Abstract

Molecular dynamics simulations using ab initio force fields and signal processing techniques are combined to analyze the dynamic properties of a minimum unit of a field programmable random molecular array also called nanocell. We analyze stretching, angular, and torsional internal modes at several temperatures of operation and their correlations as well as the possibility of signal modulation and processing at terahertz frequencies. The proposed scenario is another alternative for molecular electronics, which is being developed at very low frequencies of operation using the electronic states of molecules, clusters and other nanoscopic systems.

1. Introduction

The use of small molecules to complement silicon-based electronic devices is under intensive development [1-7]; each molecule occupies an area between $10^5$ to $10^6$ [2, 5] times smaller than conventional electronic devices
however addressability during the construction and operation is a challenge. Both self-assembling [5, 8] and direct assembling [9] have been proposed for the construction and they depend on the chemical affinity of terminal groups attached to the “electrically active” part of the molecule. Due to the non-deterministic characteristics of these processes, molecules are expected to be arranged in quasi-random configurations, which together with their small molecular size, make them no directly addressable. The conversion, reconfiguration, or reprogramming during operation of a randomly constructed circuit relies on the use molecules with highly nonlinear features that allow the system to have alternative states externally settable after construction to perform a specific function [1, 10-12].

In this work, we study one of the possible minimum programmable structures, a square consisting of four active molecules interconnected by four Au clusters. This arrangement is one of the two most likely allowed to take place when self-assembling on a substrate (the other being a triangle) [12]. We focus this study on the thermal stability of the system and the correlation among vibrations in the molecules. Ab initio calculations, molecular dynamics simulations, and signal processing techniques are combined for this aim. MD simulations provide time dependent information of the system, and signal processing techniques are used for the analysis of the time-domain signal in order to show the strong correlations among the dynamics of internal degrees of freedom and to suggest a new scenario for the use of molecular arrangements as signal processing devices.

2. Procedure and Methods

This study focuses on a molecular unit consisting of four Au405 clusters interconnecting four active molecular devices (Figure 1). The Au clusters are roughly spherical with diameter of ~2.3 nm. The molecule, 2,5-dinitro-1,4-diethynylphenylthiolate-benzene, dinitro hereafter, is a phenyl-based oligomer known to perform negative differential resistance NDR, a very important feature for molecular electronics applications [13-15]. We combine molecular dynamics simulations, able to simulate time evolution of the system at different temperatures, with digital signal processing techniques, able to analyze the time-domain signals obtained by the MD simulations.

The initial geometry of the system is obtained minimizing the energy of the whole structure using the fast minimizer tool [16] from the Cerius² [17] suit of programs. The MD runs solve Newton’s equations simultaneously for all atoms in the system using the leap frog algorithm [18] as implemented in Cerius² [17]. We use the universal force field (UFF) [19], which is
parameterized for all the elements in the periodic table and validated using experimental data for organic molecules [20], main-group compounds [21], and metal complexes [22]. UFF uses combination rules based on elements, hybridization, and connectivity to determine interaction parameters from a set of parameters characterizing each atom type. In this work, modifications are performed for Au-Au and Au-S interactions with respect to those in the UFF [19, 23]. We chose a 12-10 potential

\[ V(r) = D_o \left\{ S \left( \frac{x_{ij}}{x} \right)^{12} - 6 \left( \frac{x_{ij}}{x} \right)^{10} \right\} \]

with \( x_{Au-Au} = 2.884 \) Å and \( x_{S-Au} = 2.350 \) Å. For a more general description of the UFF, the reader is referred to the original work of Rappé [19], and to the compilation and implementation done by Senn [23].

The Au-Au interaction with a 12-10 potential, which is an approximation from a more realistic Sutton-Chen many-body potential [24, 25]. The equilibrium distance Au-Au is set to 2.884, which corresponds to the Au-Au distance between nearest neighbors in an fcc Au lattice,[26] and it is within the equilibrium geometries of 2.6 and 3.0 Å, depending of the size and shape of the cluster obtained from ab initio calculations [27]. The interaction energy \( D_o \) of 14.7 kcal/mol is obtained from the experimental cohesive energy of 87.5 kcal/mol [26], which accounts for 12 bonds per atom, but each bond involves two atoms; thus, the interaction energy is six times smaller than the cohesive energy per atom.

