CENTRO DE INVESTIGACIÓN Y DE ESTUDIOS AVANZADOS DEL INSTITUTO POLITÉCNICO NACIONAL

UNIDAD QUERÉTARO

"EMULACIÓN Y SIMULACIÓN DE CIRCUITOS ELÉCTRICOS FORMADOS POR ARREGLOS DE DISPOSITIVOS MOLECULARES"

Tesis que presenta

Alejandro José Giménez Gómez

Para obtener el Grado de

Maestro en Ciencias

en la especialidad de

Materiales

Directores de la Tesis:

Dr. J. Gabriel Luna Bárcenas   Dr. Jorge Seminario

Santiago de Querétaro, Qro.   Enero de 2009

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ABSTRACT

Electronics technology in the last 60 years has provided extraordinary advances as it has evolved from simple bulb circuits of about 200 cm^3 (~10^{-4} m^3) to complex circuits built by transistors fabricated by lithography methods to sizes as small as 45 nm at gate (~10^{-15} m^3), this gives a 11 order reduction in volume and the size reduction involves other advantages like the reduction of power consumption by component, faster operation speed and lower fabrication cost by the same performance.

The world has witnessed a great advance in electronics technology and its strong influence in our lives as it has changed the communications, entertainment, data manipulation, etc. The influence of electronics has been of great relevance in every technological and human aspect in today's world.

Recently, new challenges are emerging in the silicon-based technology that we use to manufacture integrated circuits, although this technology has been very successful; it is reaching its limits in several ways including power dissipation for instance, but there are other problems associated with reducing the density of integrated circuits, like the optical limits of lithography methods at nanoscales. The existence of these limits leads the scientific community to find new ways to develop technologies which will allow this technological development to continue in the same way as in the last decades. Most of these new proposals are related to the field of nanotechnology because nanostructure devices and molecules are intended to be used to build electrical circuits.

The Negative Differential Resistance (NDR), has been pointed by several researches as a good candidate to be the base component for a new type of electronics; this is due to the fact that it has been proved that arrays of interconnected NDR devices yield multiple operation states, that feature supposes programmability for this kind of circuits, and besides the NDR rare non-linear behavior has been theoretically and experimentally demonstrated to be commonly found in many organic molecules.

In this thesis different tools are developed to comprehend and analyze the behavior of circuits formed by non-linear components like the NDR. An emulation method has been proposed using a digital programmable electronic circuit and by using this circuit we can imitate, in the macroscopic world, the behavior of molecular devices. In this way we can easily perform tests in a test bench to comprehend better how these components behave and eventually to know how to assemble these molecules into a useful device.

We also have elaborated computer software to apply deterministic and random algorithms to simulate molecular-like circuits in large quantities having in mind that this software might be a useful tool to evaluate the potential, stability and programmability of molecular circuits.

RESUMEN

La tecnología electrónica en los últimos 60 años ha presentado avances extraordinarios ya que se ha pasado de sencillos circuitos formados por bulbos de un tamaño de aproximadamente 200 cm^3 (~10^{-4} m^3) a complejos microprocesadores formados por transistores formados por medios litográficos de tamaños de hasta 45 nm en la compuerta (~10^{-15} m^3), esto supone una reducción de cerca de 11 ordenes en el volumen y la reducción en tamaño lleva de la mano otras ventajas como la reducción en potencia consumida por cada componente, incremento en velocidad de operación y disminución de costos de fabricación en relación con el desempeño, todo el mundo ha sido testigo de este gran avance ya que la electrónica ha tomado un papel muy importante en nuestras vidas y ha cambiado profundamente las tele comunicaciones, el entretenimiento, la investigación, el manejo de información, etc. La influencia de este gran avance ha impactado en todos los aspectos tecnológicos y humanos de la vida actual.

El problema que se ha presentado en la electrónica en los últimos años es que la línea de la tecnología basada en Silicio que se ha seguido para poder disminuir de manera tan exitosa la densidad de componentes dentro de un circuito integrado esta llegando a sus limites de varias maneras, al parecer el principal problema es la disipación de calor pero existen otros limitantes como por ejemplo los limites ópticos para realizar procesos de litografía a nanoescalas. La existencia de estos limites ha llevado a los científicos a proponer nuevas tecnologías que permitan continuar con el desarrollo que se ha tenido en las ultimas décadas y la mayoría de estas propuestas están relacionadas con el campo de la nanotecnologia ya que se propone usar moléculas u otros dispositivos del tamaño de unos cuantos nanometros para realizar las funciones básicas de un circuito electrónico.

La Resistencia Diferencial Negativa (NDR por sus siglas en ingles) ha sido considerada por muchos investigadores como una buena opción para ser el componente base para un nuevo tipo de electrónica ya que se ha confirmado que circuitos formados por estos componentes presentan múltiples puntos de operación lo que supone una programabilidad en estos sistemas, además que se ha comprobado teórica y experimentalmente que el comportamiento de NDR es común de encontrar en moléculas orgánicas.

En el trabajo de esta tesis se desarrollaron diferentes herramientas para conocer y analizar el comportamiento de circuitos formados por componentes con NDR, se desarrollo un método de emulación con el cual utilizando electrónica digital programable se puede imitar a macro escala el comportamiento de un dispositivo NDR y de esta manera realizar pruebas sobre este mismo para poder conocer mejor su funcionamiento y los mecanismos en los cuales estos dispositivos pueden ser usados.

También se desarrollo un software que aplica diversos algoritmos matemáticos deterministicos y no deterministicos para poder simular circuitos que contengan grandes cantidades de dispositivos NDR teniendo en mente que este software puede ser una herramienta útil para la evaluar en trabajos posteriores la estabilidad, programabilidad y potencial de los circuitos moleculares.

A mis padres y hermanos,

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1.-Introduction

1.1.-Molecular Electronics

The work in this thesis is related to Molecular Electronics, an interdisciplinary theme pretending to use molecules as the main components of electrical circuits[1, 2] capable to process, store and transmit information.[3-6]

A transistor, the basic unit of digital integrated circuits, is composed by approximately one billion atoms; if we were able to use instead molecular devices formed by a hundred atoms, we will be talking of a reduction around seven orders which implies a revolution in electronics without precedents.[2]

Since Feynman in his famous lecture "There's plenty of room at the bottom"[7] at Caltech in 1960, he depicted the benefits of building things at atomic scale, and he even dimensioned these benefits explaining how all the human knowledge from all the books at that time, assuming 24 millions of volumes could be stored using a very small piece of matter barely visible by the human eye.

