

Molecular vibration sensor via transport measurements in carbon nanotubes

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When a molecule adsorbs to the surface of a carbon-based nanostructure the local binding potential and the molecule mass determine the natural characteristic frequency with which it vibrates after being slightly perturbed from its equilibrium position. We perform phonon-assisted inelastic quantum transport calculations for carbon nanotubes with a single molecule attached to its surface and show that the differential conductance spectra may be used to identify the presence of the adsorbed molecule.

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The search for high-sensitive sensors capable of detecting specific chemical and biological agents in real time and at the lowest possible concentrations is presently a topical subject. The use of carbon-based nanostructures has been attracting a great deal of interest for this purpose because their properties may change considerably upon exposure to certain agents. Various methods have been devised for developing carbon-based molecule nanosensors.¹⁻⁵ However, the possibilities of exploiting molecule vibrations for this aim has been less investigated. Actually, the effects of intrinsic electron-phonon (e-ph) interaction on the transport properties of carbon nanotubes have been largely exploited.⁶⁻⁹ In a recent very interesting work, vibrational modes in a single molecule were observed by measuring the differential conductance as function of the applied bias voltage across the molecular junction.¹⁰

Here we propose a spectroscopic technique that may effectively detect the presence of a particular molecule down to very low concentrations by exploring molecular-vibrational features. The physical principle of detection is rather simple, resembling inelastic electron tunneling spectroscopy techniques,¹¹ and is described as follows. Suppose we wish to detect the presence of a specific molecule that gets attached to the surface of a carbon-based nanostructure. There is a characteristic angular frequency ω_0 with which the attached molecule vibrates in the vicinity of its stable equilibrium position that is determined by the local potential describing the connection between the molecule and the nanostructure surface. The energies of the local mode are quantized in multiples of $\hbar\omega_0$. We shall consider, as an example, a sensor made of a single-wall carbon nanotube (CNT) where electrical contacts are made to allow measurements of the current-voltage (I - V) characteristic of the device. If one sweeps the applied voltage V through $\hbar\omega_0/e$, where e is the magnitude of the electron charge, when eV reaches $\hbar\omega_0$ a new channel opens up, by means of the electron-phonon interaction, because the electron may inelastically emit or absorb a vibrational quantum in the process. As a consequence, the conductance varies when this occurs, and one shall find very sharp features in the dI/dV and d^2I/dV^2 curves which distinctively identify the fingerprint of the molecule presence.

It should be also possible to functionalize the carbon-based surface to attract individual species of interest. In this case, a considerable shift in ω_0 may be observed when the

desired molecule binds to the attractor, provided the mass of the specific molecule we wish to detect is not relatively small in comparison with the one employed in the functionalization.

Our interest is in very low concentrations of molecules, a regime where they may be approximately treated as noninteracting. Therefore, we shall consider a single molecule coupled to an infinite carbon nanotube. It is convenient to label a CNT site by a pair of indices (i, α) which specify the CNT ring i to which it belongs and the position α within this ring where it is located. We assume that the single molecule is attached to the CNT site labeled by $(0,0)$. The electronic structure is described by a single π -band tight-binding model, taking into account the electron interaction with a local-vibrational mode. The Hamiltonian operator is written as

$$\hat{H} = \sum_{i\alpha} \epsilon_{i\alpha} c_{i\alpha}^\dagger c_{i\alpha} + \sum_{ij\alpha\beta} t_{\alpha\beta}^{ij} c_{i\alpha}^\dagger c_{j\beta} + \hbar\omega_0 b^\dagger b + f c_{00}^\dagger c_{00} (b^\dagger + b), \quad (1)$$

where, $c_{i\alpha}^\dagger$ and $c_{i\alpha}$ represent the electronic creation and annihilation operators at the site (i, α) , respectively; $\epsilon_{i\alpha}$ describes the on-site potential energy profile, including external potentials, $t_{\alpha\beta}^{ij}$ denotes the electronic hopping integral between sites (i, α) and (j, β) ; b^\dagger and b are the local-phonon creation and annihilation operators, and f measures the strength of the e-ph interaction that takes place at $(0,0)$.

