Effects of molecular length and carbon parity on iets of alkanethiols

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Abstract: First-principles calculations were employed to investigate the inelastic electronic tunneling spectra of thiol molecule clusters in a series of alkanes. The results demonstrate that the inelastic electron tunneling spectrum is highly sensitive to parity changes in the number of carbon atoms within the molecular junction.Theoretical analysis indicates that the CH_2 symmetric stretching vibration mode originates from the methylene group at the sulfur end; when the number of carbon atoms is even, this vibration mode is stronger, primarily because, in this case, the $C-H$ bond of the group is perpendicular to the electrode surface, and its coupling with the gold electrode is significantly stronger than when the number of carbon atoms is odd.These results explain the origin of the symmetric stretching vibration of the CH_2 group in alkanes and validate the orientation bias observed in inelastic electron tunneling spectroscopy.

Keywords: molecular electronics, inelastic electron tunneling spectroscopy, hybrid density functional theory, molecular devices

1. Introduction

1.1. Background for molecular device research

As semiconductor device manufacturing processes have advanced, silicon-based electronic devices have become increasingly smaller; however, due to the limitations imposed by photolithography technology and the physical effects within semiconductors, device dimensions cannot be reduced indefinitely, and Moore's Law is approaching its end. Consequently, the discovery and development of a new generation of electronic devices has become imperative.Against this backdrop, organic molecular devices have emerged as a viable alternative to silicon-based semiconductor devices, owing to their advantages of small size, low power consumption, and high speed.Since Richard Feynman proposed the concept of molecular devices, researchers have not only employed self-assembled molecular films (Self-Assembled Monolayers, SAMs), LB (Langmuir–Blodgett) techniques combined with scanning tunneling microscopy (Scanning Tunneling Microscope, STM), and other methods to prepare and characterize molecular devices, but have also developed and applied various theoretical approaches to analyze the operating principles of these devices, achieving significant progress [1-2].However, because molecular devices are extremely small in size, some researchers have questioned whether stable molecular junctions truly exist. They argue that it is impossible to confirm whether current is transported through the organic molecules; instead, it may be transmitted directly through the two electrodes of the molecular junction—that is, what we macroscopically refer to as a "short circuit."Consequently, determining the internal structure has become a major bottleneck in the development of molecular devices.[3]

1.2. Principles of non-elastic electron tunneling spectroscopy

The advent of inelastic electron tunneling spectroscopy (IETS) technology has resolved this constraint [4-10]. The tunnel effect in quantum mechanics demonstrates that electrons can penetrate the potential barrier of a molecular junction and undergo tunneling; there are two mechanisms for tunneling: if a tunneling electron passes through the tunnel junction without energy loss, this is elastic tunneling; if the

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tunneling electron undergoes an inelastic collision with an organic molecule within the molecular junction and loses energy, this is inelastic tunneling. In the latter case, the energy lost by the tunneling electron excites vibrational modes on the surface of the organic molecule; one surface vibrational mode of the molecular junction corresponds to a spectral peak in the inelastic electron tunneling spectrum.Due to the high sensitivity of inelastic electron tunneling spectroscopy to the structure of molecular devices, the measured spectral results not only confirm the existence of stable molecular junctions within these devices but also enable the determination of their microscopic structure.

1.3. Research motivation of this paper

In recent years, significant breakthrough progress has been made in the study of the structure and transport properties of molecular devices through the use of inelastic electron tunneling.Recently, JEONG et al. employed scanning tunneling microscopy (STM) to investigate the inelastic electron tunneling spectra of dodecanethiol molecules [11].The study results indicate that the peak located near 360 mV does not always appear clearly,In light of previous reports, we have found that this peak is sometimes clearly observable [12] and at other times undetectable; accordingly, we designed a series of molecular junctions and primarily investigated the effects of chain length and the parity of the number of carbon atoms on the vibrational modes and intensities of thiol molecular junctions in chain hydrocarbons.

2. Calculation details

A series of alkanethiol molecules (propanethiol to decanethiol, denoted as M1–M6) were taken as research objects. Considering the locality of interatomic interactions, a metal cluster composed of a finite number of metal atoms was selected to simulate the interaction between bulk metal electrodes and organic molecules.Therefore, a Au(111) surface composed of 12 gold atoms was selected as the electrode and connected to both ends of the molecule, respectively.,The S atom and the C atom of the methyl group at the other end each occupy a vacant site on the gold electrode, while the gold electrodes at both ends are parallel to each other,The S − Au bond length is 2.853 Å, and the carbon atom at the methyl terminus is 3.51 Å from the gold surface.Given the orientation bias inherent in nonelastic electron tunneling spectra, the relationship between the intensity of the CH_2 stretching vibrational mode near 360 mV and molecular orientation was investigated while keeping the position of the terminal methyl carbon atom and that of the gold electrode fixed.For M1, M3, and M5 molecules with an odd number of carbon atoms, the angle between the S − C bond and the Au electrode surface is approximately 72°,For M_2, M_4, and M_6 molecules with an even number of carbon atoms, the S − C bond makes an inclination of approximately 5.6° with the substrate, while the angle between the C − H bond and the substrate is denoted by α, as shown in Figure 1.