To fabricate transistors at micrometric scale, expensive and complex processes are required. On the other hand, to fabricate astronomical amounts (10^{26}) of molecules capable to perform as electrical components, we only require chemical reactions which result to be much cheaper and simpler compared with silicon electronics fabrication.

There are very high expectations about the operation speeds of molecular circuits due to the fact that theoretical analysis have shown that using molecular vibrations from the molecules it might be possible to obtain processors running up to 100 Terahertz (10^{12} Hz).[8, 9] It is also expected a great reduction in the power consumption using this kind of electronics.

1.2.-Molecular Electronics Justification

It could be thought that nowadays silicon processors are fast enough to fulfill our needs, but the truth is that there is a big demand for more processing power for several applications; as research, design and simulation in every area of science and technology. This processing power demand also exists in leisure fields as in video gaming and cinematography.

The electronics consumer market has based its growth in the exponential increasing capacity predicted by Moore[10]. This growth capacity from the electronics circuits has continuously offered new life changing gadgets like cell phones and laptops, and we can expect that a pause in this economical motor may cause financial crisis worldwide.

1.3.-General objective

The main objective of this thesis work is to develop tools to understand how electrical circuits formed by molecules with highly non-linear response, such as the Negative Differential Resistance will behave. This kind of tools will be useful to know which mechanisms are followed when these molecules are interconnected. This will be of great help to know about how to use molecular circuits.

Among several benefits of understanding molecular circuits; we will have a better estimation of the potentials and limitations of these circuits, we will identify the best suited architectures to be used for different purposes and also we may find what electrical properties from the molecules are the most desirable to implement working devices.

1.4.-Specific objectives

In this thesis, in order to understand molecular circuits, we have developed two different kinds of tools; in the first one, we have made an electronic circuit capable to emulate or mimic highly non-linear behaviors found in molecules. The goal of this emulator circuits is as a proof of concept to analyze the basic nature of a molecular circuits when having a few components. The use of this kind of circuit comes from the fact that performing real measurements in real molecular circuits is very difficult and also that the highly non-linear properties we want to emulate are not present in macroscopic electrical components as resistors and diodes for example.

The second tool developed is a software simulator capable of analyzing how a circuit of several non-linear devices would work. This is due to the fact that the non-linear behaviors we want to analyze are very different to the ones from typical electrical components; consequently we have chosen to develop a custom-made simulator for molecular circuits instead of using a SPICE (Simulation Program with Integrated Circuit Emphasis) circuit simulator. The advantage of this software over the emulator devices is that in this simulator we can test and analyze circuits formed by several molecules in a more practical way.

2.-Theoretical background

2.1. - Molecular Electronics Proposals

Many and different methods have been proposed as candidates to develop technologies in which it would be used molecules to transmit, process or store information. The main idea is to take advantage of molecular characteristics for these goals.

One of these proposals consists to employ the molecular electrostatic potentials MEPs to perform electronics work; these potentials could be calculated using the next equation:

$$V(r)=\sum\frac{Z_i}{|R_i-r|}-\int\frac{\rho(r')}{|r-r'|}dr'$$

Where $\rho(r')$ is the charge density, it can be obtained from the molecular wave function. These potentials are well known in some cases like in water where we know it is a negative potential in the oxygen vicinity and a positive potential in the hydrogen atoms vicinity.

Using this same idea we can build a logic gate with a trifluorobenzene molecule [1, 8] [11] [12]. In Figure 1 it can be appreciated how water molecules strategically placed can alter the MEPs from the molecule making it work like a logic AND gate.

