

# Length dependence of the thermal conductance of alkane-based single-molecule junctions: An *ab initio* study

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Motivated by recent experiments, we present here a systematic *ab initio* study of the length dependence of the thermal conductance of single-molecule junctions. We make use of a combination of density functional theory with nonequilibrium Green's function techniques to investigate the length dependence of the phonon transport in single-alkane chains, contacted with gold electrodes via both thiol and amine anchoring groups. Additionally, we study the effect of the substitution of the hydrogen atoms in the alkane chains by heavier fluorine atoms to form polytetrafluoroethylenes. Our results demonstrate that (i) the room-temperature thermal conductance is fairly length independent for chains with more than 5 methylene units and (ii) the efficiency of the thermal transport is strongly influenced by the strength of the phononic metal-molecule coupling. Our study sheds light on the phonon transport in molecular junctions, and it provides clear guidelines for the design of molecular junctions for thermal management.

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## I. INTRODUCTION

Heat conduction by phonons is a fundamental physical process with great relevance in numerous problems in science and engineering as well as in technological applications [1]. In the context of macroscale systems, phonon conduction is, to some extent, well understood thanks to the use of semiclassical theoretical methods such as the Boltzmann transport equation [2] or molecular-dynamics-based approaches [1], which are often used in combination with *ab initio* techniques for the determination of the phonon spectra and coupling constants. However, with the advent of novel nanoscale systems and devices it has become possible to study phonon conduction in a new regime, where the system size can be smaller than the inelastic mean free path for phonons (due to phonon-phonon interactions) and in some cases even smaller than the corresponding elastic mean free path leading to quasiballistic transport [3–6]. In this new regime, phonon conduction has to be described by purely quantum-mechanical means, which poses a very interesting and challenging problem for the theory.

In this work we are interested in the heat conduction via phonons in single-molecule junctions, which constitute the ultimate limit of miniaturization of electronic devices. These nanojunctions have emerged in recent years as ideal platforms to study the quantum theories that describe both the charge and energy transport in nanoscale devices [7]. In particular, recent experimental advances have made it possible to investigate different aspects of energy and heat conduction in molecular junctions such as thermoelectricity [8–10], Joule heating [11], and thermal conductance [12]. These advances stimulate the development of fully *ab initio* methods, which in turn should elucidate the main aspects and physical mechanisms

of phonon conduction in atomic-scale junctions. In this sense, the goal of this paper is to use an *ab initio* approach, based on a combination of density functional theory (DFT) and non-equilibrium Green's function (NEGF) techniques, to study one of the most fundamental questions in the context of phonon transport in atomic-scale systems, namely, the length dependence of the thermal conductance of a molecular chain.

The theoretical discussion of the thermal conductance of a linear one-dimensional (1D) chain has a long history [13–15]. The general conclusion is that in long ideal chains (of more than 100 identical units) exhibiting nonlinear interactions, momentum conservation, and no disorder, the thermal conductance decays algebraically as  $\kappa_{\text{ph}} \propto L^{\alpha-1}$ , where  $L$  is the chain length and the exponent  $\alpha$  is found to be  $\alpha = 1/3$ . Although these results are of fundamental interest, it is not clear that they are very relevant for actual experiments on nanoscale systems due to the long chain lengths required.

In the context of molecular junctions, the issue of the length dependence of the thermal conductance has already been addressed both experimentally and theoretically. Often, the molecules of choice have been alkane chains [16,17], which are saturated molecules whose electrical properties have been widely studied in the context of molecular electronics [18–31]. From the experimental side, the length dependence of the thermal conductance of alkane-based molecular junctions was investigated by Wang *et al.* [32] making use of alkanedithiol self-assembled monolayers (SAMs) that were sandwiched between Au and GaAs electrodes. It was found that the thermal conductance of junctions with 8, 9, and 10 CH<sub>2</sub> units did not depend significantly on the molecule length. More recently, Meier *et al.* [33] reported thermal conductance measurements of monothiolated alkane monolayers, self-assembled on Au(111) surfaces as a function of their length (ranging from 2 to 18 methylene units). Making use of a scanning thermal microscope with a Si tip, it was found that the thermal conductance first increases for short chains, reaching

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a maximum for 4 units, and then it exhibits an (arguably) slow decay for lengths above 8 units. From the theory side, Segal *et al.* [34] made use of semiempirical methods to predict that the thermal conductance of alkane chains approaches a constant value for more than 15 CH<sub>2</sub> units for a weakly coupled junction, while it decreases inversely proportionally to the length for the strongly coupled case. On the other hand, Duda *et al.* [35], using a diffusive transport model combined with Hartree-Fock calculations of the vibrational modes of alkane chains, suggested that the thermal conductance should be fairly length independent for chains with more than 5 CH<sub>2</sub> units. In the only *ab initio* study of this issue that we are aware of, Sadeghi *et al.* [36] explored the phonon transport in alkane-based single-molecule junctions with 2, 4, 8, and 16 CH<sub>2</sub> units and found a very pronounced decay of the thermal conductance for the longest molecular length. These seemingly contradictory theoretical results call for new inspections of the fundamental issue of the length dependence of the thermal conductance of molecular junctions.