The S-Au is also chosen to be a 12-10 potential in order to allow the S alligator clip to attach to or to dissociate from the Au clusters. The equilibrium bond length is set to 2.35 Å, which is based on several density functional theory calculations on similar systems, some of them already reported,[28] however, \( D_o \) is set to 14.7 kcal/mol in order to make this bonded interaction simulated by nonbonded fields and compatible with calculated geometrical structures. Therefore, the Au-S interaction is chosen based on a precise reproduction of geometrical features, rather than energetic ones. Nevertheless, the bond energy of a S-Au bond is 38 kcal/mol, which can be directly associated with roughly three Au atoms, thus corresponding to an average of 13.0 kcal/mol per interaction, which is consistent with the 14.7 kcal/mol chosen for geometrical purposes. This is simply an average to have an idea of the magnitude of the energies involved; it does not mean that the S atom bonds equally to three Au atoms as already shown theoretically [29-32] [13] and experimentally [33-35].
Fig. 1. Minimum programmable unit in square conformation consisting of four Au clusters interconnected with four “dinitro” molecules consisting of four Au$_{36}$ clusters interconnecting four active molecular devices. The Au clusters are roughly spherical with diameter of ~2.3 nm. The molecule, 2,5-dinitro-1,4-diethynylphenylthiolate-benzene, also called dinitro is a phenyl-based oligomer known to perform negative differential resistance NDR.

The vibrational analysis is performed using a series of simple filters applied to the time dependent atomic displacement signals. Briefly, a Hamming window is first applied to reduce spectral leakage. Lowpass filters, bandpass filters, and signal rectifiers are then used to isolate selected vibrations of interest. A very detailed description of the methods used in this paper can be found elsewhere [36].

3. Results

Table 1 shows average bond length and vibrational frequencies obtained for all the bonds analyzed in this study, when available, comparison to experimental values of the corresponding bond stretching modes are provided. We focus our study on the top and central rings of the three-ring molecule
(Figure 1). It is expected that the bottom ring behave similarly to the top ring. Two CH bonds, one located on the top ring and the other in the central ring, are chosen for this study since they represent two different environments and can provide complementary information about other vibrations in the molecule. The C-H on the top ring (C-H$_{CC}$) is located nearby the ethynyl group separating the two rings; the C-H bond in the central ring (C-H$_{NO2}$) can provide information about the NO$_2$ substituents.

![Fig. 2. Time and frequency domain plots of the C-H bond vibration at 10 K for a) the C-H in the top ring closer to the central ring and b) the C-H in the central ring. Time domain signals are shown on the left and frequency spectra are on the right. The analyzed bonds are boxed on the molecule.](image)
Table 1. MU4 molecular dynamics results for bond stretchings. We show more than one value of frequency when more than one peak of high intensity is observed in the frequency spectrum.