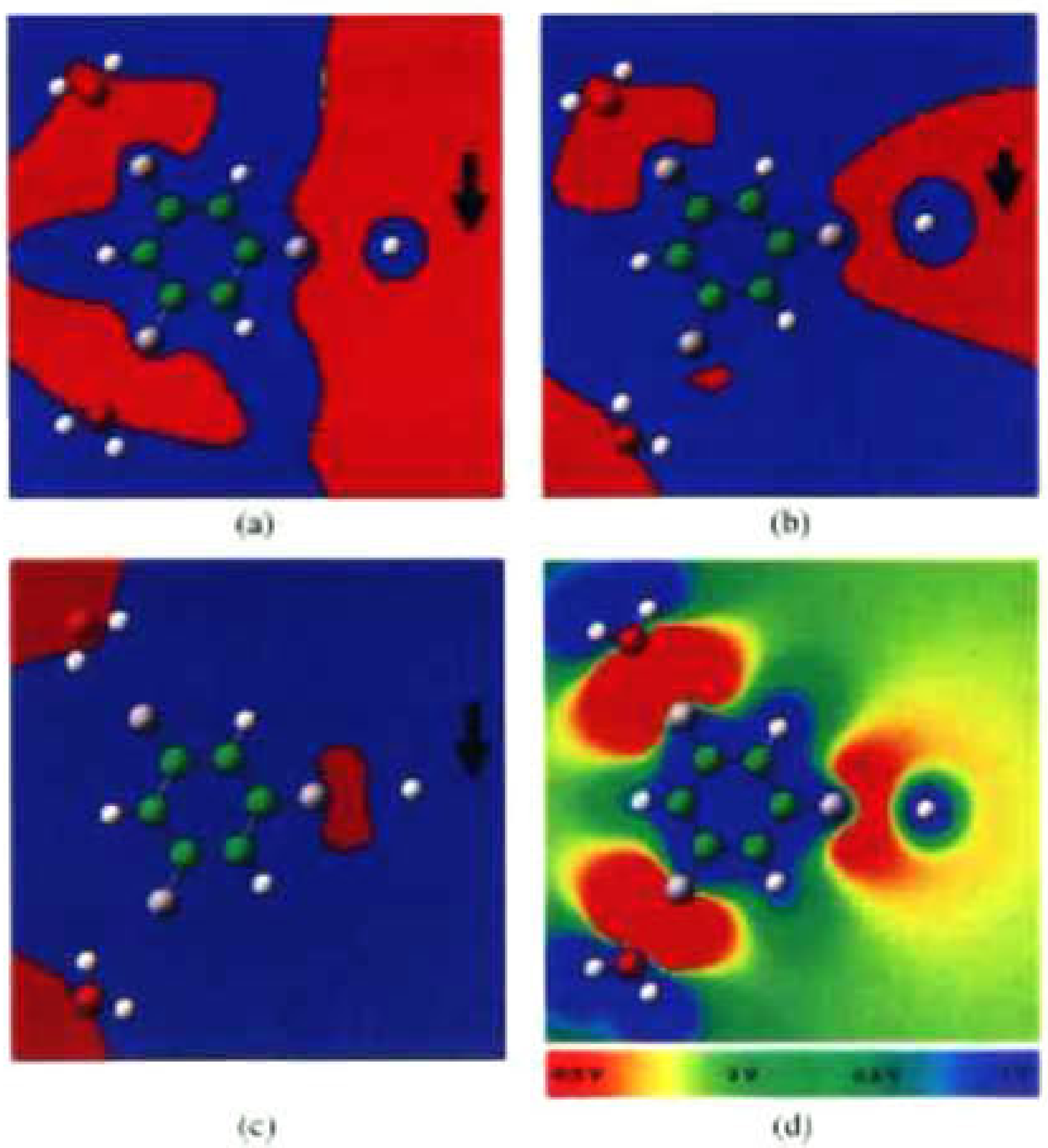


Figure 1, It can be seen the way the molecular electrostatic potentials from a trifluorobenzene molecule are modified externally by nearby water molecules, negative potentials are considered as logic zeros and are market in red color and positive potentials as logic ones and are market in blue color, a) case for inputs 0 0 output 0, b) and c) case for inputs 0 1 output 0, d) case for inputs 1 1 output 1[13].

The proposal to use MEPs has many inherent advantages; the most attractive probably is the low power consumption. Theoretical studies [12] show this technology may consume about 1.2 billion times less energy compared to actual silicon technology, which is a remarkable statistic.

Other proposed method consists in employing the vibration modes of a molecule to realize electronics functions [9, 14]. It is well known that every molecule presents different vibration frequencies due to the nuclei masses and the bonds between atoms behaving like mass-spring systems; frequencies in these systems lay in the Terahertz region and it has been theoretically demonstrated that long molecules can transport signals at relatively large distances [9]. In the Figure 2 it can be seen how a long molecule can transmit a modulated signal presenting only small distortions.

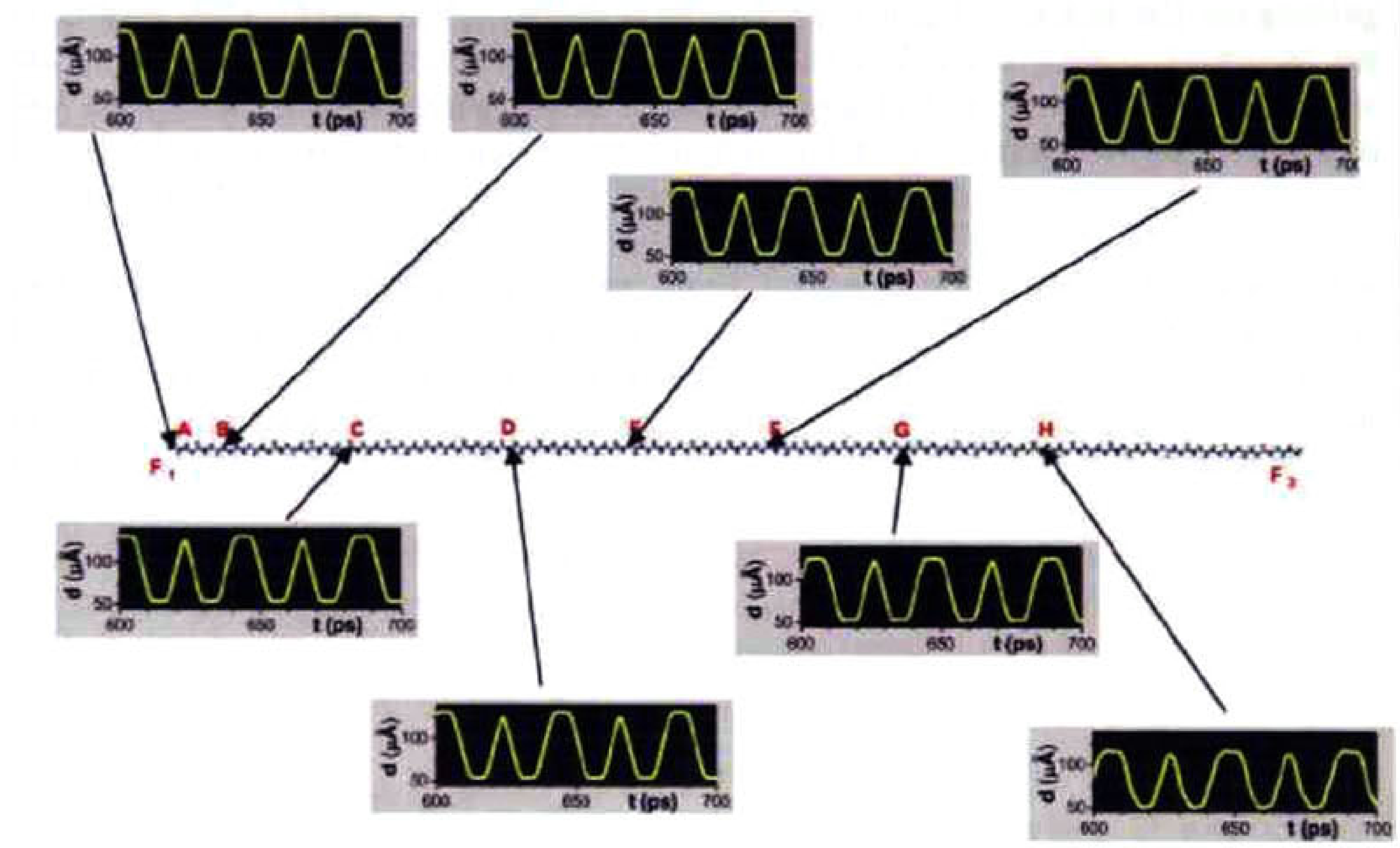


Figure 2, Signal transmitted trough a Ala30 molecule using Amplitude Modulation, this signal is introduced in point A and is recovered at point B-H presenting only an small degradation [13].

The third proposal is probably the most studied and perhaps the one having the better chances to yield useable technology in a near future; we are talking about using molecules as electrical components in which we apply some voltage and we obtain as a result an electrical current through the molecule. To be able to use the molecules in this way we need to use molecules having very special characteristics.

These molecules need to be able to conduct electrical current in a linear or non-linear way; the molecules conducting current in a linear way will be used as resistors or junctions to transmit information between points inside a molecular circuit and the non-linear molecules might be used to realize amplification or digital logic functions. Many research groups have found theoretically and experimentally molecules able to behave as diodes or other non-linear devices [6, 15-17].