In this work we present a systematic *ab initio* study with no adjustable parameters of the phonon transport in alkane-based single-molecule junctions and also discuss electronic contributions to the heat transport. Making use of a combination of DFT and NEGF techniques, we analyze the thermal conductance of Au-alkane-Au molecular junctions as a function of the length of the alkane chains ranging from 2 to 30 methylene units. Moreover, in order to elucidate the role of the metal-molecule interface, we investigate two different anchoring groups, namely, thiol (SH) and amine (NH<sub>2</sub>). Additionally, we determine the impact of the substitution of the H atoms in the alkane chains by F atoms for both types of anchoring groups. The ensemble of our results shows that the room-temperature phonon thermal conductance of all investigated junctions is fairly length independent for chains with more than 5 CH<sub>2</sub> units. This statement also holds for the total thermal conductance that consists of phononic and electronic contributions since we show that the electronic contribution plays a significant role only for the shortest chain lengths below 4 units. Moreover, we demonstrate that the relative efficiency of the phonon heat conduction is mainly, although not exclusively, dictated by the strength of the metal-molecule phononic coupling. Our results yield novel insights into the heat conduction in molecular wires and provide clear predictions that will surely be possible to test in the near future due to the recent rapid advances in the experimental techniques.

The rest of the paper is organized as follows. First, in Sec. II we briefly describe the theoretical approach employed to obtain the results presented in this work. Then, in Sec. III we describe and analyze the main results of this paper on phonon heat transport. Section IV is devoted to additional discussions of our results such as electronic contributions to the thermal conductance and to the comparison with published experimental and theoretical work. Finally, we present in Sec. V our conclusions.

## II. THEORETICAL APPROACH

Our primary goal is to compute the thermal conductance due to phonon transport in single-molecule junctions. For

this purpose, we make use of the first-principles formalism developed by us and reported in Ref. [37]. Our approach is based on a combination of DFT and NEGF that allows us to compute both the electronic and phononic contributions to all basic linear response transport properties of a nanoscale system. In what follows, we briefly describe the main features of our method and refer the reader to Ref. [37] for further details.

### A. Contact geometries, electronic structure, and vibrational properties

The first step in our modeling is the construction of the molecular junction geometries. We use DFT to compute equilibrium geometries through total energy minimization and to describe their electronic structure. Vibrational properties of the optimized equilibrium contacts are subsequently obtained in the framework of density functional perturbation theory. We use both procedures as implemented in the quantum chemistry software package TURBOMOLE 6.5 [38–40] and employ the Perdew-Burke-Ernzerhof exchange-correlation functional [41,42], the “default2” basis set of split-valence-plus-polarization quality def2-SV(P) [43], and the corresponding Coulomb fitting basis [44]. To make sure that the vibrational properties, i.e., vibrational energies and force constants, are accurately determined, we use very stringent convergence criteria. Thus, total energies are converged to a precision of better than 10<sup>-9</sup> a.u., while geometry optimizations are performed until the change in the maximum norm of the Cartesian gradient is below 10<sup>-5</sup> a.u.

### B. Phonon transport

We compute the phononic contribution to the heat conductance within the framework of the Landauer-Büttiker picture; that is, we ignore inelastic and anharmonic effects that are expected to play a minor role in short molecular junctions. Within this picture, the heat current due to phonons can be expressed as [45–47]

$$J_{\text{ph}}(T_L, T_R) = \frac{1}{h} \int_0^\infty dE E \tau_{\text{ph}}(E) [n(E, T_L) - n(E, T_R)], \quad (1)$$

where  $\tau_{\text{ph}}(E)$  is the phonon transmission,  $n(E, T) = [\exp(E/k_B T) - 1]^{-1}$  is the Bose function describing the phonon occupation in the left (L) or right (R) electrode, and  $T_X$  is the temperature in electrode  $X = \text{L, R}$ . In this work, we focus on the linear response regime in which  $J_{\text{ph}} = -\kappa_{\text{ph}} \Delta T$  is proportional to the temperature difference  $\Delta T = T_L - T_R$  and the phonon thermal conductance is given by

$$\kappa_{\text{ph}}(T) = \frac{1}{h} \int_0^\infty dE E \tau_{\text{ph}}(E) \frac{\partial n(E, T)}{\partial T}. \quad (2)$$

