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Quantum phonon transport of molecular junctions amide-linked with carbon nanotubes: A first-principles study

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Quantum phonon transport through benzene and alkane chains amide-linked with single-walled carbon nanotubes (SWCNTs) is studied within the level of density-functional theory. The force-constant matrices are obtained from standard quantum chemistry software. The phonon transmission and thermal conductance are from the nonequilibrium Green's function and the mode-matching method. We find that the ballistic thermal conductance is not sensitive to small compression or stretching of the molecular junction. The terminating groups of the SWCNTs at the cutting edges only influence the thermal conductance quantitatively. The conductance of the benzene and alkane chains shows large difference. Analysis of the transmission spectrum shows that (i) the low-temperature thermal conductance is mainly contributed by the SWCNT transverse-acoustic modes, (ii) the degenerate phonon modes show different transmission probability due to the presence of molecular junction, and (iii) the SWCNT twisting mode can hardly be transmitted by the alkane chain. As a result, the ballistic thermal conductance of alkane chains is larger than that of benzene chains below 38 K and becomes smaller at higher temperature.

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I. INTRODUCTION

The electronic transport properties of a molecular device depend much on the underlying nuclear configuration and the electron-phonon coupling.[1] The mutual interaction between them induces Joule heating in the molecule, which may have important consequences on the functionality and reliability of a molecular device. Study of the heat transport by phonons in molecular junctions is crucial for a better understanding of their electronic transport properties. Phonon thermal transport itself is also interesting. Detailed understanding of the underlying transport mechanism is especially useful for the design of novel phononic devices.[2,3] Furthermore, combined study of the electronic and phononic transports in molecular junctions is the first step toward the design of molecular thermoelectric devices.[4] Great experimental progress has been made in these directions recently, which enables one to measure the thermal and thermoelectric transport properties of molecular junctions.[4,5] Advances in experimental technique call for a different theoretical method to predict the thermal conductance of molecular junctions. Although semiempirical or minimal model calculation is helpful to understand the underlying physics,[6,7] for a detailed quantitative study, a parameter-free first-principles method is highly desirable.[8]

In this paper we introduce such a method based on a standard quantum chemistry software, the GAUSSIAN03 package.[9] Given the molecule structure, we can obtain the force-constant matrices after performing the structure relaxation. The thermal conductance can be calculated via available theoretical methods. Among them are the nonequilibrium Green's function (NEGF) method,[10–14] which has been successfully used to predict the electronic conductance of molecular junctions.[15–17] To study the transport of each phonon mode, we will also use the mode-matching method,[18] which is equivalent to the NEGF method in the ballistic limit.[19] Using these methods, we first compare the thermal conductance of a benzene ring amide-linked with two (6, 0) single-walled carbon nanotubes (SWCNTs) under different compression or stretching conditions. Then we study the effect of SWCNT terminating group at the cutting edges. Finally, we compare the phonon transmission probability and the thermal conductance of benzene and alkane chains with the same leads. Although the electron contribution to the thermal conductance may be comparable with or larger than that of phonons, inclusion of this effect is out of the scope of the present study.

II. MOLECULAR STRUCTURE AND THEORETICAL METHOD

In this section we first introduce the system Hamiltonian and the procedure to obtain it from the GAUSSIAN03 package. Then we briefly outline the NEGF, the mode-matching method, and their relationship. For a detailed discussion, please refer to Ref. 14. The system we are interested in is a molecular junction connected with two periodic semi-infinite leads at both sides. It is a standard treatment to divide the whole structure into three parts: the center junction and two leads acting as thermal baths. The boundaries between the center and the baths may be at arbitrary positions and may not correspond to any physical interface. But it is desirable to include a part of the leads into the center region, since we need to make sure that there is no direct interaction between the two baths, which is required by the NEGF formalism. By doing this, we can also include the charge-transfer effect between the leads and the molecule junction. With this setup, the system Hamiltonian can be written as

$$\mathcal{H} = \sum_{\alpha=L,C,R} H_\alpha + (u^L)^T V^{LC} u^C + (u^C)^T V^{CR} u^R + V_n, \qquad (1)$$

where $H_\alpha = \frac{1}{2}(\dot{u}^\alpha)^T \dot{u}^\alpha + \frac{1}{2}(u^\alpha)^T K^\alpha u^\alpha$ represents harmonic oscillators, u^α is a column vector consisting of all the mass normalized displacement variables in region α, and $\dot{u}^\alpha$ is the corresponding conjugate momentum. K^α is the spring constant matrix and $V^{LC}=(V^{CL})^T$ is the coupling matrix of the left lead to the central region, which is similar for V^{CR}. V_n is the nonlinear interaction in the center, which could be $V_n = \frac{1}{3}\sum_{ijk} t_{ijk} u_i u_j u_k$ for cubic nonlinearity. We ignore the nonlinear interaction in this paper and only briefly discuss its effect in Sec. III.