<table>
<thead>
<tr>
<th>Bond</th>
<th>T (K)</th>
<th>Average bond length (Å)</th>
<th>Vibrational Frequency (THz)</th>
<th>Vibrational Frequency (cm$^{-1}$)</th>
<th>Experimental Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H$_{CC}$</td>
<td>10</td>
<td>1.084</td>
<td>92.4</td>
<td>3082</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.084</td>
<td>92.4</td>
<td>3082</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>1.085</td>
<td>92.5</td>
<td>3085</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1.089</td>
<td>92.6</td>
<td>3089</td>
<td>3051$^1$</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.084</td>
<td>92.3</td>
<td>3079</td>
<td>3002 [37]</td>
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<tr>
<td></td>
<td>100</td>
<td>1.084</td>
<td>92.3</td>
<td>3079</td>
<td>3100-3000 [38]</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>1.085</td>
<td>92.5</td>
<td>3085</td>
<td></td>
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<tr>
<td></td>
<td>1000</td>
<td>1.090</td>
<td>92.4</td>
<td>3082</td>
<td></td>
</tr>
<tr>
<td>C-H$_{SO2}$</td>
<td>100</td>
<td>1.206</td>
<td>61.1</td>
<td>2038</td>
<td>2260-2100 [38]</td>
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<tr>
<td>C-C Triple</td>
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<td>1.206</td>
<td>61.1</td>
<td>2038</td>
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<tr>
<td></td>
<td>300</td>
<td>1.206</td>
<td>61.1</td>
<td>2038</td>
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<tr>
<td></td>
<td>1000</td>
<td>1.208</td>
<td>61.1</td>
<td>2038</td>
<td></td>
</tr>
<tr>
<td>C-C</td>
<td>10</td>
<td>1.400</td>
<td>34.3/47.6</td>
<td>1144/1588</td>
<td></td>
</tr>
<tr>
<td>Resonant 1,6</td>
<td>100</td>
<td>1.400</td>
<td>47.6</td>
<td>1588</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>1.401</td>
<td>47.6</td>
<td>1588</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1.404</td>
<td>27.7/47.4</td>
<td>924/1581</td>
<td>1600-1500 [38]</td>
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<tr>
<td>C-C</td>
<td>10</td>
<td>1.401</td>
<td>49.2/55.9</td>
<td>1431/1865</td>
<td></td>
</tr>
<tr>
<td>Resonant 4,5</td>
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<td>1.402</td>
<td>48.9</td>
<td>1631</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>1.402</td>
<td>55.7</td>
<td>1858</td>
<td></td>
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<td>1.406</td>
<td>55.7/48.9</td>
<td>1858/1631</td>
<td></td>
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<tr>
<td>C-S</td>
<td>10</td>
<td>1.789</td>
<td>---$^2$</td>
<td>1434</td>
<td>794 [39]</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.789</td>
<td>---$^2$</td>
<td>1434</td>
<td>624 [40]</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>1.791</td>
<td>---$^2$</td>
<td>1441/1144</td>
<td>582 [41]</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1.796</td>
<td>---$^2$</td>
<td>1194/530/1438</td>
<td></td>
</tr>
</tbody>
</table>

$^1$ Average value for the C-H vibration is 3035 cm$^{-1}$, 3044 cm$^{-1}$, 3059 cm$^{-1}$, and 3067 cm$^{-1}$, corresponding to the Wilson vibrational modes 2, 7, 13, and 20, which belong to the C-H stretching region in a benzene molecule [42].

$^2$ There are too many peaks, several of them around the experimental frequencies; however, it is not possible an unambiguous determination.
Table 2. MU4 molecular dynamics results: NO\textsubscript{2} scissoring and rotational modes. We show more than one value of frequency when more than one peak of high intensity is observed in the frequency spectrum.

<table>
<thead>
<tr>
<th>Mode</th>
<th>T (K)</th>
<th>Average Value (degree)</th>
<th>Vibrational Frequency (THz)</th>
<th>Vibrational Frequency (cm\textsuperscript{-1})</th>
<th>Experimental Values (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-N-O scissoring</td>
<td>10</td>
<td>118.6</td>
<td>27.4/26.3</td>
<td>914/877</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>118.4</td>
<td>48.5/27.4</td>
<td>1618/914</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>118.3</td>
<td>26.3/27.4/48.5</td>
<td>877/914/1618</td>
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<td></td>
<td>1000</td>
<td>118.0</td>
<td>27.4/26.3</td>
<td>914/877</td>
<td></td>
</tr>
<tr>
<td>NO\textsubscript{2} rotational</td>
<td>10</td>
<td>23.6</td>
<td>1.6</td>
<td>53.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>24.1</td>
<td>1.3/1.6</td>
<td>43.4/53.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>26.7</td>
<td>1.3/1.6</td>
<td>43.4/53.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>77.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The other vibrations considered in this work are the C-C triple bond in the ethynyl group joining the top ring to the central ring, two resonant bonds on the top ring, the C-S bonds and C-S-Au angle, the scissoring and rotation of the NO\textsubscript{2}, and the relative rotation between the top and the central ring. Table 2 summarizes the results obtained for NO\textsubscript{2} modes (scissoring, rotation).

4. C-H Bonds

These bonds only differ on their van der Waals (vdW) interactions showing only different magnitudes around the same frequency in the spectra. The C-H\textsubscript{CC} and C-H\textsubscript{NO\textsubscript{2}} time and frequency domains plots at 10 K are shown in Figure 2a and b, respectively. Their equilibrium bond length and a vibration frequency are very similar and not affected by their environment; however, the maximum displacement, which is 0.016 Å for C-H\textsubscript{CC} is only 0.010 Å for C-H\textsubscript{NO\textsubscript{2}} because the NO\textsubscript{2} restricts the H movement. In fact, the frequency spectrum for C-H\textsubscript{NO\textsubscript{2}} (Figure 2c) shows a strong line located at about 27 THz, which is the characteristic frequency for the scissoring modes of the NO\textsubscript{2} (Table 2). Two other strong lines at 49 and 55 THz are also common to both the C-H vibrations and the scissoring mode; however, these lines are associated with the C-C resonant bond vibration (vide infra).
Fig. 3. Time and frequency domain plots of the C-H bond vibration at 100 K for a) the C-H in the top ring closer to the central ring and b) the C-H in the central ring. Time domain signals are shown on the left and frequency spectra are on the right. The analyzed bonds are boxed in the molecule.

