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Transmission of Vibronic Signals in Molecular Circuits

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It is proposed and demonstrated using molecular dynamics and digital signal processing techniques that molecular vibrations can be used to transport signals in molecular circuits, revealing that signals transmitted along polypeptide molecules by a frequency-modulated carrier in the terahertz domain consume only 0.2 eV to successfully transfer one information bit; this energy is several orders of magnitude smaller than the several thousands of electronvolts needed using electrons in present electronic devices.

Progress in integrated circuit miniaturization needed for faster computation is slowing down because of problems associated with heat removal, device addressing, and fabrication;[1] data are encoded as charges and transmitted as electron currents; as circuits become denser, these currents cannot be properly scaled down because of thresholds in signal-to-noise ratios required for signal integrity. Physical limits such as speed of light, atom size, electron delay, and Planck constant strongly affect the nanoregime regardless of materials used, and searching for new materials only yields marginal improvements. Another way to encode and transfer information is needed to continue the desired exponential computational growth. To satisfy present and future computational needs of our society, electronic devices are scaled down with the intention of making them faster. Under the so-called complementary metal-oxide-semiconductor (CMOS) technology of integrated circuits, the strategic reduction of size in a circuit yields smaller resistances and capacitances and hence smaller activation times, which in turn permit higher frequencies of operation, and therefore faster computation. This size reduction is carried out regardless of the fact that smaller and denser devices imply higher heat removal, higher leakage currents due to tunneling, and higher fabrication costs. All these problems drive us to search other possible avenues for improvement such as developing new materials, creating new architectures, or changing the way information is encoded and transmitted. A change or improvement in one of these alternatives demands adjustments or perhaps radical changes on the other two. Although a great deal of effort has been oriented toward the use of small molecules, nanoclusters, and nanotubes, and possible changes of architectures have been proposed for these nanodevices, information encoded as electron charges and transmitted as electron currents makes any nanodevice or architecture practically useless for further scaling down, because electron currents are large perturbations to the small devices; electrons lose considerable energy to the material, tunnel at short distances, and migrate to atoms. Electron currents cannot be scaled down further in small structures; otherwise, signals are washed out by natural noise. This problem is already affecting CMOS devices as this technology approaches the 10 nm feature size limit, which at the present rate of growth is expected by the year 2010 and is being perceived as the end of CMOS technology.[2] Proposed alternatives beyond the 10 nm limit consist of the use of several variants of Si nanostructures and the use of carbon nanotube transistors; however, at best they yield slight improvements over CMOS.[2] However, several other possible chargeless alternatives of encoding information might require much less energy than transporting electrons, such as molecular electrostatic potentials,[3] spin and quantum computing,[4,5] vibrational mode communication,[6,7] bond creation/destruction,[8] photonics, mechanical bonds,[9−11] torsional and conformational effects,[12−14] and other alternatives using the charge approach.[15−17] None of these have yet proven to stand as the best alternative, raising the question of which of these alternatives would be the most suitable for rapid implementation.

Signals can be transmitted as electromagnetic waves or photons, which propagate at the velocity of light. The best way to transmit signals is in free space, but because of the massless nature of the photon, practical wavelengths are too large to be confined in small circuits. The best alternative was the electron (electronics) instead of the photon, but we have already reached the point in which the devices are too small for the electrons' associated lengths. The next step is to find a media for the information with larger mass than the electron, such as the proton, neutron, ions atoms, and so forth. However, they are too large to be practical; thus, some interaction between electron and nuclei need to be considered. Molecular potentials, vibronic states, spin states, and plasmonic states are strong candidates. Given the advantage of organic molecules to be perfectly tailored with feature sizes much smaller than 1 nm yielding switches with less than 100 atoms,[18] vibronics and molecular potentials are strong alternatives, as plasmonics and spintronics might require elements with bulk properties or contacts, which would be detrimental to the nanodevices.