Following the approach developed in Refs. 12–14, we choose a suitable basis set $[|ian\rangle = \frac{1}{n!} c_{i\alpha}^\dagger (b^\dagger)^n |0\rangle]$ to construct a matrix representation of \hat{H} given by

$$H_{i\alpha, j\beta}^{n, m} = (\epsilon_{i\alpha} + n\hbar\omega_0) \delta_{ij} \delta_{\alpha\beta} \delta_{nm} + t_{\alpha\beta}^{ij} \delta_{nm} + f \delta_{i0} \delta_{j0} \delta_{\alpha 0} \delta_{\beta 0} (\sqrt{m+1} \delta_{nm+1} + \sqrt{m} \delta_{m-1n}), \quad (2)$$

where n, m are the number of phonons. In this representation, the problem is exactly mapped into a single-particle one, though in a higher dimension which is specified by the number of phonons considered, as schematically illustrated in Fig. 1. At zero temperature, electrons enter the scattering region via the zero-phonon channel only, and have a finite probability of being transmitted to any of the outgoing leads. In this case just phonon-emission processes are allowed. At finite temperatures, however, a number n of phonons may be

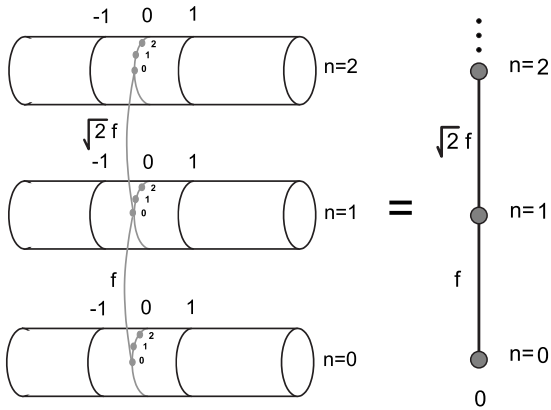


FIG. 1. Schematic representation of Eq. (2), which maps the problem of a CNT coupled to a local phonon modes into a single-particle problem in a higher dimension. The CNTs shown in the figure represent incoming and outgoing electronic channels of a virtual multiterminal system with 0, 1, and 2 phonons. Note that channels associated with n and $n+1$ phonons are coupled via single sites with a coupling energy given by $f\sqrt{n+1}$. Transitions between different channels correspond to emission and absorption of phonons which are made possible by the local electron-phonon interaction.

excited with a probability given by¹⁴ $P_n = e^{-n\hbar\omega_0/k_B T} (1 - e^{-\hbar\omega_0/k_B T})$. An elastic process takes place when an electron is transmitted between two channels associated with equal phonon numbers, whereas all other routes correspond to inelastic events.

We employ the Landauer approach to calculate the phonon-assisted transport properties of the system, namely, its conductance and I - V characteristic curves. The conductance is given by $\mathcal{G} = (2e^2/h) \sum_{n,m} P_n \mathcal{T}_{nm}$, where \mathcal{T}_{nm} represents the transmission coefficient between the incoming n and outgoing m channels. \mathcal{T}_{nm} can be expressed in terms of one-electron retarded and advanced Green's function,¹⁵ which are determined by an efficient real-space renormalization method.^{16–18}

In our calculations we consider nearest-neighbor hopping only and its value t is chosen as our energy unit. For carbon nanotubes $t \approx 2.7$ eV.¹⁹ The phonon energy $\hbar\omega_0$ and the value of the e-ph coupling constant f depend upon the specific molecule we are dealing with and on the nature and characteristics of its bonding to the CNT surface. In principle, the precise value of $\hbar\omega_0$ may be either estimated by first-principles calculations or determined by other experimental means such as vibrational spectroscopy measurements.

As an illustrative example of our model calculation we first consider a single molecule attached to an atomic linear chain. Characteristic curves of current versus voltage are shown in Fig. 2, for null temperature. Two electron-phonon coupling intensities and a phonon vibration energy $\hbar\omega_0 = 0.1t$ were considered. In both panels the dotted-dashed curves are zero-phonon results whereas dashed and solid lines describe elastic and total contributions for $N=8$, respectively, N being the maximum number of phonon channels allowed in the calculation. A current reduction takes place when phonon scattering mechanisms are present, changing

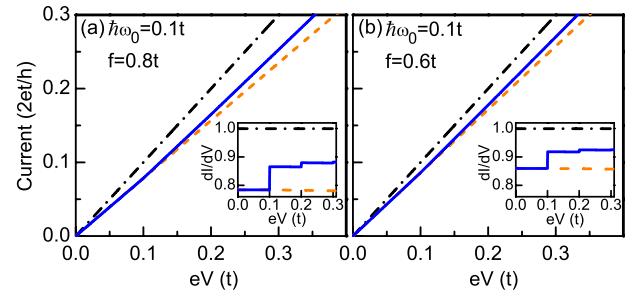


FIG. 2. (Color online) Current as function of the bias voltage for a linear chain coupled to a single phonon mode $\hbar\omega_0 = 0.1t$ ($N=8$) at $T=0$ and electron-phonon couplings (a) $f=0.8t$ and (b) $f=0.6t$. Elastic and total current are represented by dashed (orange online) and solid (blue online) lines, respectively. The case of zero phonons ($N=0$) is depicted with a black dotted-dashed line, for comparison. Inset: differential conductance as a function of the potential bias.