The characteristic spectra at 100 K are shown in Figure 3 for the two C-H bonds. Frequency and bond length do not change with respect to those at 10 K; however, the oscillation amplitude increases almost three times for C-H_{CC} (0.044 Å), and more than three times for C-H_{NO2} (0.036 Å) with respect to the observed amplitudes at 10 K.
Fig. 4. Time and frequency domain plots of the C-H Bond vibration at T = 300 K for a) the C-H in the top ring closer to the central ring and b) the C-H in the central ring. Time domain signals are shown on the left and frequency spectra are on the right. The analyzed bonds are boxed in the molecule.

At 300 K (Figure 4), both the equilibrium bond length and the oscillation frequency slightly increase (0.001 Å and 0.1 THz respectively) and the maximum displacement increases three times with respect to that at 100 K (0.095 for C-HCC and 0.087 Å for C-HNO2).
At 1000 K (figure 5), the peak at the characteristic frequency of the C-H vibration spreads out and increases in intensity. All other peaks in the spectra are very small; as a consequence, modulation is small. The equilibrium bond length shows the largest increase but still limited due to the harmonic force field used to simulate this bond, which does not allow bond dissociations only allowed for Au-Au and Au-S bonds [36]. The vibrational frequency did not change with the temperature. The maximum displacement duplicates with respect to the case at 300 K (0.186, and 0.205 Å, respectively, for C-HCC and C-HNO2). 1000 K is likely beyond the operating temperature for this system.
Fig. 6. Time and frequency plots of the upper C-C bond in the top benzene ring at a) 10, b) 100, c) 300, and d) 1000 K. Time domain signals are shown on the left and frequency spectra are on the right. The analyzed bond is boxed on the molecule.

The dominant frequency of each of the C-H vibrations we analyzed for the 10, 100, 300, and 1000 K simulations ranges from 92.3 THz (3079 cm^{-1}) to 92.6 THz (3089 cm^{-1}) (Table 1). For these cases, the stretching vibrational frequencies lie very close to the experimental values 3035 cm^{-1}, 3044 cm^{-1}, 3059 cm^{-1}, 3067 cm^{-1} corresponding to the Wilson vibrational modes no. 2, 7, 13, and 20, of the C-H stretching region in a benzene molecule [42].

5. C-C Resonant Bonds

The time and frequency domain spectra for two C-C resonance bonds in the upper benzene ring are shown in Figure 6 and 7. Each figure shows the vibration spectra of the 10, 100, 300, and 1000 K simulations for each of these bonds. These vibrations are much less symmetric across their mean value than the C-H bond vibrations.

Figure 6 shows the results for the upper C-C bond in the benzene ring. The average length of this bond ranges from 1.400 Å to 1.404 Å (Table 1) as the temperature increases from 10 K to 1000 K. The bond length is almost the same up to 300 K (1.400 Å for 10 and 100 K and 1.401 Å for 300 K) and goes to 1.404 at 1000 K. The frequency spectra for these vibrations have many well-defined peaks that are present at all temperatures, but with varying magnitudes. The peak that is consistently dominant relative to other peaks over the entire range of temperatures is located at 47.6 THz (1586 cm^{-1}) and could be assigned to the characteristic frequency for this vibration; however, this is not the highest peak for all the cases. A second peak at ~49 THz is also present and could be due to the bottom C-C resonant bond as explained in the following paragraph. The presence of several dominant peaks at all temperatures is an indication of a strong correlation that the C-C resonant bond has with other vibrations in the system. There is an isolated peak located above 90 THz, which comes from the C-H vibration.