The phonon transmission appearing in the previous equations can be determined with the help of Green’s function techniques [37,46,47]. Briefly, the starting point is the description of the phonons or vibrational modes of the junction within the harmonic approximation. In this approximation, the phonon Hamiltonian for small displacements  $\{Q_\xi\}$  of the atoms around

their equilibrium positions  $\{R_\xi^{(0)}\}$  adopts the following form:

$$\hat{H} = \frac{1}{2} \sum_{\xi} \hat{p}_{\xi}^2 + \frac{1}{2\hbar^2} \sum_{\xi\chi} \hat{q}_{\xi} \hat{q}_{\chi} K_{\xi\chi}, \quad (3)$$

where we have introduced mass-weighted displacement operators  $\hat{q}_{\xi} = \sqrt{M_{\xi}} \hat{Q}_{\xi}$  and mass-scaled momentum operators  $\hat{p}_{\xi} = \hat{P}_{\xi} / \sqrt{M_{\xi}}$  as conjugate variables. These variables obey the following commutation relations:  $[\hat{q}_{\xi}, \hat{p}_{\chi}] = i\hbar\delta_{\xi\chi}$  and  $[\hat{q}_{\xi}, \hat{q}_{\chi}] = [\hat{p}_{\xi}, \hat{p}_{\chi}] = 0$ , where  $\xi = (i, c)$  denotes a Cartesian component  $c = x, y, z$  of atom  $i$  at position  $\vec{R}_i = \vec{R}_i^{(0)} + \vec{Q}_i$ . The phonon system is characterized by its dynamical matrix  $K_{\xi\chi} = \hbar^2 \mathcal{H}_{\xi\chi} / \sqrt{M_{\xi} M_{\chi}}$ , which is the mass-weighted Hessian of the DFT total ground-state energy with respect to the Cartesian atomic coordinates,  $\mathcal{H}_{\xi\chi} = \partial_{\xi\chi}^2 E$ . These harmonic force constants are computed within density functional perturbation theory.

The use of a local displacement basis enables the partitioning of the dynamical matrix into three parts, a central (C) scattering region and the two semi-infinite L and R electrodes, i.e.,

$$\mathbf{K} = \begin{pmatrix} \mathbf{K}_{LL} & \mathbf{K}_{LC} & \mathbf{0} \\ \mathbf{K}_{CL} & \mathbf{K}_{CC} & \mathbf{K}_{CR} \\ \mathbf{0} & \mathbf{K}_{RC} & \mathbf{K}_{RR} \end{pmatrix}. \quad (4)$$

Notice that there is no direct coupling between L and R. The phonon transmission can be expressed as [46,48]

$$\tau_{\text{ph}}(E) = \text{Tr}[\mathbf{D}_{\text{CC}}^{\text{r}}(E) \mathbf{\Lambda}_{\text{L}}(E) \mathbf{D}_{\text{CC}}^{\text{a}}(E) \mathbf{\Lambda}_{\text{R}}(E)], \quad (5)$$

where  $\mathbf{D}_{\text{CC}}^{\text{r,a}}(E)$  are the retarded and advanced phonon Green's functions of the central region that can be computed by solving the following Dyson equation:

$$\mathbf{D}_{\text{CC}}^{\text{r}}(E) = [(E + i\eta)^2 \mathbf{1} - \mathbf{K}_{\text{CC}} - \mathbf{\Pi}_{\text{L}}^{\text{r}}(E) - \mathbf{\Pi}_{\text{R}}^{\text{r}}(E)]^{-1}, \quad (6)$$

with  $\mathbf{D}_{\text{CC}}^{\text{a}}(E) = \mathbf{D}_{\text{CC}}^{\text{r}}(E)^{\dagger}$  and an infinitesimal quantity  $\eta > 0$ . On the other hand, the linewidth-broadening matrices

$$\mathbf{\Lambda}_X(E) = i[\mathbf{\Pi}_X^{\text{r}}(E) - \mathbf{\Pi}_X^{\text{a}}(E)] \quad (7)$$

are related to the corresponding contact self-energies

$$\mathbf{\Pi}_X^{\text{r}}(E) = \mathbf{K}_{\text{CX}} \mathbf{d}_{\text{XX}}^{\text{r}}(E) \mathbf{K}_{\text{XC}}, \quad (8)$$

describing the coupling between the central region C and electrode X. In the expressions  $\mathbf{d}_{\text{XX}}^{\text{r}}(E)$  is the surface Green's function of lead  $X = \text{L, R}$  and  $\mathbf{\Pi}_X^{\text{a}}(E) = \mathbf{\Pi}_X^{\text{r}}(E)^{\dagger}$ .