the slope of the characteristic curve. When $eV \geq \hbar\omega_0$, inelastic scattering is also allowed through other channels corresponding to emission of one phonon with energy $\hbar\omega_0$. This effect is clearly shown in the $I \times V$ diagrams: the curves corresponding to total currents (elastic plus inelastic contributions) present a slope increase exactly at the characteristic energy $\hbar\omega_0$. Higher n -phonon processes may be detected in the $I \times V$ curves for $eV = n\hbar\omega_0$ ($n=2, 3, \dots, 8$). These effects are more evident in the corresponding differential conductance (dI/dV) shown in the insets of both Figs. 2(a) and 2(b). The increase in the slopes are clearly indicated by the steps exhibited in the dI/dV curves at the phonon energies $n\hbar\omega_0$. The results, therefore, reveal the expected signatures of the phonon mode energy $\hbar\omega_0$. As expected, the intensity of electron-phonon coupling f dictates the current slope change.

In the following, we consider a single molecule attached to metallic CNTs. Since we are mainly interested in a proof of concept rather than in a particular molecule, we shall assume a generic value of $\hbar\omega_0 = 5 \times 10^{-2}t$ which is on the order of magnitude of a typical CNT-molecule covalent-bond stretching mode, and values of the e-ph coupling constant in the range of 0.1–0.4 t , which are on the order of magnitude of those quoted in Ref. 20. Figure 3(a) shows the transmission coefficients \mathcal{T} through a (5,5) CNT, coupled to $N=4$ phonons, calculated as functions of energy for different values of the e-ph coupling constant. The corresponding elastic contributions to \mathcal{T} are also displayed for comparison. The transmission coefficients exhibit noticeable reductions at regular energy intervals that are multiples of $\hbar\omega_0$. Although not visible in the chosen scale of Fig. 3(a), the transmission suppression, marked by the main dip associated to $n=1$ phonon mode, lies between 2% and 8% with respect to $\mathcal{T}=2$. Calculations of the density of states (DOS) for the Hamiltonian given by Eq. (2) in the limit $f \rightarrow 0$ helps elucidating where this behavior stems from. Figure 3(b) depicts the corresponding DOS associated with n -phonon virtual quantum channels ($n=0, 1, 2, 3, 4$), which are all independent in this case. The signatures of the absorbed molecule appear in \mathcal{T} at the van Hove singularity energies of the CNTs representing higher order ($n > 0$) phonon channels, where the on-site potential energies are shifted by $n\hbar\omega_0$. We have performed

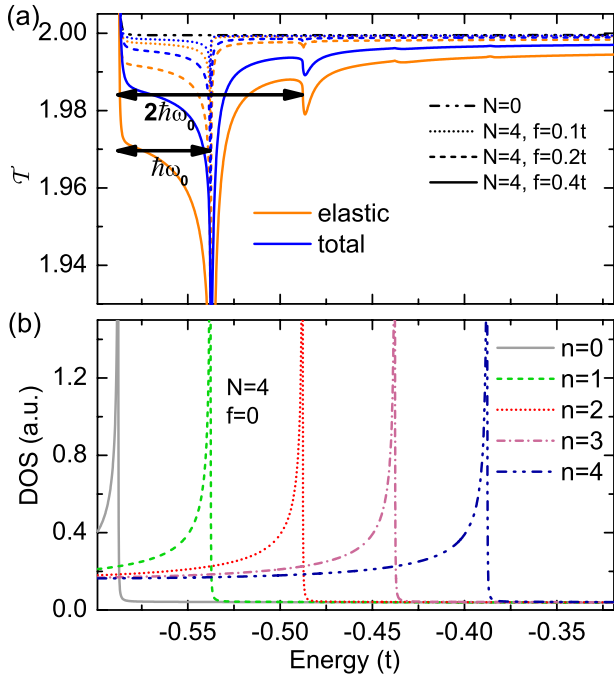


FIG. 3. (Color online) (a) Transmission coefficient and (b) DOS calculated as functions of energy for a (5,5) CNT. The transmission coefficients are calculated at zero temperature for various values of the e-ph coupling constant. The DOS associated with the Hamiltonian given by Eq. (2) are computed in the limit $f \rightarrow 0$. In all calculations we consider $\hbar\omega_0 = 5 \times 10^{-2}t$. The correlation between the dips in the transmission coefficients and the Van Hove singularities in the DOS is evident.

similar calculations for a (12,0) CNT obtaining basically the same results.