Figure 7 shows the results for the lower C-C bond in the top benzene ring. The average length of this bond ranges from 1.401 Å to 1.406 Å as the temperature increases from 10 K to 1000 K. The frequency content of this bond vibration spectrum is similar to that of the upper C-C bond shown in Figure 6. A well-defined peak at 49 THz (1633 cm^{-1}) dominates the spectra for the lower C-C resonant bond. This frequency was also observed in the top C-C resonant bond with less intensity than the one at ~47 THz. Conversely, a
small peak at ~47 THz is also observed in the spectra of the bottom C-C resonant bond. We can conclude, based on the relative intensity of these two peaks that the top C-C bond vibrates with a characteristic frequency of 47.6 THz while the bottom C-C bond characteristic frequency is slightly shifted to 49 THz.

The C-C resonance bond vibration spectra vanishes after 60 THz, and a well-defined peak takes place in the neighborhood of the C-H vibration, which is around 92.5 THz. For the most part, the C-C vibration spectra are characterized by several well-defined peaks in the range of about 0 to 70 THz. These characteristics peaks can also be observed in the C-H vibration spectra. This confirms the correlation between the C-H bond vibrations and the vibrations of their neighboring C-C bonds. We can conclude that within the C-C vibrations, we also find the contribution of the C-H bond vibrations, and vice versa.
Fig. 7. Time and frequency plots of the lower C-C bond in the top benzene ring at a) 10, b) 100, c) 300, and d) 1000 K. Time domain signals are shown on the left and frequency spectra are on the right. The analyzed bond is boxed on the molecule.
6. C-C Triple Bond

The C-C triple bond located between the upper and middle rings in the molecular device is analyzed in Figure 8. The average length is 1.206 Å up to 300 K, and 1.208 Å for 1000 K. These values are really close to the experimental bond length for ethyne (1.203 Å [43]). At 10 K (Figure 8a), the dominant peak in the frequency spectrum is located at 54.9 THz (1831 cm⁻¹), which is intermediate between the expected vibrational frequency of C-C resonant bond (~48 THz) and C-C triple bond of about 61 THz (Table 1).
showing the strong effect that the ring vibrations have on this bond. For the 100, 300, and 1000 K spectra shown in Figure 8b to d, the dominant peak is located at ~61 THz (2033 cm$^{-1}$), which is in perfect agreement with the experimental C-C vibrational frequency of 2011 cm$^{-1}$ [44] for ethyne HCCH. A line at ~61 THz is also present at 10 K, but is not dominant.
7. C-S Bond

The vibrational spectra for the C-S bond located at the top of the molecular device are shown in Figure 9. The dominant frequency for 10, 100, and 300 K is around 43 THz (1434 cm$^{-1}$), which is certainly not due to the intrinsic C-S expected to be $\sim$20 THz [39-41] (Table 1), but rather to contributions from other vibrations that have been mixed into the C-S bond vibration. The resonant C-C bond on the top of the ring has a vibration around this value, for instance. A line at around 17 THz is present in the frequency spectrum at all temperatures and it corresponds to the characteristic frequency for this vibration. The spectrum in this range of frequencies shows several peaks from neighbor atoms vibrations that makes difficult to characterize it.
8. Angle Au-S-C

The results of the Au-S-C angle bending mode are shown in Figure 10. The average value for this angle increases from 98° to 120° as the temperature increases from 10 to 1000 K. Ab initio calculations of the C-S-Au predict for this angle a value in that range (~105°) [13, 31], and a temperature increase is expected to yield a wider distribution of angles due to thermal agitation. Notice that we have not calculated ab initio values for this angle within the force field; S is not ligand to Au in our simulation thus a Lennard-Jones (LJ) type of interaction is responsible for this grouping. LJ force field potential is a two-body interaction, which is a particular case of the many-body Sutton-Chen many-body potentials [24, 25]. Then it follows that the Au-S-C equilibrium angle is a result mainly of the one to one interactions with surrounding atoms. It can be inferred, when comparing to ab initio values, that the model used for the S to Au atom interactions reproduces similar physical parameters of the S-Au contact.

The vibration of the S to Au distance yields a spectra showing low frequencies contributions. These contributions have several very close peaks of similar amplitude indicating that the angle along Au-S-C is affected by low frequency vibrations of nearby atoms, like the Au-Au vibration in the contact. As for the C-S bond, the abundant low frequency contributions from the contacts makes difficult to characterize this vibration.