Other characteristics required from these molecules are to be reproducible by chemical reactions and to present self-assembling mechanisms in order to facilitate building a large circuit using these components. Otherwise it would be extremely expensive and time consuming to assemble one by one every molecule of a computer processor formed by several billions of molecules.

2.2.-Architectures to implement Molecular Electronics

Architectures are a key point in molecular electronics; Scientifics and Engineers are working to find new configurations to make possible to fabricate devices using molecules as basic components. These configurations need to have in mind chemical self-assembling methods and interface communication between micro and nano scales. Many of the proposed approaches suggests using micro electronics as a tool to be able to operate at the nano regime, in some way that micro electronics would be a intermediary between nano and the macro world.

There exists one architecture involving many proposed approaches, this one is the Crossbar [18, 19]. In this architecture crossed nanoWires[17, 20-23] are used in a way in which at the crossing points of the nanoWires it is deposited or self-assembled some material with special electrical properties. Depending on the deposited material behavior this architecture can yield many different uses; for example as digital programmable logic or as memory arrays, some of the proposals to use this kind of architecture are: nanoFabrics [24], majority logic arrays [25] and nano-PLA [26, 27]. Some Crossbar arrays like the Majority logic arrays implement Negative Differential Resistances (NDR) as components, this kind of components are a key point in this thesis and because of this they will be better explained later.

Some groups like Stanley Williams's from HP and Kuekes from UCLA have achieved to build memory devices using this architecture. In Figure 3 it can be seen an atomic force microscope image of a Crossbar.

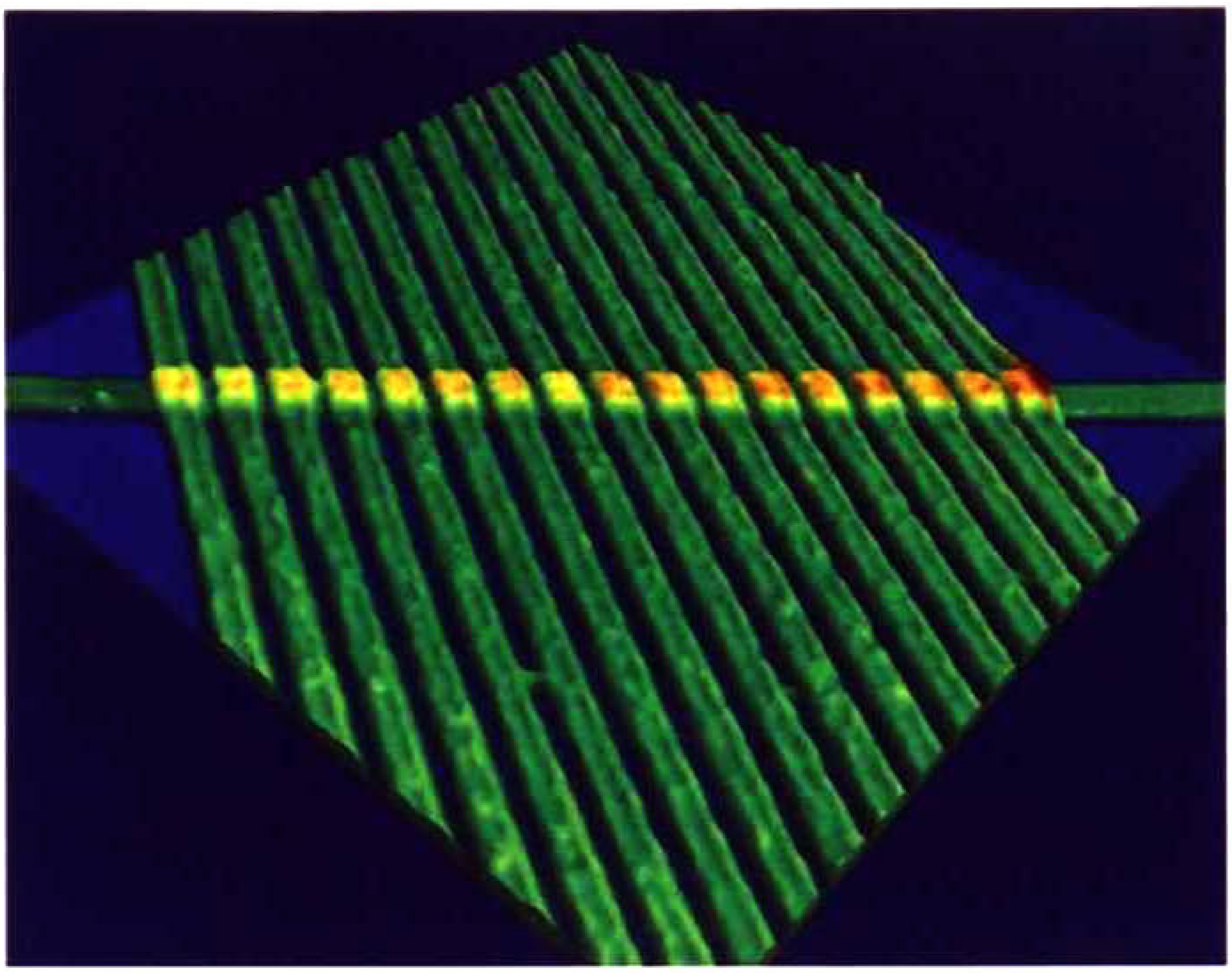


Figure 3, Image generated by an AFM, 17 nanoWires with a diameter of 50 nm are being Crossed by a nanoWire of the same diameter forming a Crossbar array. Photographed by J. J. Yang, HP Labs.

Other proposed Architecture is the nanoCell [13, 28-31], in this approach the idea is to deposit over an insulator substrate gold nano clusters, then molecules are attached over this clusters interconnecting them, in this way having a self-assembled circuit which may contain a very large amount of nets and nodes randomly assembled. The molecules used to interconnect the gold clusters will be chosen to present a special highly non-linear behavior called Negative Differential Resistance (NDR). It is well known that circuits having this kind of components yield multiple operational states; this fact involves a potential use for these circuits to be configured or programmed. Configuration would be done by using input voltages or currents, then allowing these randomly assembled circuits to realize deterministic mathematical or logical functions, as a final goal putting together a large amount of these nanoCell we eventually would be able to construct a computing processor.