In analogy with the concept of conduction channels in coherent electron transport [7], it is interesting to decompose the total phonon transmission in terms of individual transmission coefficients of the different phononic scattering eigenfunctions that contribute to the phonon conduction at each energy. The total phonon transmission in Eq. (5) can be rewritten as a sum of independent contributions,

$$\tau_{\text{ph}}(E) = \text{Tr}\{\mathbf{t}_{\text{ph}}(E) \mathbf{t}_{\text{ph}}^{\dagger}(E)\} = \sum_n \tau_{\text{ph},n}(E), \quad (9)$$

where  $\mathbf{t}_{\text{ph}}(E) = \mathbf{\Lambda}_{\text{R}}^{1/2}(E) \mathbf{D}_{\text{CC}}^{\text{r}}(E) \mathbf{\Lambda}_{\text{L}}^{1/2}(E)$  is the phonon transmission matrix and  $\tau_{\text{ph},n}(E)$  are the energy-dependent eigenvalues of  $\mathbf{t}_{\text{ph}} \mathbf{t}_{\text{ph}}^{\dagger}$ .

To conclude this discussion, let us remark that to compute the different parts of the dynamical matrix in Eq. (4) we follow

the strategy of our cluster-based approach for charge quantum transport [49]. In this approach, we first compute the dynamical matrix for an extended central cluster including the molecule and large parts of the leads. Subsequently, we extract from there the matrices  $\mathbf{K}_{\text{CC}}$ ,  $\mathbf{K}_{\text{XC}}$ . On the other hand, the surface Green's functions of the electrodes  $\mathbf{d}_{\text{XX}}^{\text{r}}(E)$  are obtained by extracting bulk force constants from a separate calculation of a big cluster of several hundred atoms and then using these extracted parameters in combination with a decimation technique to describe the surface of a semi-infinite perfect crystal (see Ref. [37] for details). In this way, we achieve a consistent, parameter-free *ab initio* description of the phonon system in nanoscale devices.

### C. Electronic transport

For completeness, in this work we also investigate the electronic contribution to the thermal conductance. In this way we can assess the relative importance of electrons and phonons in the studied molecular junctions. Like in the phononic case, we assume that the electronic transport is dominated by elastic tunneling processes. Under these circumstances the electronic contribution to the thermal conductance in the linear response regime can be computed within the Landauer-Büttiker formalism. It is given by [7,50]

$$\kappa_{\text{el}}(T) = \frac{2}{hT} \left( K_2(T) - \frac{K_1(T)^2}{K_0(T)} \right), \quad (10)$$

where the  $K_n(T)$  coefficients are defined as

$$K_n(T) = \int_{-\infty}^{\infty} dE \tau_{\text{el}}(E) \left( -\frac{\partial f(E)}{\partial E} \right) (E - \mu)^n, \quad (11)$$

$\tau_{\text{el}}(E)$  is the energy-dependent electron transmission, and  $f(E, \mu, T) = \{\exp[(E - \mu)/k_B T] + 1\}^{-1}$  is the Fermi function. Here, the chemical potential  $\mu \approx E_F$  is approximately given by the Fermi energy  $E_F$  of the Au electrodes.

We have computed the electron transmission making use of our DFT-NEGF formalism implemented in TURBOMOLE and explained in detail in Ref. [49]. It is worth stressing that in order to correct for the known inaccuracies in DFT related to quasiparticle energies, we have made use of the DFT+ $\Sigma$  approach [51], which was implemented in our method as explained in Ref. [52].

## III. RESULTS

To investigate the length dependence of the thermal conductance of single-molecule junctions, we study alkane chains of different lengths with an even number  $n$  of methylene ( $\text{CH}_2$ ) units ranging between 2 and 30. These saturated molecules are electrically rather insulating, which ensures that the thermal transport is dominated by phonons (see below). To elucidate the role of the anchoring or terminal group in the length dependence of the phonon transport, we analyze two standard groups in molecular electronics, namely, thiol and amine groups. Moreover, we study the impact of the substitution of the H atoms in the alkane chains by heavier F atoms to investigate polytetrafluoroethylenes (PTFEs) with both thiol and amine groups. Thus, in an attempt to draw

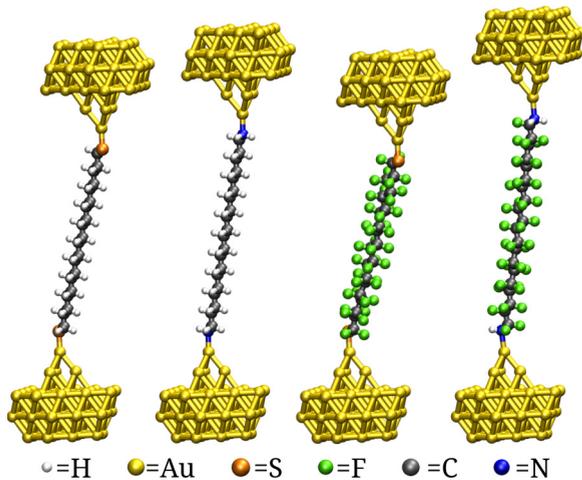


FIG. 1. Examples of the four types of molecular junctions studied in this work. The four molecules have the structure  $X - (CY_2)_n - X$ , where the terminal or anchoring group  $X$  is either S or  $NH_2$ , while the  $Y$  atom in the repeated unit is either H or F. The integer number  $n$  denotes the number of  $CY_2$  segments in the molecules. In all cases, the electrodes are made of gold, and the contact geometries are such that molecules are bonded to the electrodes in an atop position via the anchoring groups.

general conclusions, we investigate four different families of molecules attached in all cases to gold electrodes.