We study the phonon thermal conductance of benzene and alkane chains covalently bonded with two (6, 0) SWCNTs via the amide group. This is relevant to a recent experimental setup,[20] where the SWCNT is oxidatively cut and the cutting edges are covalently bonded with molecular chains via the amide group. To get the force constants of the system, we do two separate runs for the center and the leads using GAUSSIAN03. For the center, we include extra one and a half periods of SWCNT at each side, which is terminated by hydrogen atoms at the outer boundaries. The cutting edges may be terminated by H or COOH group. We optimize the center at the level of B3LYP density-functional method using the 6-31G basis set. We first relax the structure by constraining the leads to be coaxial to get an optimized distance between the two leads. Then we fix the outer half period of the SWCNTs and the H atoms at both sides and allow all other atoms to move freely. The optimized structure is used to get the dynamical matrix. The inset of Fig. 2 shows the optimized benzene structure terminated by the H and COOH groups at the cutting edges. For the lead, it is desirable to use periodic boundary condition to compute the dynamical matrix but this is out of the ability of GAUSSIAN03. So we optimize seven SWCNT periods and extract the force constant from the central period to minimize the finite-size effect. To connect the molecule with the two leads, we remove the outer fixed atoms in the molecule and connect the remaining period of SWCNT with one semi-infinite SWCNT at each side. For the coupling matrix between the center and the leads, we only include coupling between one period of SWCNT atoms in the center and one period in the leads. This is a good approximation so long as we include enough SWCNT atoms into the center molecule. In the present case, if we replace the force constants of SWCNTs included in the molecule by ideal ones, the maximum thermal conductance change within the temperature range studied here is less than 5%.

In the NEGF method as described in Refs. 10–14, thermal conductance of the molecular junction can be calculated from the Landauer formula ($\hbar=1$ throughout the formula)

$$\sigma = \frac{1}{2\pi}\int_0^\infty d\omega \omega T[\omega]\frac{\partial f(\omega)}{\partial T} \tag{2}$$

with the transmission coefficient

$$T[\omega] = \mathrm{Tr}\{G^r \Gamma_L G^a \Gamma_R\}. \tag{3}$$

$f(\omega)$ is the Bose-Einstein distribution function. The retarded Green's function G^r is obtained from

$$G^r(\omega) = [(\omega + i0^+)^2 - K^C - \Sigma_L^r(\omega) - \Sigma_R^r(\omega)]^{-1}, \tag{4}$$

where the retarded self-energy of lead α is

$$\Sigma_\alpha^r[\omega] = V^{C\alpha} g_\alpha^r[\omega] V^{\alpha C}, \tag{5}$$

and the lead surface Green's function $g_\alpha^r[\omega]$ can be calculated from the generalized eigenvalue method,[14] e.g.,

$$g_R^r(\omega) = [(\omega + i0^+)^2 - k_{11}^R - k_{01}^R F_R^+(1)]^{-1}. \tag{6}$$

k_{11}^R and k_{01}^R are the diagonal and off-diagonal parts of the right lead dynamical matrix. Their sizes are determined by the degrees of freedom M in each period of the lead. The matrix $F_R^+(s)$ translates to the right the displacement in the nth period to the $(n+s)$th period $u_R^+(n+s)=F_R^+(s)u_R^+(n)$. It is constructed from the eigenvalues and vectors of the generalized eigenvalue problem

$$\begin{pmatrix} (\omega + i0^+)^2 I - k_{11}^R & -I \\ k_{10}^R & 0 \end{pmatrix}\begin{pmatrix} \epsilon \\ \zeta \end{pmatrix} = \lambda \begin{pmatrix} k_{01}^R & 0 \\ 0 & I \end{pmatrix}\begin{pmatrix} \epsilon \\ \zeta \end{pmatrix} \tag{7}$$

as $F_R^+(s)=E_R^+\Lambda_+^s(E_R^+)^{-1}$. Here I is an $M\times M$ identity matrix. The diagonal matrix Λ_+ consists of all the eigenvalues $|\lambda_+| < 1$, and E_R^+ the corresponding eigenvectors $E_R^+ = (\varepsilon_1^+, \varepsilon_2^+, \cdots, \varepsilon_{M'}^+)$. Note that M' may be less than M, in which case the matrix inverse becomes pseudoinverse. A similar left-translation matrix $F_R^-(s)$ can be constructed from Λ_- and E_R^-, which include all the eigenvalues $|\lambda_-| > 1$ and the corresponding eigenvectors.