Part of the idea to implement a nanoCell lies in using micro electronics, doing this to configure the circuit applying pulses from a few strategically placed electrodes, as well as for feeding and reading data from the nanoCell circuit, this idea is a good example of how we could employ micro electronics as a tool to approach the nano world.

The nanoCell approach is very appealing because it responds to the addressing problem, given the small size of the components involved researchers are looking for assembling processes like this one in which we do not need to make precise connections. More importantly the configurability of the nanoCell assumes this to be a fault tolerant system which is a very desirable feature, as a matter of fact the actual Silicon technology process is very low fault tolerant this is the main reason why extremely clean environments are required for this processes. Extremely clean environments are expensive and complex, so implementing a process like the nanoCell may simplify the actual fabrication methods, In Figure 4 a nanoCell cartoon is represented.

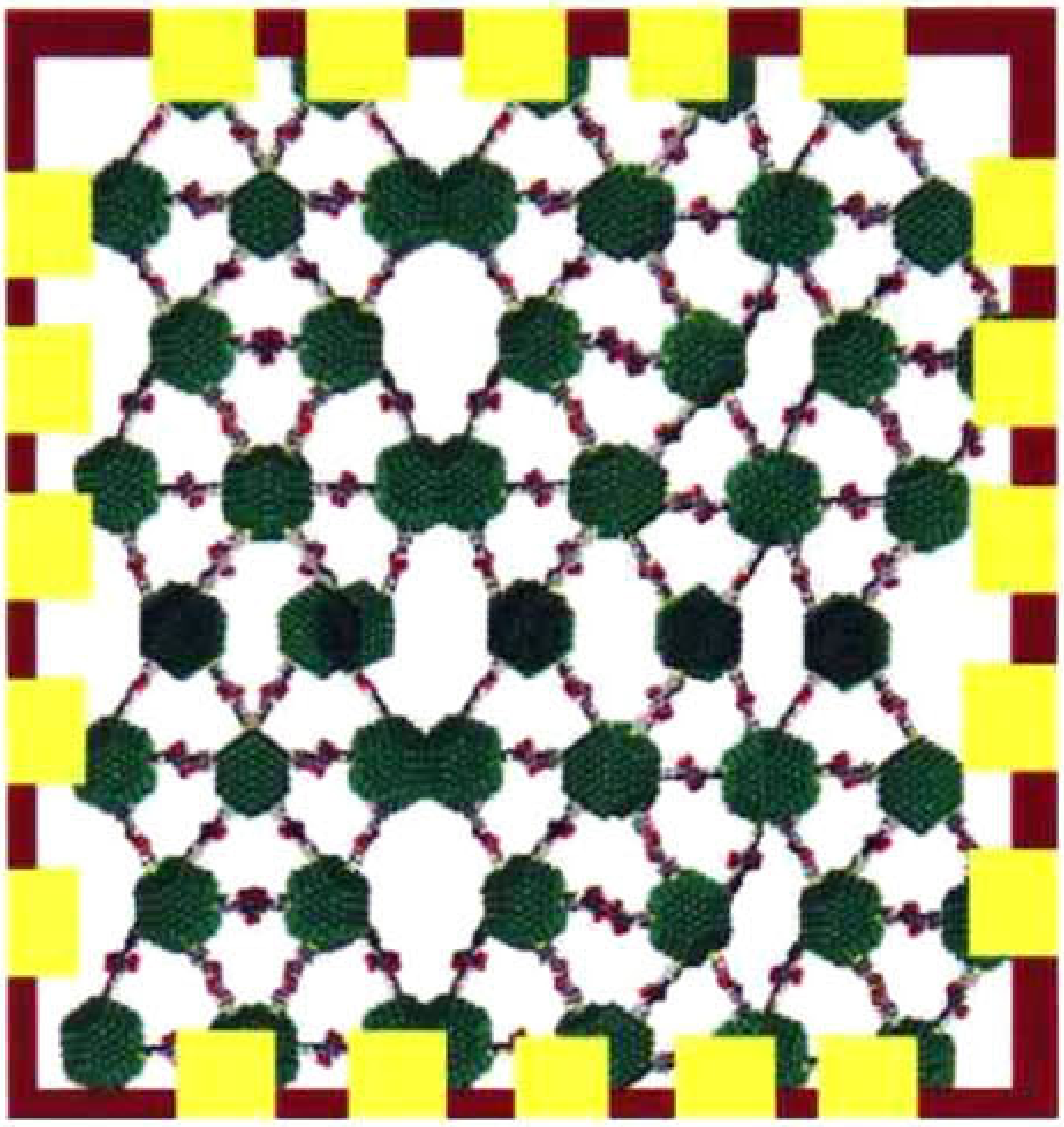


Figure 4, Cartoon representation of a nanoCell, gold clusters (green) are interconnected by molecules forming random circuit nets, at the borders there are electrodes (yellow) which are meant to be used as configuration inputs as well as for input and output data from this circuit [13].

2.3.-Electrical properties characterization of molecular devices

As it can be expected the basic blocks in Molecular Electronics are molecules, molecules are intended to be used to build circuits and for this same reason we require to know how a molecule would behave as an electrical component. Then we would be able to propose the best circuit configurations and the best molecules to employ for these purposes.

For several years Seminario et al. among other research groups have been using different methods to find out how molecules conduct electricity; they have been characterizing many different molecules to choose the best fitted to perform electronic functions.

In research done by different groups it has been decided to employ organic molecules for Molecular Electronics purposes, due to the fact that organic molecules can be chemically synthesized in a large variety of sizes and shapes. At the other hand these organic molecules can be easily altered by using well known substituents, this which can be an useful tool to modify or tune characteristics to produce a large amount of different molecular devices having different functions [2].

Several molecules have been analyzed experimentally and theoretically using simulation, there are already many candidate molecules for Molecular Electronics; for example in one of the firsts papers on this topic Aviram and Ratner propose to use molecules formed by a donor-acceptor groups to create molecular diodes [6].

For the case of Jorge Seminario's research group molecules characterized have been simulated using quantum chemistry ab initio methods [32]. Using DFT (Density Functional Theory) implemented by Gaussian Software [33-35] the molecules are model as oligomers attached to a few gold atoms at its extremes, then the molecular geometry is optimized applying the Helleman-Feyman theorem [36-38].