Thus, to test whether signals can be transmitted and recovered from a molecular wire using their vibronic states, two polypeptide molecules GLY58 and ALA600 (Figure 1) with different stiffness and length are modeled. The vibrational wave transmission takes place at speeds of ∼3000 m/s, which are smaller

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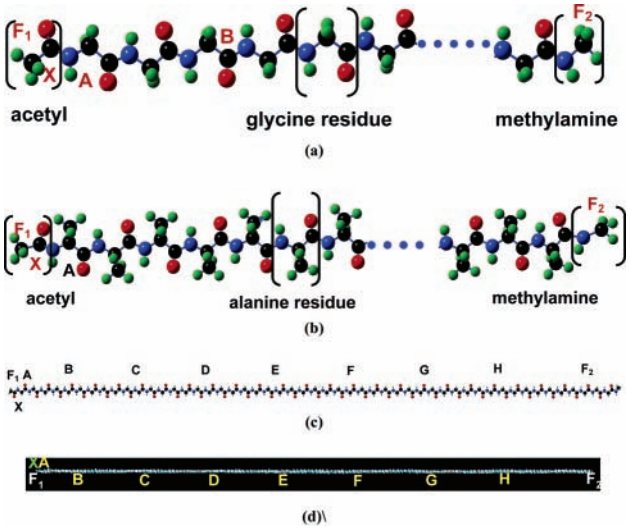

Figure 1. (a) GLY58 is a very soft polypeptide with 58 glycine residues capped by methylamine at the carbonyl terminus and acetyl at the amino terminus, with straight length of 21.8 nm, and (b) the stiffer ALA600, due to the methyl groups on the α carbon, polypeptide, with 600 alanine residues and a length of 223.5 nm. Two carbon atoms, F_1 and F_2, from each cap are held fixed during MD simulation; input signals are coupled to the carbon atom X nearest neighbor to the fixed carbon F_1 at the left. (c) The input signals transfer along the backbone of GLY58 and are detected at sites A, B, C, D, E, F, G, and H located at 1.4, 8.3, 34, 67, 90, 116, 142, and 168 Å from the input site, respectively. (d) For ALA600, the observation sites are A, B, C, D, E, F, G, and H located at 1.4, 224, 503, 782, 1062, 1341, 1620, and 1899 Å from the input site, respectively. Atoms for both molecules are color-coded, O (red), N (dark blue), C (light blue), and H (black).

but within the same order of magnitude as the electron transport in semiconductors devices (10 000 m/s).[19] However, vibronics yields wavelengths smaller than those in a vacuum and compatible with molecular sizes; thus, vibrational modes are a strong alternative for encoding and transfer information in molecular circuits interconnected by linear molecules; there is no need of any bulk material. Several linear biological molecules such as DNA, RNA, and proteins are strong candidates for the transfer and perhaps for the processing of information, and this is perhaps what nature does. Although the response of neuron cells to the external devices (muscles, senses, etc.) are ionic, the decision by which these ionic responses are triggered perhaps involves molecular potentials or vibrational states.

The vibrational spectrum corresponding to an individual bond shows peaks at several resonant frequencies, even from modes that are not associated with the specific bond (output at point H in Figure 2). This is because the internal coordinates are actually linear combinations of normal modes; thus, the time evolution of a bond stretching vibration not only provides the information of the normal modes corresponding to such a bond but also provides information from other bonds. This is consistent with the suggestion that in long molecules such as DNA and proteins each segment of the molecule has information about the others located far away. We find that signals transmit more effectively at frequencies corresponding to the bands created by the resonances; when an external signal is injected at frequencies outside the resonances, the signal decays much more rapidly with the distance along the molecule with respect to an injected signal in the range of the resonance frequencies. Signals injected at resonance frequencies can be recovered within acceptable margins of signal-to-noise ratios. The diagram of the signal flow is shown in Figure 2; we generate a hypothetical base signal of a trapezoid followed by a triangle as the information to be transmitted. The recovery of this signal (at the end of the flow diagram in Figure 2) is enough proof that encoding information into vibrational modes can handle digital binary signals, because the shape of the input signal used in this study is much more stringent than any typical binary signal.

Figure 2 shows the large difference between the signal injected at one end of the molecule (point X in Figure 2) and the one recovered at point H where noise from other modes and the environment are mixed through the molecular wire; however, after filtering and then clipping the signal, action that actually eliminates the noise at the same frequency spectrum of the signal, an amplitude-modulated signal is obtained using a slope demodulator. The wave rectification followed by the low-pass filtering allows recovery of the envelope from the carrier as shown in Figure 2, containing the same features as the input signal. The elimination of the sharp changes at the corners of the original signal is expected as those changes would require a channel with infinite bandwidth. Even at room temperature (equivalent to 26 meV), the input signal energy can be smaller than 26 meV, because as shown in Figure 2, the frequency modulation is immune to thermal perturbations. The excitation of 1 bit of information only requires 0.2 eV, which is at least 4 orders of magnitude smaller than the energy required using electrons.