Fig. 10. Time and frequency domain plots of the Au-S-C angle bending at a) 10, b) 100, c) 300, and d) 1000 K. Time domain signals are shown on the left and frequency spectra are on the right. The analyzed bond is boxed on the molecule.
Fig. 11. Time and frequency domain plots of the O-N-O angle bending at a) 10, b) 100, c) 300, and d) 1000 K. Time domain signals are shown on the left and frequency spectra are on the right. The analyzed bond is boxed on the molecule.
9. Angle O-N-O

The results for the O-N-O angle bending are shown in Figure 11. The average value for this angle decreases from 118.6° to 118.1° as the temperature increases from 10 to 1000 K. The spectra for this angle-bending mode have several well-defined peaks. At all temperatures there are three peaks located around 25, 26, and 27.5 THz from which the peak at 27.5 THz dominates at all temperatures (except at 300 K where the one at 26 THz is slightly more intense). The strong peak located at 48.5 THz is due to the stretching mode of the C-C bonds in the aromatic ring and modulates the scissoring vibrational mode of the NO₂.
Cos (dihedral)

Mean Value = 0.9°

Time (ps)

-1.5
-1
1
1.5
-0.5
0
0.5
1
1.5
-1.5

High Frequency Detail
Frequency (Hz) x10^13
0 2.5 2.15 0.5 1 3 3.5

Magnitude

0 25 20 15 5 10 30 40 35 45

Low Frequency Detail
Frequency (Hz) x10^12
200 400 100 300 500

Magnitude

50 2.5 2.15 0.5 1 3 3.5 50 2.5 2.15 0.5 1 3 3.5

(b)

(c)
10. Relative rotation between rings (Dihedral)

In order to study the relative rotation between two consecutive benzene rings, we define an “improper” dihedral angle between the planes of the top and central rings, which represents the relative orientation of the planes of each ring. The fact that the two C atoms, one in each ring, defining this dihedral are not formally bonded does not affect this definition since they are practically co-linear with the two C atoms connecting them. We study the cosine of the dihedral angle instead of the angle itself, in order to avoid discontinuities inherent to the +180 to –180 jump.

The results obtained for the C-C-C-C dihedral angle rotation at 10, 100, 300, and 1000 K are shown in Figure 12. For the 10 and 100 K dihedral rotations, shown in Figure 12a and b, the cosine of the angle stays close to 1 indicating that the dihedral in both cases oscillates around its initial value of
approximately 0°. The amplitude of oscillation increases when going from 10 to 100 K; however, it is unlikely that the rings will complete a rotation with respect to one another at these temperatures. For the 300 and 1000 K dihedral rotations shown in Figure 12c and d, several complete ring rotations are observed.

The frequency spectrum of the relative rotation of the rings, is characterized by several low frequency (less than 1 THz) peaks located very close to each other as shown in the high resolution plots shown below the corresponding time and frequency spectra in Figure 12 (notice the different vertical scale between the low and high frequency detail plot). The magnitude of the low frequency peaks is clearly much larger than the high frequency peaks. Peaks between 0.5 and 1 THz reduce their intensity with T; whereas for 10 K, the region in the spectra with important peaks goes from 0 to 1 THz, for 1000 K this region goes from 0 to 0.5 THz.

The high frequency detail is very noisy and it is very difficult to obtain information from it.
Fig. 13. Time and frequency domain plots of the O-N-C-C dihedral at a) 10, b) 100, c) 300, and d) 1000 K, a zoom to the 0-5 THz regime is provided for this case. Time domain signals are shown on the left and frequency spectra are on the right. The analyzed bond is boxed on the molecule.

11. NO₂ Rotation

To analyze the rotation of the NO₂, we defined a dihedral angle between the planes defined by O-N-C and N-C-C, respectively. We perform the analysis in the same way as for the C-C-C-C dihedral. The results for the O-N-C-C dihedral rotation are shown in Figure 13. At 10, 100, and 300 K the NO₂ does not perform a complete rotation as it can be seen in Figure 13a, b, and c, it oscillates around its initial position of approximately 0°, though the amplitude of oscillation increases with temperature. Only at 1000 K does the NO₂ make complete rotations Figure 13d.

The spectrum for the NO₂ rotation is less noisy than the one for the rings relative rotation; however, the main frequency components spread and shift to lower values when T increases, as it was observed for the C-C-C-C rotation. For 10 K, the higher intensity components are around 1.6 THz; for 100 and 300 K they are below 1.6 THz, whereas for 1000 K, they are below 0.5 THz.