The geometric structures of a series of extended molecules were optimized using the Gaussian09 software package, followed by calculations of the electronic structure. Using LanL2DZ [13] as the basis set, hybrid density functional theory (B3LYP) [14] was employed for the calculations. IETS calculations were performed using the QCME1.1 software package [15].

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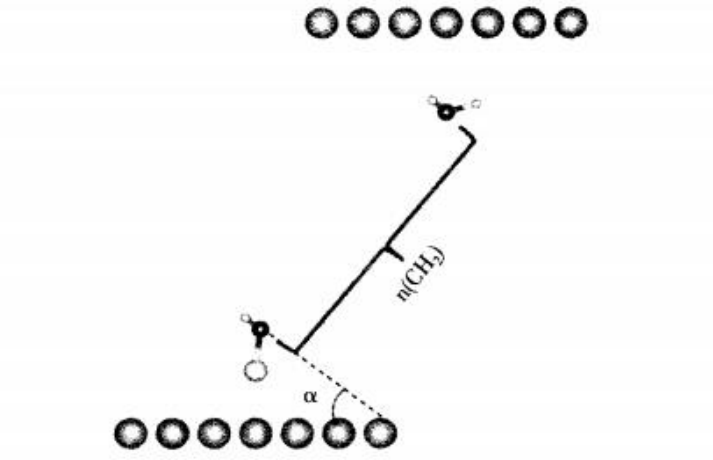

Figure 1 Schematic diagram of alkane thiol molecular association (n = 1, 2, 3, 4, 5, 6)

3. Results and analysis

3.1. Overall characteristics of the IETS spectra of alkane thiol molecules

The theoretically calculated inelastic electronic tunneling spectra for six alkane thiol molecules are shown in Figure 2. For ease of comparison, M1, M3, and M5 are shown on the left, while M2, M4, and M6 are shown on the right.In the inelastic electron tunneling spectrum, the peaks within 0.05 V correspond to the vibrational modes of the metal atoms in the electrodes; this section primarily discusses the influence of the length of the hydrocarbon chain and the parity of the number of carbon atoms on the inelastic electron tunneling spectrum of organic molecules in molecular devices. Consequently, the calculations associated with this aspect have been omitted from the results.

As can be readily seen from Figure 2, there is a marked difference between the inelastic electron tunneling spectra of systems with an even and an odd number of carbon atoms; however, there is considerable similarity among M1, M3, and M5, as well as among M2, M4, and M6.In both sets of figures, the vibrational modes that contribute significantly to inelastic tunneling are the three vibrational modes of the methylene group: CH_2 out-of-plane oscillation ($W(CH_2)$) , CH_2 symmetric deformation($\delta_8(CH_2)$)andCH_2symmetric stretching($\nu_8(CH_2)$)mode,the positions of the vibration peaks are shown in Table 1.In addition, contributions from the $S-C$ stretching vibration ($\nu(S-C)$) and the CH_2 twisting vibration (t(CH_2)) modes also exist.In the inelastic electronic tunneling spectra of M1, M3, and M5, a $C-C-C$ bending vibration ($\delta_8(C-C-C)$) appears at approximately 59 mV; this differs significantly from the behavior observed in M2, M4, and M6.The relative intensity of vibrations also varies considerably: when the number of carbon atoms is odd, the contributions of the ($\delta_8(CH_2)$) and w(CH_2) vibration modes are relatively large; when the number is even, the strongest vibration mode is the symmetric stretching vibration of the methylene group CH_2 near 360 mV. For different molecules, each vibration mode also exhibits a slight blue shift or red shift.

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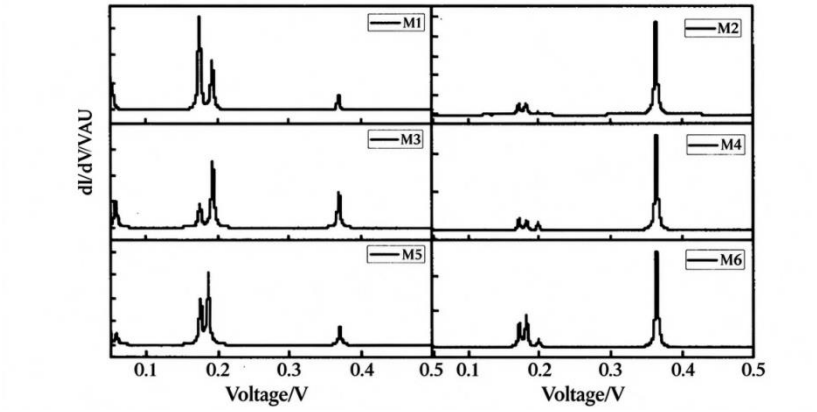