DFT is employed to obtain the KS Hamiltonian and the wave function overlap matrix S of the electric field extended molecule.

$$H_{KS}\Psi = \varepsilon S\Psi$$

$$H_{KS} = \begin{bmatrix} H_{11} & H_{1M} & H_{12} \\ H_{M1} & H_{MM} & H_{M2} \\ H_{21} & H_{2M} & H_{22} \end{bmatrix}$$

Once we have the calculation for the molecular minimum energy, the DOS (Density of States) using Gaussian and the DOS from the metal terminals using CRYSTAL. These calculations are used to simulate the current vs. voltage I-V characteristics, this is simulated by using an own Seminario's group software algorithm called GENIP [39] [40] which is a combination of DFT and Green function.

$$G_M = \left[ES_{MM} + H_{MM} - \sum_L - \sum_R\right]$$

This GENIP algorithm uses Green function to calculate the transmission function to find the probability of one electron flowing across the junction.

$$T(E) = Trace(\Gamma_L(E)G_M(E)\Gamma_R(E)G_M^{+}(E))$$

And finally the current is calculated as a function of voltage change ΔV using an adapted version of Landauer-Buttiker equation.

$$I(V) = \frac{2e}{h}\int_{Ef-V/2}^{Ef+V/2} T(E,\Delta V)dE$$

One strong candidate molecule to be used in the nanoCell as NDR is Au_n-C_6H_5-CC-$C_6H_2O_2$-CC-C_6H_4S-Au_n, this molecule has a central ring with two oxygen atoms as substituents. Due to this feature this molecule is referred as "Dioxo", and James Tour research group at Rice University has already synthesized this molecule [41].

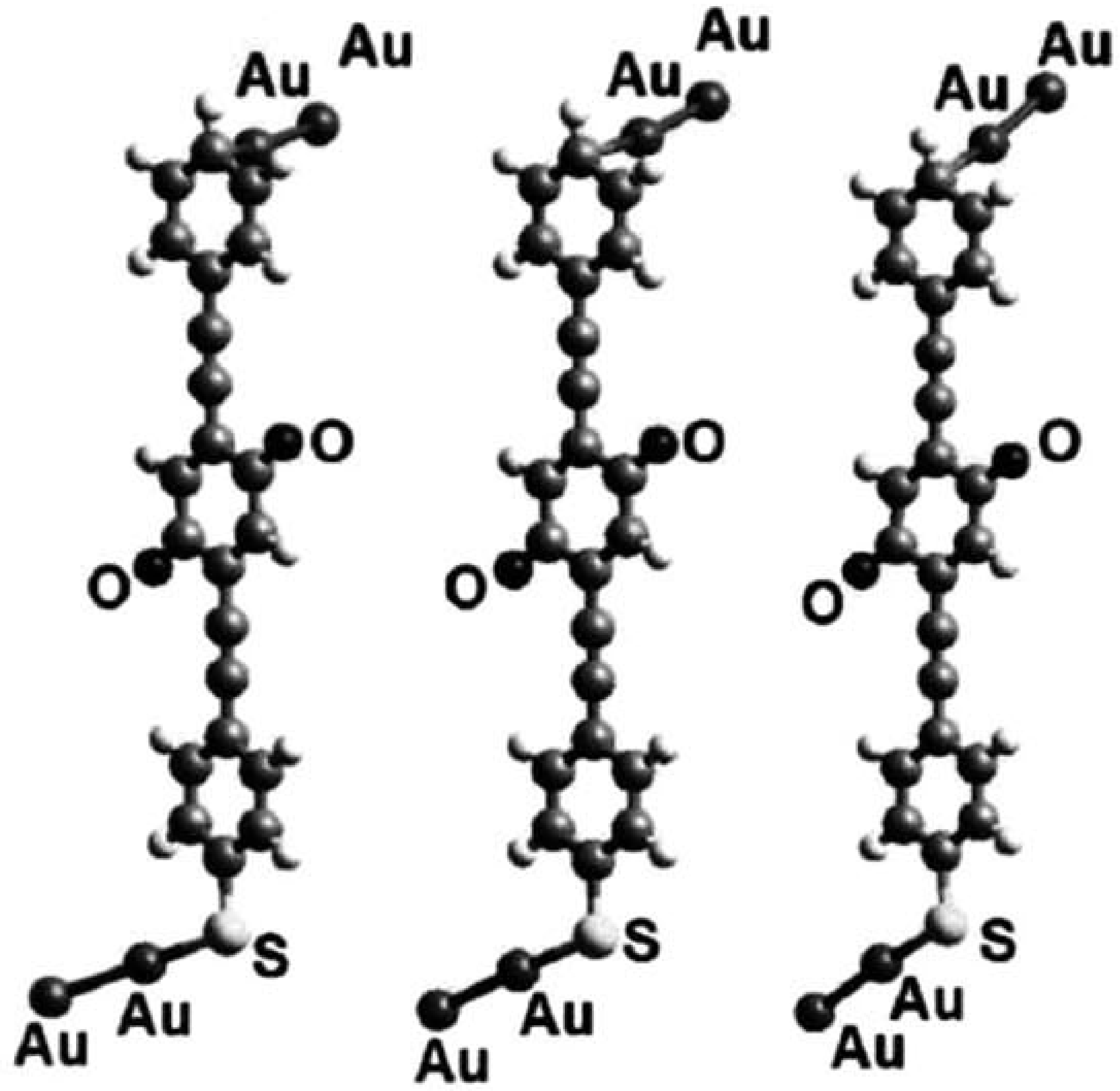


Figure 5, Au_n-C_6H_5-CC-$C_6H_2O_2$-CC-C_6H_4S-Au_n Optimized geometries for the neutral, anion and di-anion configurations. [2]

Current vs. Voltage characteristics can change due to molecular charge states. In Figure 5 it can be seen the geometry optimization for different charge states. To obtain a real I-V curve for this molecule the different charges states must be considered. The I-V theoretical curve for the Dioxo molecule is shown in Figure 6, in this I-V curve the different charge states I-V signatures have been mixed giving as result a highly non-linear negative differential resistance behavior (NDR). It can be clearly seen how there is region where the voltage increases and the current decrease.