In vibronics, no electrons are transferred; signals are coupled to the molecular wire by forcing the movement of one or a group of atoms as can be done experimentally by femtosecond time-resolved laser[20,21] or similar techniques already proposed for the analysis, design, and simulation of nanoelectronics operating in the terahertz domain.[7,22,23] Combinations of single molecules and nanoclusters provide suitable candidates for information processing devices because of their intrinsic vibrational frequencies in the terahertz range. Thus, molecules a few nanometers long can be tailored for specific analogue and digital operations and interconnected to metallic nanoclusters, which can be used as interfaces. Thus, the transfer of information can be encoded into the vibrational modes at much faster operational frequencies and with much lower energy expenditure than electrons do. This study is reminiscent of another suggesting the possibility of transmitting electrons through biomolecules such as DNA and proteins back in 1941;[24] our demonstration shows that when a signal is injected transmission can be achieved using vibrational modes which propagate along one-dimensional vibrational bands. To our knowledge, this is the first demonstration of such a possibility.

Compatible size with molecular dimensions and low dissipation energy make this approach suitable as an alternative to conventional CMOS technology that might facilitate further miniaturization as pursued by the microelectronics industry. Proof of concept experiments are needed to prove that this transfer of information approach is valuable and to stimulate further interest, as the basic issues of processing and storing information remain to be developed; however, the use of molecular electrostatic potentials for processing information is already a strong alternative to be combined with the vibronic transfer of information.

Methodology. Molecules are modeled by a collection of mass and point charge centers; the mass centers interact with each other via bonding and nonbonding forces, and the charge centers interact via electrostatic forces.[25] No viscosity effects are considered in this demonstration, as molecular circuits should resemble a solid rather than a fluid. The MD simulation is the numerical integration of Newton's equations[25,26] performed