While the NEGF method is systematic and suitable to take into account the nonlinear interaction, the transmission coefficient from it is the sum of all the eigenmodes from the leads. Thus it is difficult to analyze the contribution from each mode. The mode-matching method provides another way to calculate the transmission coefficient in the ballistic limit.[14,18,19] Single-mode transmission and mode mixing effect can be studied by this method. The transmission matrix is given by

$$t_{mn}^{RL} = \sqrt{\frac{v_{R,m}^+ a_L}{v_{L,n}^+ a_R}}\tau_{mn}^{RL} \tag{8}$$

and

$$\tau^{RL} = (E_R^+)^{-1} g_R^r V^{RC} G^r V^{CL} g_L^r k_{10}^L [F_L^+(-1) - F_L^-(-1)] E_L^+, \tag{9}$$

where $v_{\alpha,m}^+$ is the group velocity of the mth right propagating mode for the lead α. While the mode indices m and n are only for propagating modes, the matrices $E_\alpha^\pm$ include all the propagating and evanescent modes. The total transmission coefficient as in the Landauer formula is $T[\omega] = \mathrm{Tr}\{(t^{RL})^\dagger t^{RL}\}$. Similar relations hold for waves incidented from the right lead and transmitted to the left t_{nm}^{LR}.

The NEGF and the mode-matching methods are exactly equivalent in the ballistic case as shown in Ref. 19. All the matrices needed by Eqs. (8) and (9) can be obtained by solving the generalized eigenvalue problem Eq. (7). It is interesting to note that by doing a singular value decomposition on the transmission matrix t, we can get the transmission eigenchannel information without any other efforts, for which different methods have been developed in the electronic transport literature.[21]

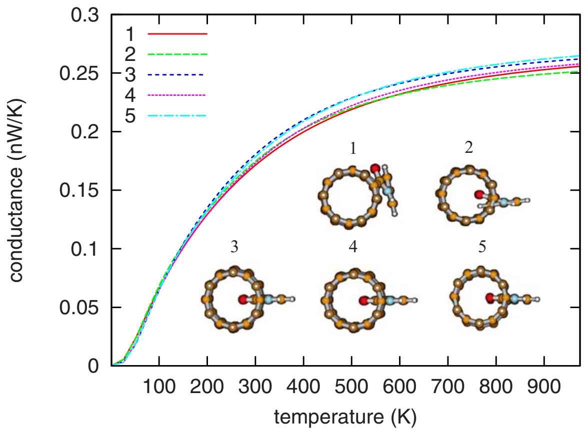

FIG. 1. (Color online) Ballistic thermal conductance of the benzene junction terminated by H atoms at different configurations. 3 is the full relaxed structure. 1–2 are in the compression state, and 4–5 are in the stretching state.

III. NUMERICAL RESULTS AND DISCUSSION

We now present our numerical results. We begin with the simplest case where there is only one benzene ring at the center. We compare the thermal conductance of the molecular junction at different compression or stretching configurations by changing the distance between the two leads. The purpose of this study is twofold. First, we want to study the effect of the compression or stretching on the thermal conductance. Second, our optimization process discussed in Sec. II cannot ensure that we have reached the lowest-energy configuration while keeping the two SWCNTs to be coaxial. This is because we have fixed the position of the outer C and H atoms at both sides. If the thermal conductance is not sensitive to the distance between the two leads, our results make sense even if we do not find the lowest-energy configuration. As we can see in Fig. 1, this is indeed the case. In Fig. 1, from 1 to 5 the distance between the two carbon atoms connecting to the amide groups is 10.07, 10.21, 10.38, 10.51, and 10.64 Å, respectively. The inset shows the atom configuration of the five cases. In the compression states (10.07 and 10.21 Å), the relative position between the benzene ring and the SWCNT leads changes compared to the full relaxed (10.38 Å) and stretching (10.51 and 10.64 Å) states (inset of Fig. 1). Although the atom configurations change a lot, the ballistic thermal conductance of the molecular junction only changes slightly in the entire temperature range studied here. So we can conclude that the ballistic thermal conductance of the molecular junction is not sensitive to small compression or stretching of the molecule.