In what follows, we shall focus on the binding geometries illustrated in Fig. 1, where the molecules are bonded to the electrodes in an atop position via the corresponding anchoring group. Let us stress that in all cases the molecular junctions were carefully optimized to find the minimum energy configuration. Moreover, in order to establish a meaningful comparison between the different compounds, special care was taken to avoid both strain effects and the appearance of defects in the molecular chains. In this sense, the alkane chains remain linear in our case, while the introduction of F atoms causes the carbon atoms to deviate from this linear structure, leading to more disordered PTFE chains. Independent of this, the distance between the carbon atoms stays nearly constant in all chains with a value of around 1.5 Å.

We summarize in Fig. 2 the main result of this work, namely, the room-temperature phononic thermal conductance for the four types of molecular junctions as a function of the number of  $CY_2$  segments ( $Y = H, F$ ) ranging from 2 to 30, which corresponds to a maximum length of around 4.5 nm. The first thing to mention is that the conductance values range from 15 to 45 pW/K. Second, for chains with more than five segments the conductance exhibits small variations, but it is basically length independent, irrespective of the molecular family. Third, the molecules with amine anchoring groups typically exhibit a lower conductance than the corresponding dithiolated ones. This is particularly evident in the case of the PTFE-diamine molecules, which exhibit thermal conductances that are about a factor of 2 smaller than those of the other families. Overall, these results show that the phononic thermal conductance of alkane-based single-molecule junctions is rather insensitive to the molecular length for up to 30 segments, which is a signature of ballistic phonon transport.

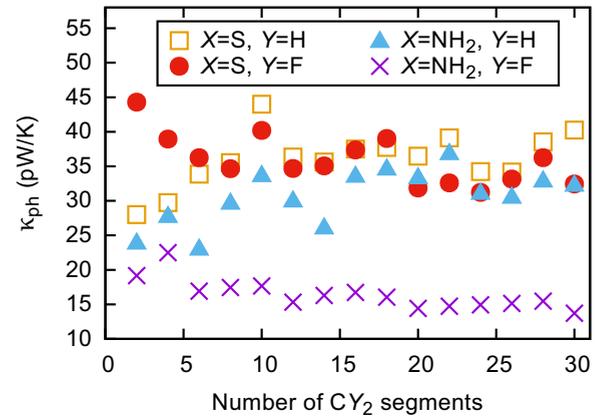


FIG. 2. Room-temperature ( $T = 300$  K) phonon thermal conductance as a function of the number of  $CY_2$  units ( $Y = H, F$ ) in the molecule for both anchoring groups, thiol and amine. The distance between neighboring C atoms in the chains of around 1.5 Å allows us to translate the number of units to a corresponding distance.

To understand these results, let us first analyze the energy dependence of the phonon transmission. An example for the four types of molecules with  $n = 10$   $CY_2$  segments is shown in Fig. 3. First of all, notice that the transmission is different from zero only in an energy region between 0 and 20 meV, which is determined by the phonon density of states of the gold electrodes (see Ref. [37]). Second, the most obvious feature in these results is the fact that for the molecules with the amine group the transmission spectra exhibit narrower peaks, which explains the lower conductance obtained for these molecules. (This is particularly well pronounced for the PTFE-diamine ones.) This strongly suggests that the phononic metal-molecule coupling for the amine group is weaker than for thiol. On the other hand, although the fluorinated molecules are expected to exhibit more vibrational modes in the transport window than the alkane chains due to the larger mass of the F atoms, one does not observe significant differences.

To further clarify how the elastic phonon transport takes place, we show in Fig. 4 the largest individual phonon transmission coefficients for molecular junctions with alkanedithiols

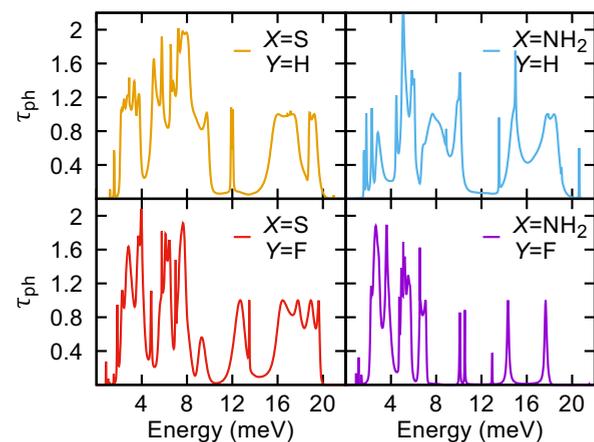


FIG. 3. Phonon transmission as a function of energy for junctions containing molecules with 10  $CY_2$  units.