Distinct features that enable the identification of the molecular vibration appear in the current-voltage characteristics and in the differential conductance dI/dV curves, which are essential for the device operation. In a metallic nanotube there is an overall decrease in the current when e-ph scattering processes are allowed. At $T=0$ and for relatively low bias only elastic scattering processes take place. However, when eV reaches $\hbar\omega_0$ new channels become available through inelastic scattering. As a consequence, the slope of the characteristic curve increases, and exhibits a very sharp transition precisely at $\hbar\omega_0$, as previously reported for the case of a linear chain. The size of the slope change is controlled by the e-ph coupling constant. In Fig. 4 we show results of dI/dV calculated as function of eV for an armchair (5,5) CNT coupled to $N=4$ phonons, for $k_B T=0$ and $0.01t$ (gray and black curves, respectively). Calculations for a pure pristine CNT with no phonons are also included for comparison (dotted-dashed curves). Actually, in the limit of no phonon scattering and null temperature the conductance should reach the value of two when the bias goes to zero. The fact that this value is not exactly achieved is partially due to a small imaginary part that is added to the energies (typically a value of $10^{-4}t$) which introduces a finite mean lifetime for the carrier. This small deviation may also be attributed to limitations of the numerical accuracy. The abrupt change in the slope of the I - V curve leads to a steplike discontinuity in the

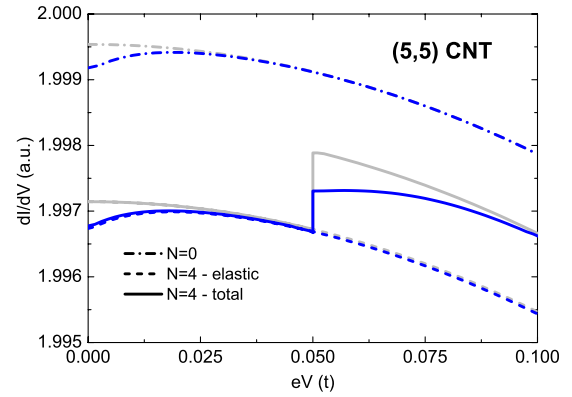


FIG. 4. (Color online) dI/dV as a function of the bias voltage for a metallic (5,5) CNT. The phonon mode parameters are $\hbar\omega_0 = 5.0 \times 10^{-2}t$ and $f = 0.3t$. The gray lines represent $k_B T = 0$ and the black (blue online) lines represent $k_B T = 0.01t$.

differential conductance (and to a very sharp peak in d^2I/dV^2) at $eV = \hbar\omega_0$, as depicted by the solid lines. As extra scattering processes are allowed for finite temperatures, phonon absorption and emission events lead to a reduction on the current and on the differential conductance. For $k_B T > 0$, inelastic processes are allowed for $eV < \hbar\omega_0$. One should remark that in Fig. 4 the second jump should appear at the voltage 0.1 eV, which is exactly the final energy considered. It is worth noticing that the higher the order of the phonon scattering the smaller is its corresponding signal in the differential conductance. In the chosen vertical scale the second and higher steps becomes very small and to make them visible one should analyze the d^2I/dV^2 . Calculations for a metallic (12,0) CNT using the same set of parameters provide similar results.

Phonon-assisted inelastic quantum transport properties of armchair and zigzag CNTs coupled locally to a single optical-phonon mode were studied within a simple tight-binding approximation. The transport results show that the characteristic molecular vibration energy $\hbar\omega_0$ can be observed in the transmission coefficients, the differential conductances, and the d^2I/dV^2 curves. Also, by analyzing the slopes of the characteristic curves one may study the effects of the electron-phonon coupling energy f on the electronic transport. Despite of the subtleness of the effects induced by molecular vibrations on the transport properties ($2et/h \sim 100 \mu A$), the state of the art in experimental measurements²¹ indicates that these effects may be measurable. At finite but very dilute molecule concentrations, which is the regime of actual interest, one expects the strength of the signal to increase linearly with the number of molecules that bind to the nanotube.

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