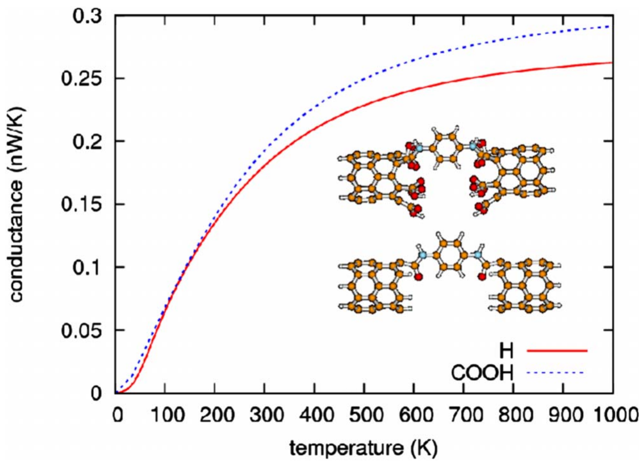

FIG. 2. (Color online) Ballistic thermal conductance of the benzene junctions terminated by H and COOH groups.

In a related experiment,[20] the cutting edge carbon atoms are expected to be saturated by the COOH group and not by the H group as shown in Fig. 1. In Ref. [22], the authors show that the electron transmission is largely affected by the terminating groups. It is also interesting to know how the terminating group affects the quantum thermal conductance. We still use the single benzene structure to study this problem. Figure 2 shows the thermal conductance of the two configurations. The full relaxed structures are shown in the inset. The electrical conductance is mainly determined by the energy channel near the chemical potential, while the thermal conductance is jointly contributed by many phonon modes. The terminating group only has a large influence on the high-energy (short wavelength) optical phonon modes. The low-energy (long wavelength) phonon modes are not sensitive to the local environment at the cutting edges. As a result, the thermal conductance only shows quantitative difference, which becomes larger at high temperatures.

We now compare the conductance of the benzene rings and that of the alkane chains with the SWCNTs terminated by H atoms. We expect that the COOH terminating structures show similar behavior. To ensure that the two molecules have comparable length, we include two benzene rings for the benzene structure and eight CH_2 groups for the alkane chain. The total transmission probability and the thermal conductance are shown in Figs. 3 and 4, respectively. Since the nonlinear interaction is not considered here, phonon modes with different energies are independent of each other. The transmission probability is nonzero only in the overlapped energy range of the SWCNT leads and the center molecule. Strong coupling with the leads gives rise to wide broadening and strong shifting of the discrete molecule phonon energy. It is hard to make a one-to-one correspondence

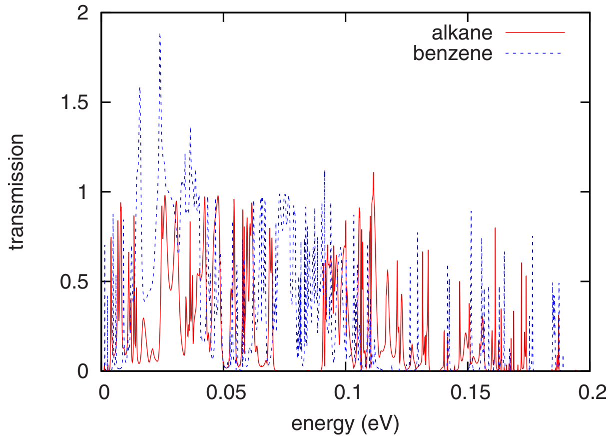

FIG. 3. (Color online) Phonon transmission probability as a function of energy for the benzene and alkane chains.

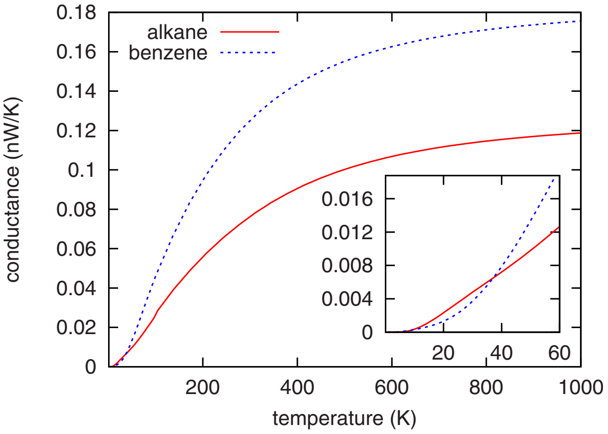

FIG. 4. (Color online) Ballistic thermal conductance as a function of temperature for the benzene and alkane chains. The inset shows the crossing point of the thermal conductance at about 38 K.