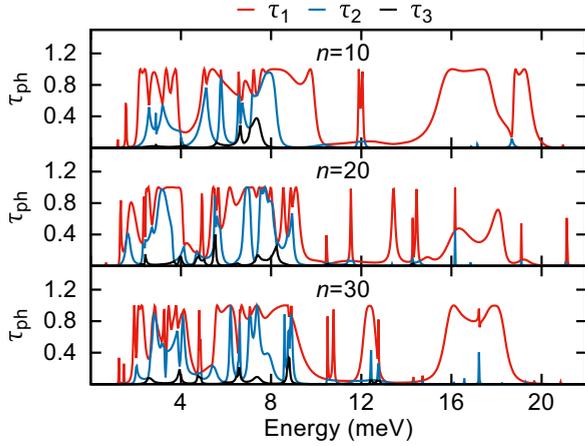


FIG. 4. Individual phonon transmission coefficients as a function of the energy for three alkanedithiols with different lengths (10, 20, and 30 methylene units). We show the coefficients of the three most transmissive channels.

of three different lengths ( $n = 10, 20,$  and  $30$  methylene units). The first thing to notice is that the total transmission is dominated by a single or two phonon channels, with a third one giving only a small contribution. The number of channels is controlled in this case by the rather linear molecules, and the three channels correspond to the three polarizations of the vibrational modes. It is important to realize that this number of channels cannot be altered by the number of vibrational modes in the molecular chains, which determine only the actual values of the transmission coefficients. More important for our discussion of the length dependence is the fact that the dominant channel is fully open (transmission equal to 1) over a wide range of energies, irrespective of the length of the molecule. This is indeed the true signature of ballistic phonon transport, which is realized here with alkane and alkane-related molecular chains.

To gain further insight into our *ab initio* results, we have developed a simple 1D model that is schematically represented in Fig. 5(a). In the following we will use the notation  $k_{ij}$  for elements of the dynamical matrix coupling atoms  $i$  and  $j$  in the toy model, compared to  $\mathbf{K}_{ij}$  in the full *ab initio* results. In the model we consider only nearest-neighbor couplings between segments in the molecular chain  $k_{CC}$ , and the leads are modeled as 1D Au chains with an analogous nearest-neighbor coupling  $k_{AuAu}$ . Finally, the metal-molecule coupling is described by a single constant,  $k_{AuC} = k_{AuX} \sqrt{M_X/M_C}$ , with  $X = S, N$ . We extracted these parameters from the DFT calculations as the highest eigenvalue of  $\mathbf{K}_{ij}$  [see Eq. (4)]. These parameters depend on the molecular species but not on the molecular length, and we summarize their values in Table I.

Using these parameters, we computed the corresponding thermal conductance with the Green's function method described in Sec. II, and the results are displayed in Fig. 5(b). As we can see, this simple model is able to reproduce all the salient features of our *ab initio* results in Fig. 2. In particular, it nicely reproduces the fact that the amine-terminated molecules exhibit a lower thermal conductance, which is especially evident in the case of the PTFE-diamine chains. Now we can confirm that this lower thermal conductance is due to a weaker

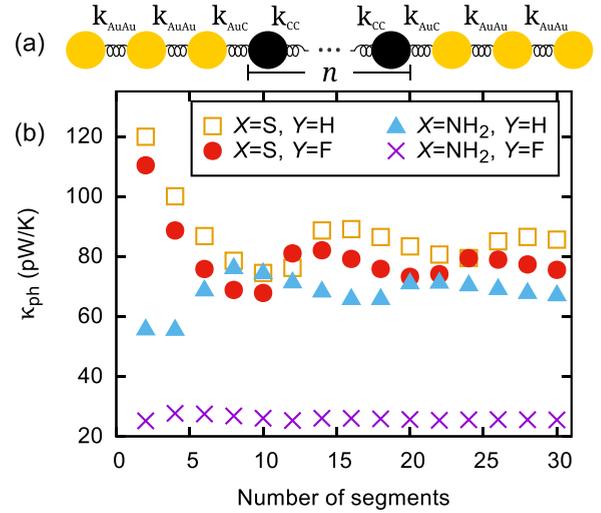


FIG. 5. (a) Schematic representation of the 1D model used to understand our findings. The meaning of the different parameters is explained in the text. (b) Results obtained with the 1D model for the room-temperature phonon thermal conductance as a function of the number of  $CY_2$  units ( $Y = H, F$ ) in the molecule for both anchoring groups, thiol and amine.

coupling to the leads (see values of  $k_{AuX}$  in Table I). The strongly reduced coupling for PTFE-diamine chains compared to their alkane-diamine counterparts results in practice from the larger distance (about  $0.15 \text{ \AA}$ ) between the Au electrodes and the N atoms in these molecular junctions. Let us also mention that we attribute the higher conductance values obtained with the 1D model compared to those from the *ab initio* results to the fact that we extract the parameters  $k_{ij}$  from the largest eigenvalues of the dynamical submatrices  $\mathbf{K}_{ij}$ .