Figure 2 Inelastic electron tunneling spectra of the various molecules

Table 1 Primary vibrational modes and spectral peak positions of CH_2

Position of vibrational peaks (mV)						
M1	M2	M3	M4	M5	M6	Vibrational modes
171.8	171.5	174.7	171.6	174.1	171.6	$W(CH_2)$
174.9	181.3	175.4	181.5	174.8	181.3	$\delta_8(CH_2)$
369.1	364.5	369.1	364.4	369.9	364.4	$\nu_8(CH_2)$

3.2. Peak assignment and vibration orientation effects

In inelastic electron tunneling spectra, different vibrational modes correspond to distinct inelastic electron tunneling channels; whether these inelastic tunneling channels can be activated is closely related to factors such as the coupling energy between the various atoms (or functional groups) in the molecule and the metal electrode, as well as the angle between the molecule (or its constituent atoms or functional groups) and the electrode.By identifying the corresponding spectral peaks, it can be determined that the $\nu(CH_2)$ vibration near 360 mV is primarily contributed by the methylene group adjacent to the S atom and is virtually unrelated to the methylene groups within the molecule; this result is entirely consistent with the findings reported in reference [12].Given the orientation bias of the inelastic electron tunneling spectrum, we investigated the angle α between the $C-H$ bond and the substrate electrode under both odd and even conditions.For an odd number of carbon atoms, the angle α between the $C-H$ bond and the gold substrate is approximately 23°; therefore, for an even number of carbon atoms, as the angle between the $S-C$ bond and the substrate changes, the angle α between the $C-H$ bond and the gold electrode correspondingly becomes 89.4º, approaching perpendicularity to the gold surface. Consequently, the $\nu_8(CH_2)$ vibrational intensity of the latter is far greater than that of the former.

3.3. Molecular–electrode coupling energy analysis

The magnitude of the coupling energy between the C atom of the methylene group near the S atom in the thiol molecules of various alkanes, as theoretically calculated, when it replaces that group, and the substrate electrode (Drop electrode). As shown in Figure 3, this explains why, for even-numbered carbon atoms, $\nu_8(CH_2)$near 360 mV dominates the entire inelastic electron tunneling spectrum. For M1, M3, and M5, the values of this coupling energy are approximately equal, at about 0.3 eV; for the M2, M4, and M6 molecules, the values are all approximately 2.3 eV. This explains why, when all are odd or all are even, the shapes of the spectral lines differ little from one another. Clearly, the coupling energy values for M2, M4, and M6 are far greater than those for M1, M3, and M5; at the same time, the distance between the CH_2 group and the substrate electrode is also far smaller than that of the former. Consequently, the strongest vibrational mode of the former is $\nu_8(CH_2)$.

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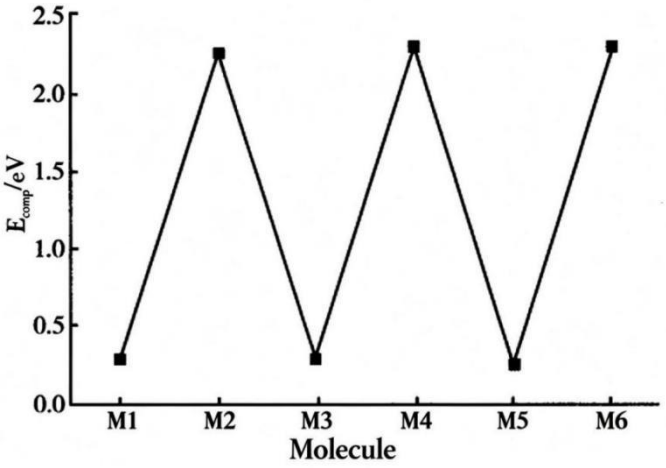

Figure 3 Coupling energy between terminal carbons of molecules and gold substrate

4. Conclusion

A series of alkane thiol molecules (from propyl thiol to decyl thiol) was selected as the subject of study to investigate the influence of molecular length and the parity of the number of carbon atoms on the inelastic electron tunneling spectra of organic molecules. The computational results indicate that the parity of the number of carbon atoms has a significant effect on the inelastic electron tunneling spectra, whereas, when the number of carbon atoms is likewise even (or odd), molecular length has essentially no effect on the shape of the spectral lines.Under these conditions, the dominant vibrational mode is the symmetric stretching vibration of the methylene group CH_2 near 360 mV; this vibration originates from the methylene group adjacent to the sulfur atom and is unrelated to the other $C-H$ bonds.Theoretical analysis indicates that this is primarily because, in even-numbered cases, the $C-H$ bond of this group is nearly perpendicular to the electrode surface; under these conditions, the coupling energy between the carbon atom of the group and the metal electrode is relatively large.These results confirm the origin of the symmetric stretching vibration of the CH_2 group in alkane molecules and the anisotropy observed in nonelastic electron tunneling spectra.

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