12. Correlation between vibrations

Several correlations between vibrations can be observed; for instance, the C-H bond affects neighboring vibrations, C-C resonant bonds, sharing one C atom with a C-H bond on the top ring, show a lone peak above 90 THz at all temperatures (Figure 6 and 7). The influence of the CH vibration is instead
very small on the C-S bond, where a very small peak appear about 90 THz (Figure 9), and it is inexistent on the C-C triple bond (see Figure 8).

The effect of the scissoring mode of the NO$_2$ in the central ring seems to be more delocalized along the molecule than other vibrations; it affects the dynamics of other bonds, and angles even if they are not close by. A peak around ~27 THz appears in several other vibrations located even on the top ring. Both C-H resonant bonds, one on the top ring and the other on the central ring, at all temperature, show a distinguishable peak at 27 THz (Figures 2 to 5). A very small peak at 27 THz can be observed on the C-C triple bond (Figure 8) and the C-S vibration (Figure 9), although the peak in those vibrations is just too small to conclude beyond doubt that NO$_2$ is influencing these vibrations. The C-S-Au angle seems not to be affected by the NO$_2$ scissoring mode (Figure 10).

The two C-C resonant bonds we treat in this work, both located on the top ring, show a well defined, and of a relatively high intensity, peak located at ~28 THz (Figure 6 and 7), a small isolated peak at 28 THz is also observed in the spectra of the NO$_2$ rotation (Figure 13). It is expected that the NO$_2$ rotation have some correlation to the scissoring mode, we can conclude then, that the peak at 28 THz is due to the NO$_2$ scissoring mode, slightly shifted to higher frequencies. Several peaks around 27 THz exist in the relative ring rotation spectrum that could correspond to the three peaks observed in the NO$_2$ scissoring mode (Figure 12), although the spectra in that region is very noisy and it is difficult to assure such a correlation.

Two main frequencies, close to each other, are found for the C-C resonant bonds on the top ring; however, the relative amplitude depends on the position of the bond in the ring, the bond on the top has a main frequency of ~47 THz whereas for the C-C at the bottom, the frequency at 49 THz dominates. The NO$_2$ scissoring mode also shows a peak at 48 THz corresponding to a nearby C-C resonant bond.

It is difficult to follow the relative ring rotation and the NO$_2$ rotation in other vibrations due to the low frequency the former two rotations have and the very noisy nature of the spectra at low frequency.

13. Discussion and Conclusions

Frequency analysis applied to individual bonds, angles, and dihedrals, is proposed as an alternative to the usual vibrational mode analysis. The analysis we carried out in this work has several advantages, it is simpler than identifying normal modes that in a system as big as the one in this work is a nearly impossible task. Normal modes are perpendicular to each other, thus
correlations between different vibrations in the molecule cannot be obtained from that analysis. Normal modes usually involve several vibrations along the molecule, all vibrating at the same frequency; conversely, each vibration can be part of several normal modes. The vibration of a bond, angle, or dihedral is projected onto several normal modes thus analyzing normal modes only partial aspects of the dynamics of each vibration can be seen.

The analysis we perform here, provides the entire frequency spectra involved in each vibration; then correlating vibrations by identifying similar frequency components, the effect that a particular vibration has on one part of the molecule can be inferred.

Of particular interest is the correlation between a vibration in the molecule that can be controlled externally and other vibrations. For instance the relative rotations between the central ring and the other two, can be controlled by an external field if, for instance a dipole moment is created in the central ring by adding adequate substituents.

We found that some vibrations, such as the C-H vibration, affects strongly neighboring vibrations, however, the rotation of the NO$_2$ group also affects vibrations relatively further from it, C-C resonant bond, C-S vibration and C-H vibration are affected by NO$_2$ rotation.

In addition to the vibrational properties, MD is also used to obtain operational information, we determine that 1000K is most probably beyond the operational T for this device.

The procedure used in this work is very promising although simple. By analyzing spectral information on one bond, we can infer how to excite another bond; thus, the dynamics of a different bond can be modified and therefore applications in molecular electronics, and signal processing, among others, are possible.