#### IV. FURTHER DISCUSSION

So far we have focused on the phononic contribution to the thermal conductance, and we may wonder whether the electrons play any role. Alkanes are known to be poor electrical conductors [18–31]. Thus, on the basis of the Wiedemann-Franz law [7,37], one therefore does not expect the electrons to give a significant contribution to the thermal conductance. To check this, we have studied the electronic contribution to the thermal conductance  $\kappa_{el}$  in all of our molecular junctions using the *ab initio* methodology briefly described in Sec. II C. Using  $T = 300 \text{ K}$ , we show in Fig. 6 the results for the ratio between the electronic and phononic

TABLE I. Parameters for the 1D model schematically represented in Fig. 5(a). All elements  $k_{ij}$  of the dynamical matrix are given in units of  $\text{meV}^2$ . Notice that the same value of  $k_{AuAu}$  was used in all cases.

$X$	$Y$	$k_{AuX}$	$k_{CC}$	$k_{AuAu}$
S	H	485	6150	100
S	F	426	4850	100
N	H	218	6150	100
N	F	55	4850	100

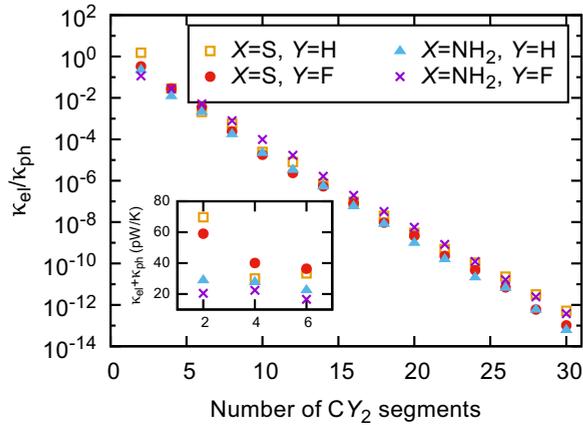


FIG. 6. Ratio of the electronic ( $\kappa_{el}$ ) and phononic ( $\kappa_{ph}$ ) room-temperature thermal conductance as a function of the molecular length for the four different types of molecules studied in this work. In the inset the thermal conductance due to both electronic and phononic contributions is displayed for short chain lengths.

thermal conductances as a function of the molecular length for the four families of molecules investigated here. As one can see, when molecular chains have more than four segments, the electronic contribution is negligible. Notice that the exponential decay of the conductance ratio is a simple consequence of the exponential decay of the electrical conductance with length in the off-resonant transport situation. It follows from the proportionality of  $\kappa_{el}$  and the electrical conductance and a rather length-independent  $\kappa_{ph}$ .

In the previous section we discussed the results for the thermal conductance at room temperature. For completeness, we now briefly address the issue of the temperature dependence of the phonon transport. Figure 7 displays the temperature dependence from 0 to 300 K of the phonon thermal conductance for junctions with the four molecular species and featuring  $n = 10$   $CY_2$  segments. This temperature dependence is relatively insensitive to the molecular length, and thus, the results of Fig. 7 are representative of the four molecular species studied in this work. As one can see, the thermal conductance

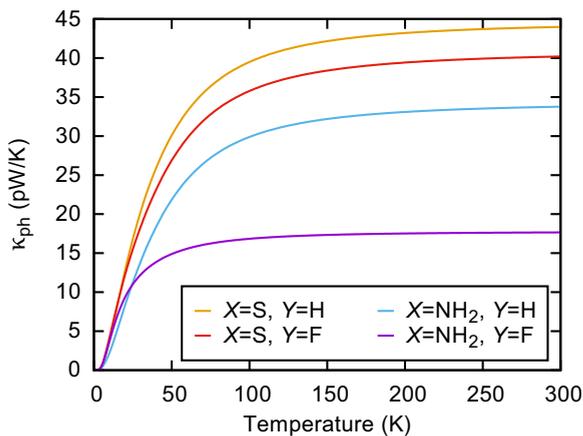


FIG. 7. Phonon thermal conductance as a function of the temperature for junctions containing molecules with 10  $CY_2$  units.

raises abruptly at low temperatures; it tends to saturate, depending on the molecule, above approximately 100 to 200 K, and around room temperature it is fairly constant. This overall behavior simply reflects the fact that for temperatures above the Debye temperature of gold, all the phonons of the metal electrodes as well as the vibrational modes of the molecule with energies within the transport window are thermally occupied, while below this temperature the higher-lying modes are only partially occupied and the thermal conductance hence becomes sensitive to the temperature.

