transmission are absent until rather low energies. This finding is due to the fact that the regions of high DOS due to van Hove singularities and molecular states in the two CNTs do not match at the same energies. Therefore, the conductances of junctions between doped semiconducting and metallic CNTs are expected to be low.

The intra- and intertube transmission functions in Fig. 7 resemble those computed for a similar CNT junction of two AuCl₄-doped (10,0) CNTs [6]. The intratube transmission function for the NO₃-doped system, however, is smoother, i.e., has fewer peaks per energy unit, than that of the CNT junction with AuCl₄ molecules. This difference indicates that there are fewer molecular states in the NO₃ molecules, and they do not hybridize with those of the CNT so strongly causing less electron scattering than the AuCl₄ molecules on the same CNT. Correspondingly, the number of peaks in the vicinity of the Fermi level in the intertube transmission function for (10,0) CNTs with NO₃ molecules is smaller than in the same region in the intertube function for AuCl₄-doped (10,0) CNTs, and doping with NO₃ is expected to be less efficient than doping with AuCl₄.

Increases in the conductances of the junctions of doped CNTs are related to the Fermi-level crossing van Hove singularities and the high and wide peaks of the intertube transmission functions. Similar to the junctions of AuCl₄-doped (10,0) CNTs [6], the conductances of the junctions of NO₃-doped semiconducting (10,0) or metallic (8,8) CNTs enhance due to doping when the Fermi level shifts to a region where the DOS is high. The Fermi level shifts to a region where the DOS is high. The Fermi level can be pinned to the van Hove singularities or localized molecular states leading to a robust mechanism for the improvement of the conductivity of CNT networks [6]. The pinning of the Fermi level at regions of high DOSs can also increase the conductances between dissimilar CNTs such as in the case of semiconducting (10,0) and metallic (8,8) CNTs that we discuss above.

G. Comparison between experimental and theoretical results

Using atomic force microscopy, Znidarsic [13] *et al.* measured the resistances of single-wall CNTs and their junctions forming CNT networks before and after nitric acid treatments. They analyzed the measured data for junction resistances as a function of the diameters of the two CNTs forming X- or Y-shape junctions and as a function of the angle between the CNTs. The smallest contact resistances found were 29 k Ω . The contact resistances decreased with increasing CNT radii and decreasing the contact angle. The Y junctions show smaller resistances than the X junctions. Because the unity transmission corresponds to the conductance quantum $2e^2/h$, the junction resistance of 29 k Ω will correspond to a transmission of about 0.5. According to our results in Figs. 7, 8, and 10, these kinds of transmission values are not plausible for the

rather small radii (10,0) and (8,8) CNTs forming a perpendicular junction outside the transmission singularity peak regions unless the Fermi level has crossed three van Hove singularities. According to Ref. [13], the nitrogen acid treatment decreased the average junction resistance by a factor of around 3, which may signalize the lowering of the Fermi level in CNTs and also its pinning around the van Hove singularities as a function of increased doping.

In a recent experimental work, Tsebro et al. [8] measured, as a function of temperature, sheet resistances of CNT networks before and after iodine or CuCl doping. The CNT radii were rather large, around 2 nm, and the dopants filled the CNTs. Tsebro et al. analyzed their data in terms of intra- and interbundle contributions corresponding to phonon scattering and fluctuation-assisted tunneling, respectively. With the help of calculated phonon dispersion relations and electronic band structures, they were able to conclude that iodine and CuCl doping lower the Fermi levels by 0.6 and 0.9 eV, respectively. The latter figure means that the Fermi level has crossed in semiconducting (metallic) CNTs three (one) van Hove singularities (singularity). The sheet resistances of the CNT networks decreased almost by a decade in the CuCl doping, and the effect did not decay, indicating that the internal doping of the CNT is stable. Our results show that the crossing of the Fermi level below a van Hove singularity causes a decrease of the junction resistance, which is of the same order of magnitude. Related to this decrease of the junction resistance, we also note that Tsebro et al. proposed that the main cause for the sheet resistance of the CNT network is the junction resistance and that doping mainly decreases this contribution.

IV. CONCLUSIONS

The influence of NO₃ molecules on the band structures and electronic transmission functions of semiconducting and metallic CNTs is explored to understand the nitricacid-doping process used to improve the conductivity of CNT thin films. In the present work, (10,0) and (8,8) CNTs are used in our density-functional modeling to represent semiconducting and metallic CNTs, respectively. Our results show that electrons are transferred from the CNT to the NO₃ molecule, and this results in *p*-type doping of the CNT. The average doping efficiency per NO₃ molecule decreases when the number of molecules on the CNT is increased. However, the doping efficiency enhances considerably when the NO₃ molecules form complexes with H₂O molecules.

Electron-transport calculations of individual NO_3 -doped semiconducting CNTs reveal that doping convert them into metallic, although sharp dips in the transmission function due to scattering "off" localized molecular states appear. The transmission functions increase stepwise over the van Hove singularities of the CNT electronic structures. Reflecting qualitatively different band structures, shifting the Fermi level toward the next singularity requires less doping in the case of semiconducting CNTs in comparison with metallic CNTs. This difference will favor semiconducting CNTs in CNT networks.