A potential scenario for the implementation of molecular electronic circuits is introduced by applying digital signal processing techniques to results from classical molecular dynamics simulations of a molecular system interconnected by nanosize gold clusters. Under this new scenario, signals can be introduced, processed, and read through interactions with the internal vibrational modes of the small molecular unit. At least modulation operations are intrinsically inherent to any molecular system. We demonstrated how molecular dynamics techniques can be used for the analysis of molecular electronic circuits; this is important since it will provide ideas as how the molecular circuits can be implemented to perform signal processing. A modified force-field is implemented for Au-Au and S-Au reproducing very well geometrical features of these interactions, and yielding calculated frequencies in very good agreement with available experimental information. On the other hand, analyzing the vibrational spectra of each bond, angle or
The dihedral of interest provides an alternative to normal mode analysis, which can be complicated for a system as big as the one treated in this work. Since normal modes are orthogonal to each other, an internal vibrational mode, such as a bond stretching, may be part of more than one normal mode; thus the analysis of normal modes only yields partial information for each internal vibration. The frequency analysis focuses on oscillations to obtain all the frequencies involved, rather than focusing on normal modes where several oscillations of the same frequency are combined. Depending on a proper selection of molecules, temperatures of ~300 K are acceptable, and the possibilities for analog signal processing using molecules are wide open. Low frequency oscillations can be externally controlled by electric fields, thus modulating higher frequency oscillations.

Thus, we demonstrate numerically how molecular dynamics techniques can be used for the analysis of molecular electronic circuits, and how a molecular circuit can be implemented to perform signal processing. It is also shown that the level of coupling between modes is enough to allow its decoupling using standard techniques.

Analyzing the vibrational spectra of bonds using digital signal processing techniques provides an alternative to normal mode analysis. A particular internal vibrational mode, such as a bond stretching, may have contributions from more than one normal vibrational mode. The analysis of normal modes only yields partial information for each particular internal vibration; however, the analysis reported in this brief finds correlations between different vibrational modes, allowing signal modulation and processing.

The application of an input signal in one region of the molecular circuit yields the modulation of bonds in other regions. Depending on the range of the vibrations wavelengths, we can find out if they can be excited (optically, bias potential, or in other ways), thus we find that modulation can be performed using standard IR and Raman spectroscopies. A near-future application is the development and design of molecular-size filters and the implementation of cellular automata techniques. Thus chemical derivatives of particular molecules can be proposed in order to use a characteristic of a particular bond to perform signal processing; therefore, a carefully study of the effect of several types of bonds when more than one signal is applied needs to be determined. This detailed analysis of the frequency spectra yields correlations between several local vibrations that can be used to include vibrational signals externally introduced through the contacts of the molecular device. Although these correlations between internal modes are not surprising, the question is if using the natural amplitude oscillations of the vibrational modes, which can be experimentally detected, will allow the detection of mixed signals in localized sites. If this were possible, several single operations...
could be implemented, enabling molecular processors dealing with signals in the THz range of frequencies. We propose that signals can be encoded as the movement of atoms that can be detected observing the changes in the electrical characteristics of the molecule. For instance, when the displacement, $\vec{r}$, of atoms associated to a vibrational mode changes the dipole moment of the molecule $\vec{\mu}$, a signal proportional to the so called infra red (IR) intensity is obtained from

$$IR \text{ Intensity} \propto \left( \frac{\partial \vec{\mu}}{\partial \vec{r}} \right)^2$$

and when atoms displacements affect the polarizability, $\vec{\alpha}$, a signal proportional to the so called Raman intensity is obtained,

$$Raman \text{ Intensity} \propto \left( \frac{\partial \vec{\alpha}}{\partial \vec{r}} \right)^2$$

These two intensities correspond to the most common experimental spectroscopic techniques, and can be unambiguously determined theoretically, and are potential candidates to be used as means for encoding information because, on the other hand, induced external changes in the dipole and polarizability by external fields yield changes in the displacements of the atoms in the molecule. Thus, signals are internally represented by atom displacements and transduced to IR and Raman intensities. The specific aspects of the theoretical and computational procedures used in this work are

Depending on a proper selection of molecules, temperatures of ~300 K are acceptable, and the possibilities for analog signal processing using molecules are wide open. Low frequency oscillations can be externally controlled by electric fields, thus modulating higher frequency oscillations. For example, inducing a motion pattern on the Au clusters (input signal), can modulate the C-H oscillation amplitude (output signal).

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