Let us now discuss the comparison with existent results. From the theory side our results, showing a thermal conductance relatively insensitive to the molecular length, are qualitatively compatible with the findings of Segal *et al.* [34] for weakly coupled alkane chains. This is also the case for the results of Duda *et al.* [35]. Our results are also in agreement with the molecular dynamics calculations performed by Luo and Lloyd [53], who studied octanedithiol SAMs sandwiched between gold electrodes and estimated a thermal conductance per molecule of 43 pW/K. However, our results are clearly at variance with the strong decay for the longest molecule reported by Sadeghi *et al.* [36], which indeed is the only *ab initio* study published to date on the length dependence of the thermal conductance of alkane single-molecule junctions. The reason for the discrepancy is unclear to us, but it is worth pointing out that those authors analyzed only a very limited number of molecules (with 2, 4, 8, and 16 methylene units), and they used a different anchoring group (hydrobenzothiophene).

With respect to existent experiments on the length dependence, we cannot establish a direct comparison, but our length independence is compatible with the experiments of Wang *et al.* [32] in junctions based on alkanedithiol SAMs sandwiched between Au and GaAs electrodes. On the other hand, the experiments of Meier *et al.* [33], which represent the most systematic study of the length dependence of the thermal conductance of alkane junctions to date, exhibit some basic differences with the junctions studied in this work. First, the tip electrode was made of Si. Second, the alkanes were monothiolated. Third, the temperature difference used in the experiment was between 200 °C and 300 °C, which is most likely beyond the linear response regime addressed in our work. Finally, in this experiment the number of contacted molecules is not directly determined, and it is inferred only with the help of tip models. Having said all that, let us mention that the estimated conductance values per molecule lie in the range of our calculated values, and a careful inspection of the experimental data shows that the conductance is indeed fairly independent of the molecular length for chains with more than 8 methylene units. Anyway, a rigorous comparison with experiment to settle the issue of the length dependence of the thermal conductance requires true single-molecule experimental techniques, and our results provide clear predictions that we hope will be tested experimentally in the near future.

Related to the role of the anchoring group, let us mention that Losego *et al.* [54] investigated experimentally with the time-domain thermoreflectance technique its impact on heat transport in SAMs of alkanes contacted to quartz and gold films. They observed that the replacement of amines as the binding group to the Au film by thiols led to a 60% increase of the thermal conductance per unit area for chains with 11

methylene units. This is consistent with the general trend found here in the sense that the amine-terminated molecules exhibit in general a lower thermal conductance than their thiolated counterparts.

Let us conclude this section by stressing that in spite of the fact that we are using an approach where anharmonic effects are not taken into account, the finding of a length-independent thermal conductance, as reported here, is by no means trivial. The intrinsic disorder in the molecular chains, which is present, e.g., in the PTFE chains, can, in principle, lead to a diffusive transport regime, where the conductance decays linearly with length, or ultimately to an Anderson-localized regime, where the conductance is exponentially suppressed with length. In our study we see that for chains of up to 30 segments (with a length of up to 4.5 nm) the conductance exhibits a weak length dependence, indicating that the elastic mean free path is larger than the system size. It would be interesting to study the limits of this quasiballistic transport, and we hope to address this issue in the near future. Let us also emphasize that Segal *et al.* [34] showed that anharmonicity in the alkane chains is rather weak, and it is not expected to play a crucial role in the range of lengths studied in this work. Therefore, our approach is well justified.

## V. CONCLUSIONS

In summary, we have presented a systematic *ab initio* study of the length dependence of the thermal transport through alkane-based single-molecule junctions. In particular, we have investigated the role of the anchoring group in this length dependence, and we have compared the results for alkane chains with those for PTFE chains, which are obtained from the alkanes by substituting the H atoms by F atoms. By investigating the phonon transport for chains with up to 30

segments, we find that the phonon thermal conductance is rather insensitive to the molecular length, irrespective of the molecule. These results strongly suggest that the phonon transport in these molecular wires is quasiballistic. On the other hand, our analysis of the role of the anchoring group shows that these groups ultimately determine the efficiency of the phonon transport, and in particular, we find that the thiol group leads to higher conductance values than the amine group. Electronic contributions to the thermal conductance do not modify these conclusions since we demonstrate that they are negligible for alkanes with four or more segments. Overall, our results provide clear predictions that we hope will be tested experimentally in the near future given the rapid advances in the field of nanothermometry. Moreover, our work sheds light on the thermal transport mechanisms in molecular wires and provides clear guidelines for the design of molecular junctions for thermal management.

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