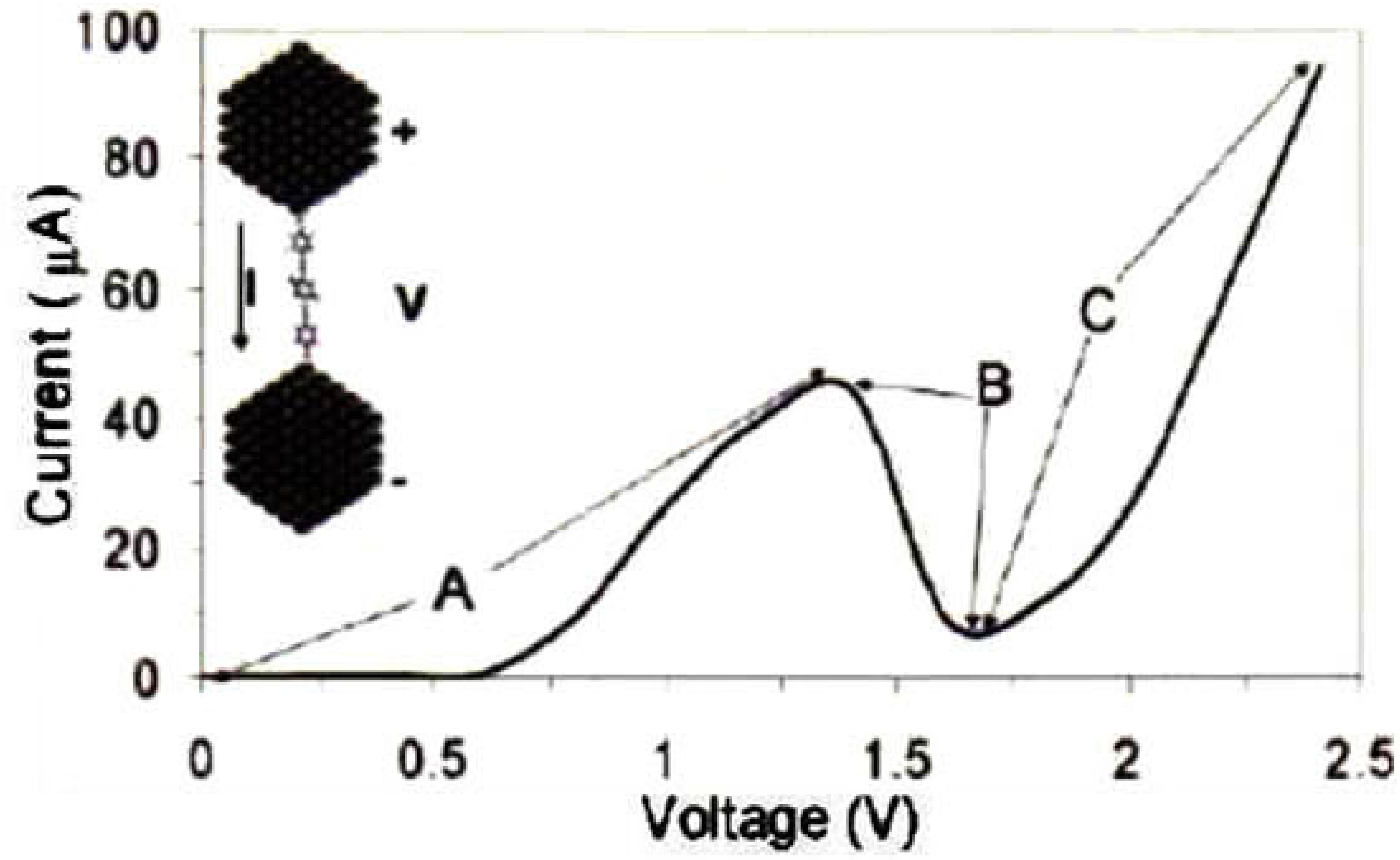


Figure 6. Dioxo molecule Current vs. Voltage signature this curve is result of mixing Current vs. Voltage curves for different charge states of the molecule [2].

2.4.-Negative Differential Resistance

As it has been shown by research done by Seminario et al. the way the Dioxo molecule conducts current as a function of voltage (as it can be seen in Figure 6) results to be highly non-linear having a non-monotonic behavior very rarely seen in electrical components, that behavior is called Negative Differential Resistance. NDR behavior in spite to be rarely seen in macro electronics components; is proved to be common at nano scales due to the highly non-linear effects caused by quantum mechanics effects.

We meant by non-monotonic that there exists a range in which the current decreases while the voltage increases, this can be clearly seen in Figure 6. This range is present approximately between 1.3 and 1.7 volts. From some time ago it is well known that circuits formed or having NDR components will yield multiple operation states [42, 43]. In Figure 7 it can be observed how in some voltage regions a two in series circuit of NDR devices has more than one operation current.

These different operation states are easily recognized in the Figure 7, for example if 3.5 volts are applied these circuit can yield a current of 10 or 40 micro amperes approximately.

Is not entirely understood how the NDR behavior is present in molecules, it seems that there exist many mechanisms making this to be possible, in the case shown from Dioxo molecule the presence of NDR region seems to be due to a saturation of the Molecular Orbitals when the molecule is charged. In other cases it seems to be caused by charge movement, anyway the important point for this work is that the NDR behavior exist and have been predicted theoretically and measured experimentally; so we can say it is a good bet to take advantage of this non-linear behavior to build useful molecular circuits.