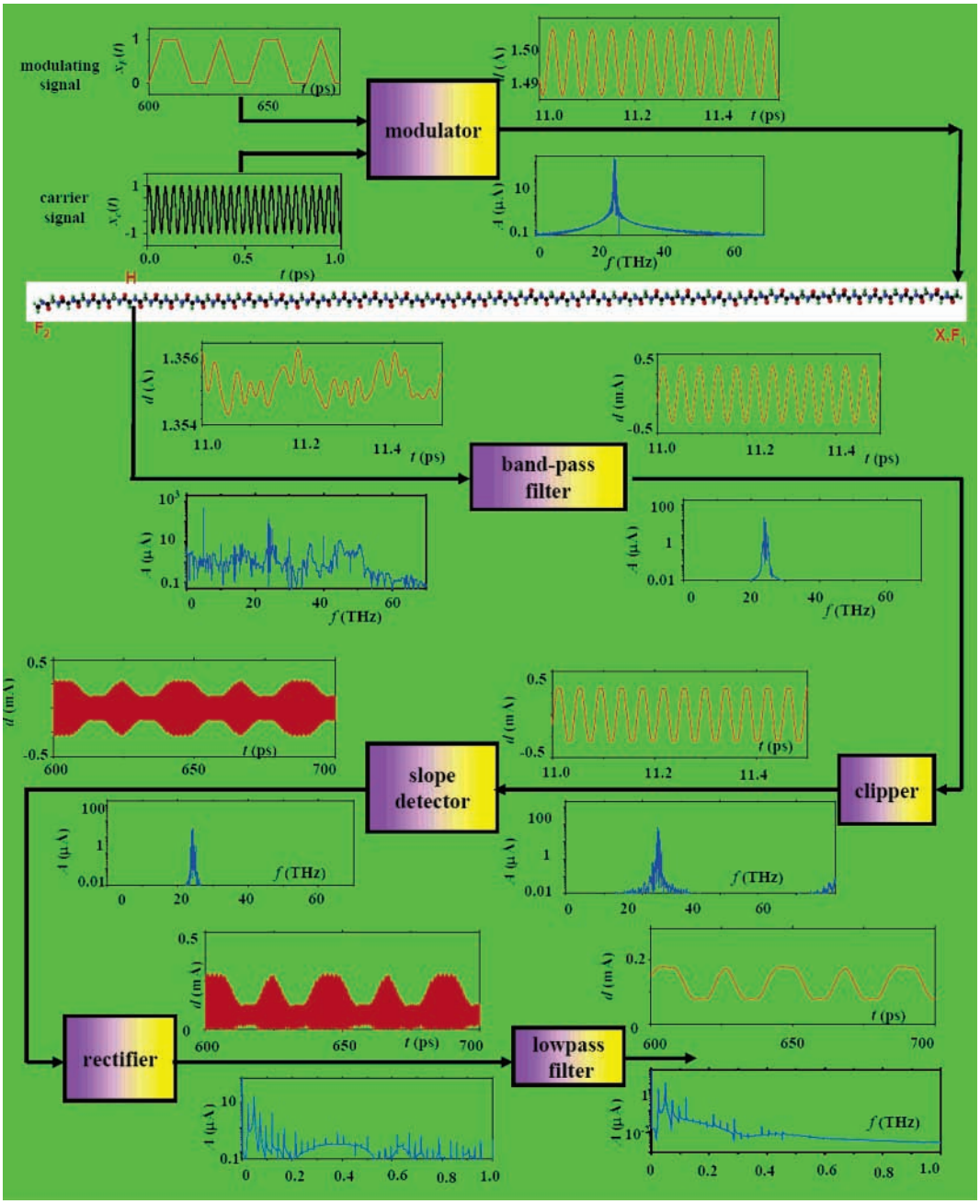

Figure 2. This flow diagram shows the results and the sequential analysis of the signals. The base signal (modulating signal) is a sequence of intercalated trapezoids and triangles formed by seven straight line segments of 6 ps each yielding a period of 42 ps or a frequency of 24 GHz. The carrier signal is a sinusoidal of 24 GHz. A variation of ±0.2 THz is allowed to modulate the carrier according to the base signal. The modulated FM signal is shown together with their Fourier transform or frequency spectrum, which is injected into the molecule at the atom X next to the fixed atom F_1 at the right end of the molecule. The signal travels along the molecule toward the left side and is recovered and analyzed in several points shown in Figure 1. This flow diagram shows the results only for the signal recovered at point H (in Figure 1). The FM signal recovered shows no resemblance to the one injected by the transmitter. The receiver output shows a signal that contains the oscillations from other vibrational modes and also the noise from the thermal oscillations at room temperature (297 K). The recovered signal is passed through a Bessel band-pass filter centered at the carrier frequency of 24.0 THz and with a bandwidth of 1 THz to recover the frequencies of interest; notice that other frequencies have been eliminated as shown in the frequency spectrum but thermal noise at the same frequencies of the signal are still included. The signal is then clipped to make the amplitude constant; this eliminates noise at the same frequencies of the carrier. Then, the clipped signal is demodulated by the slope detector, which is another Bessel filter properly centered at a frequency larger than the carrier frequency of the FM signal such that the frequency deviations for the FM signal fall on the left almost linear slope of the frequency response curve of the filter (not shown); the center and the bandwidth of the slope detector are set to 24.9 and 2.6 THz, respectively. The output signal of the slope detector is a frequency and amplitude modulated signal from which we just need its envelope, which is recovered by a full rectification and a low-pass filter with a cutoff frequency of 0.1 THz. The output from the low-pass filter shows a slightly distorted signal with resemblance to the base or modulation signal. Notice that we impose stricter conditions on the shape of the testing signal. Practical situations would only require detecting two distinct levels.

using the NAMD program[27] and the CHARMM all-hydrogen parameter force field.[28] The molecular simulation step time for the integration is set to 1 fs, and 200 ps equilibration is run before the production stage, then; 1 ns trajectories are collected containing the configurations of all the atoms at each step. From this trajectory, a time series of bond lengths are calculated at each time step, and digital signal-processing techniques are used to analyze the signal transmission through the molecule.[29,30] The

base signal modulates the frequency of the bond variations $r(t)$ around the equilibrium distance r_0 at discrete intervals t_i determined by the molecular simulation step size, which is also used as the sampling frequency for all signals and is small enough to avoid affecting the quality of the results.[6,7] The carrier frequency of $f_c = \sim 24$ THz corresponds to one of the intrinsic vibrational modes of the backbone polypeptide. The signal injected into the molecule drives displacements of atom X (Figure 1) at times t_i along the direction of its bond (from the bond equilibrium distance r_0) with atom F_1 given by the expression

$$r(t_i) = r_0 + 0.01 \times \sin\{2\pi[f_c t_i + \Delta f_m \int x_F(t)\, dt]\}$$

where Δf_m is the allowed shift in frequency to encode the signal $x_F(t)$.

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