between the transmission peaks and the isolated molecule phonon eigenfrequencies. This is especially true for low-energy phonon modes, which have relatively large spatial extent. The high-energy modes are highly localized and show sharp peaks in the transmission spectrum. Due to the highly localized nature and low Bose-Einstein weighting, these modes can hardly transfer energy. There is a wide zero transmission gap around 0.07 eV for the alkane chain, which is a characteristic of the alkane chain phonon spectrum.[6]

To gain further insight into the transmission spectrum, we also study the single-mode transmission using the mode-matching method. Figure 5 shows the transmission of several important branches in SWCNT phonon spectrum: two transverse-acoustic (TA) phonon modes, one longitudinal-acoustic (LA) mode, one twisting mode, and the lowest two degenerate optical modes. These low-frequency modes are expected to contribute much to the thermal conductance. The degenerate phonon modes of SWCNTs show different transmission in both cases. This is consistent with the fact that the junction structure destroys the symmetry in transverse directions. At the energy range below 0.01 eV, the main contribution comes from the TA modes of the SWCNT. The alkane chain shows larger transmission than the benzene chain in this energy range. Above 0.01 eV, the benzene chain shows larger transmission in most cases. The twisting mode shows the largest difference in two structures. While it can hardly be transmitted by the alkane chain, it has a large contribution in the benzene chain.

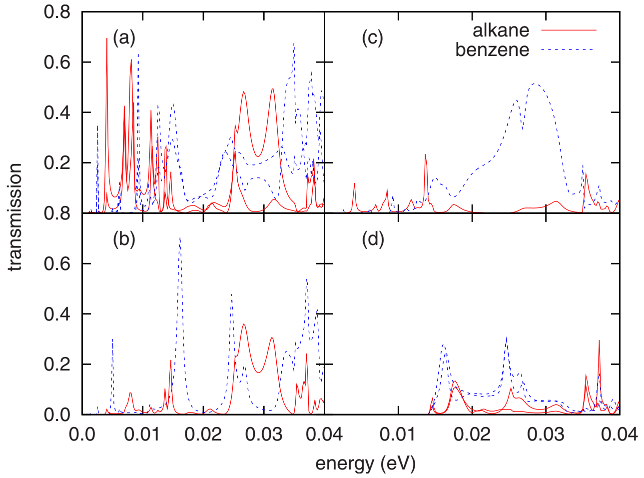

FIG. 5. (Color online) Transmission probability of different phonon branches: (a) TA modes, (b) LA mode, (c) twisting mode, and (d) lowest optical modes.

The thermal conductance of the molecular junction depends not only on the transmission coefficient but also on the phonon occupation number, which is the Bose-Einstein distribution in the Landauer formula. According to the analysis of the transmission spectrum, we may expect that the alkane chain has larger thermal conductance at low temperatures, while at higher temperatures the order reverses. This is confirmed in Fig. 4. The crossing temperature is about 38 K. The room-temperature thermal conductance is about 0.075 nW/K for alkane chains and 0.125 nW/K for benzene chains. This is about 20 times smaller than the ballistic thermal conductance of pure SWCNT (2.034 nW/K). In a recent experiment,[5] the thermal conductance of alkane chain is found to be smaller than our theoretical value. This difference comes from the effect of the leads. We are using SWCNTs here, while in the experiment it is the bulk gold connected with the alkane chain via the sulfur atom. At least two factors from the leads may account for this decrease. The first is the smaller phonon spectrum overlap between gold and alkane chains, and the second is the weaker coupling between them.

Some comments are worthwhile. The nonlinear interaction may change the transmission spectrum and lead to a decrease in the thermal conductance. A perturbative analysis of the single benzene structure shows that the room-temperature thermal conductance drops about 30% of the ballistic value if we include the cubic force constant calculated from GAUSSION03. Mean-field approximation in the NEGF formalism only works well for simple structures with relatively weak nonlinear interaction.[14] It fails to converge in the self-consistent iteration in the present case. So it is still a challenge to find a good approximation for the nonlinear self-energies in the NEGF method.

IV. CONCLUSIONS

In this paper, we introduce a straightforward method to calculate the phononic thermal conductance of molecular junctions in the ballistic regime from first principles. The force-constant matrices are obtained from GAUSSIAN03 quantum chemistry software. The phonon transmission and thermal conductance are calculated using the NEGF or mode-matching method. Further information can be obtained from the transmission spectrum of each single mode. Using this method we show that the ballistic thermal conductance of the benzene ring amide-linked with SWCNTs is not sensitive to the distance between the two SWCNTs. The benzene rings show larger thermal conductance than the alkane chains. This method is general and can be easily applied to other material systems.

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