The intertube transmission functions between two semiconducting or two metallic CNTs increase around one decade when the Fermi level passes over a van Hove singularity. This improvement increases directly the conductance of the CNT junction. Moreover, the pinning of the Fermi level at the van Hove singularity and partially filled molecular states with the hybridization of the molecular and CNT states there can further increase the junction conductance and the conductivity of the CNT network. The hybridization of the molecular and CNT states is stronger for semiconducting CNTs than it is for metallic CNTs, which will also favor the former in CNT networks. The energy mismatch between the high-DOS regions for the clearly dissimilar electronic structures of metallic and semiconducting CNTs hinders to enhance the conductance of their junctions.

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APPENDIX: DETAILS OF CALCULATIONS, CNT SYSTEMS, AND BAND STRUCTURES

The geometries of metallic (8,8) and semiconducting (10,0) CNTs with NO₃ molecules are optimized using the FHI-aims code package. The concentration of NO₃ molecules on the CNTs is varied, and the atomic structures of individual doped CNTs are relaxed. The relaxation is started with the light settings defined in the FHI-aims code package. After completing the relaxation with the light settings, the relaxation is continued with the tight settings. The relaxation calculations are stopped when the maximum force component falls below the tolerance values, as we explain in the main text. The optimal geometries of doped metallic and semiconducting CNTs are discussed below. Some systems also have H₂O molecules coordinated to the NO₃ molecules. Moreover, this appendix contains a few figures of band structures for NO₃-doped CNTs. The k-point grids of the band-structure calculations for the PBE and HSE06 functionals are $1 \times 1 \times 27$ and $1 \times 1 \times 15$, respectively.

Optimizing the geometry of the computational unit cell of an (8,8) CNT with one NO₃ molecule shows that the distance between the NO₃ molecule and the CNT decreases by 0.16 Å when the Tkatchenko-Scheffler–van der Waals correction is taken into account. The CNT-molecule distance for NO₃-doped (8,8) CNTs is 3.07 Å on average, and the distance does not depend on the number of NO₃ molecules remarkably. Only a small increase occurs in the distances when the dopant concentration is increased. This change, however, is negligible. The distance between the CNT and the NO₃ molecule is an average over all CNT-molecule distances in the system and is calculated with the van der Waals correction.

When H_2O molecules are coordinated to the NO_3 molecule, the distance between the (8,8) CNT and the NO_3 molecule increases to 3.29 Å if the calculation includes the van der Waals correction. Neglecting this correction leads to an even larger CNT-molecule distance, 3.55 Å.

Optimization of the geometries of (10,0) CNTs doped with NO₃ molecules is performed with spin when there is only one molecule per computational unit cell on a (10,0) CNT. The (10,0) CNTs with two NO₃ molecules per computational unit cell are relaxed both with and without spin. In the case of (10,0) CNTs with NO₃-H₂O complexes, spin is omitted in the relaxation calculations. After optimizing the short supercell [two molecules per computational unit cell in Fig. 1(a)] of a NO₃-doped (10,0) CNT without water, the distance between the CNT and the molecule $d_{\text{CNT-NO}_3}$ is 3.05 Å. Thus, the molecule moves closer to the CNT compared with the geometry of a larger computational unit cell. The movement probably occurs because the charge of the CNT becomes larger on average when the molecular concentration is increased. As a result, the electrostatic interaction in the system pulls the molecules closer to the CNT. Adding H₂O molecules to the NO₃-doped (10,0) CNT system makes the molecular complex move farther from the CNT surface. The distance $d_{\text{CNT-NO}_3}$ is 3.16 Å, and the alignment of the molecular system changes because of the water molecules.



FIG. 11. Band structures computed (a) without and (b) with spin for the computational unit cells of (10,0) CNTs doped with two NO₃ molecules.



FIG. 12. Band structures computed with HSE06 for (a) a pristine (8,8) CNT and (b) an (8,8) CNT with one NO₃ molecule in the computational unit cell.

The down-shift of the Fermi level occurs in the band structure for a (10,0) CNT with one NO_3 molecule in the computational unit cell. A larger down-shift can be achieved by placing another molecule on the CNT in addition to the first one [see Fig. 11(a)]. Carrying out a spin-polarized band-structure calculation results in splitting of the energy levels near the Fermi energy region as shown in Fig. 11(b). The average doping efficiencies for the NO_3 molecules in this system can be found in the main text.

The band structures determined with HSE06 for the computational unit cells of metallic (8,8) CNTs without NO₃ molecules and with one NO₃ molecule [see Fig. 1(b)] are presented in Figs. 12(a) and 12(b), respectively. The down-shift of the Fermi level becomes larger when the HSE06 hybrid functional is used in the calculations. The value of the doping efficiency is 0.9 electrons per NO₃ molecules in the case of Fig. 12(b). This increase in the down-shift of the Fermi level can also be seen in the band structures of similar semiconducting (10,0) CNTs with NO₃ molecules.

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