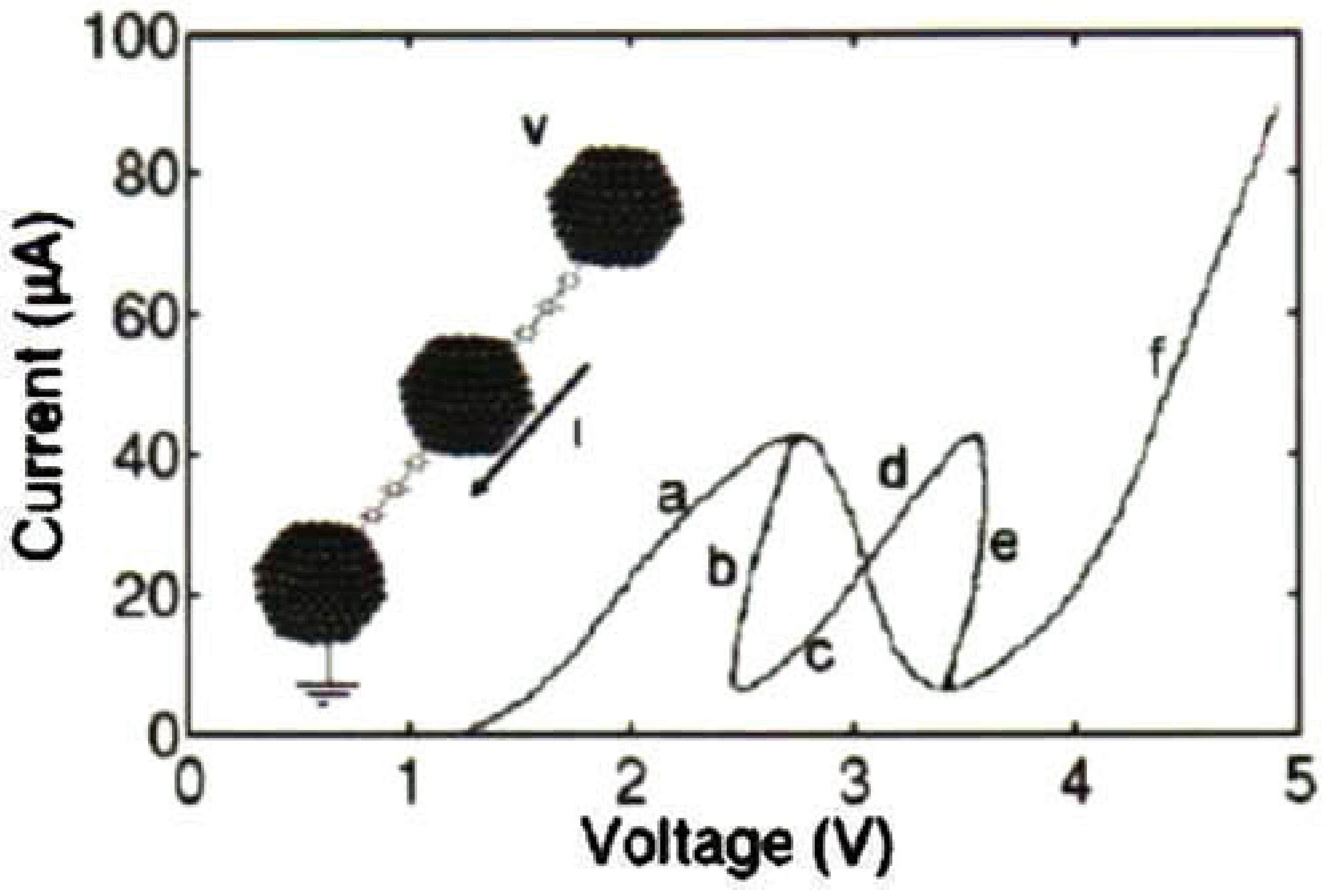


Figure 7. Plot of a current vs. voltage curve of a two in series NDR Dioxo devices, it can be observed in some regions for one applied voltage there exist two possible currents [2].

3.-Methodology

3.1.-Emulation of non-linear devices by programmable electronics

Our first approach to obtain a better understanding of basic circuits of highly non-linear components like the NDRs was by experimental emulation of the behavior of two non-linear devices in series configuration. For this we have built electronic circuits that perform as molecular emulators. Our emulators are capable of mimicking the current vs. voltage (I-V) behavior measured and predicted [44] in real molecules. This experimental demonstration is of paramount importance for the implementation of any scenario of molecular electronics which is able to "address" individual molecules using the "molecular programmability" characteristics on molecules with strongly non–linear I-V characteristics.

The electronic devices work around a microcontroller (µc), an integrated circuit programmed to perform the tasks of reading the voltage drop across the device and modifying its own resistance accordingly to the voltage drop. The program operates in this way in order to respond to the non-linear characteristic desired to emulate the ones from a NDR device. The microcontroller controls its own resistance by supplying a controlled current through a light emitting diode (LED) pointing to a photo-resistor which determines the device resistance as programmed in the microcontroller.

The microcontroller is the ATtiny26 from Atmel [45]. This chip is capable of analogical-to-digital conversion (ADC) and digital-to-analogical conversion (DAC). The DAC is implemented by using a pulse width modulator; it yields pulses of variable width (input voltage dependant) to trigger the LED. A simplified circuit schematic is shown in Figure 8; main devices are a LED, a photo-resistor and a few extra components including a couple of clamps as emulator terminals. An actual photograph of the complete circuit can be seen in Figure 9.

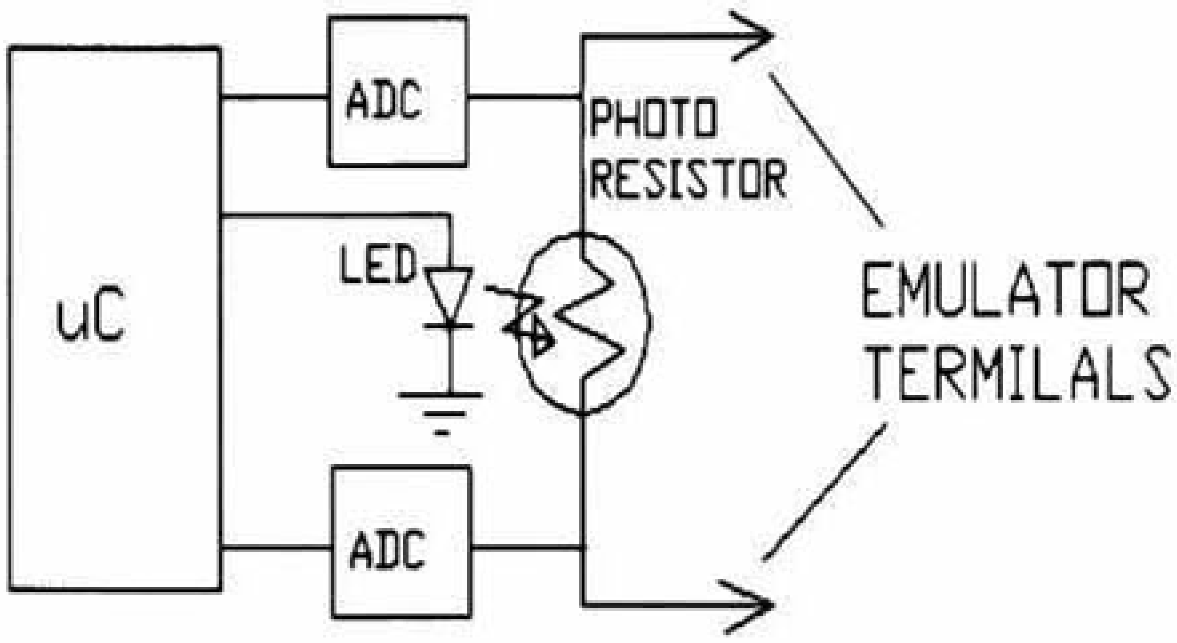


Figure 8, Simplified schematics for the non-linear emulator device

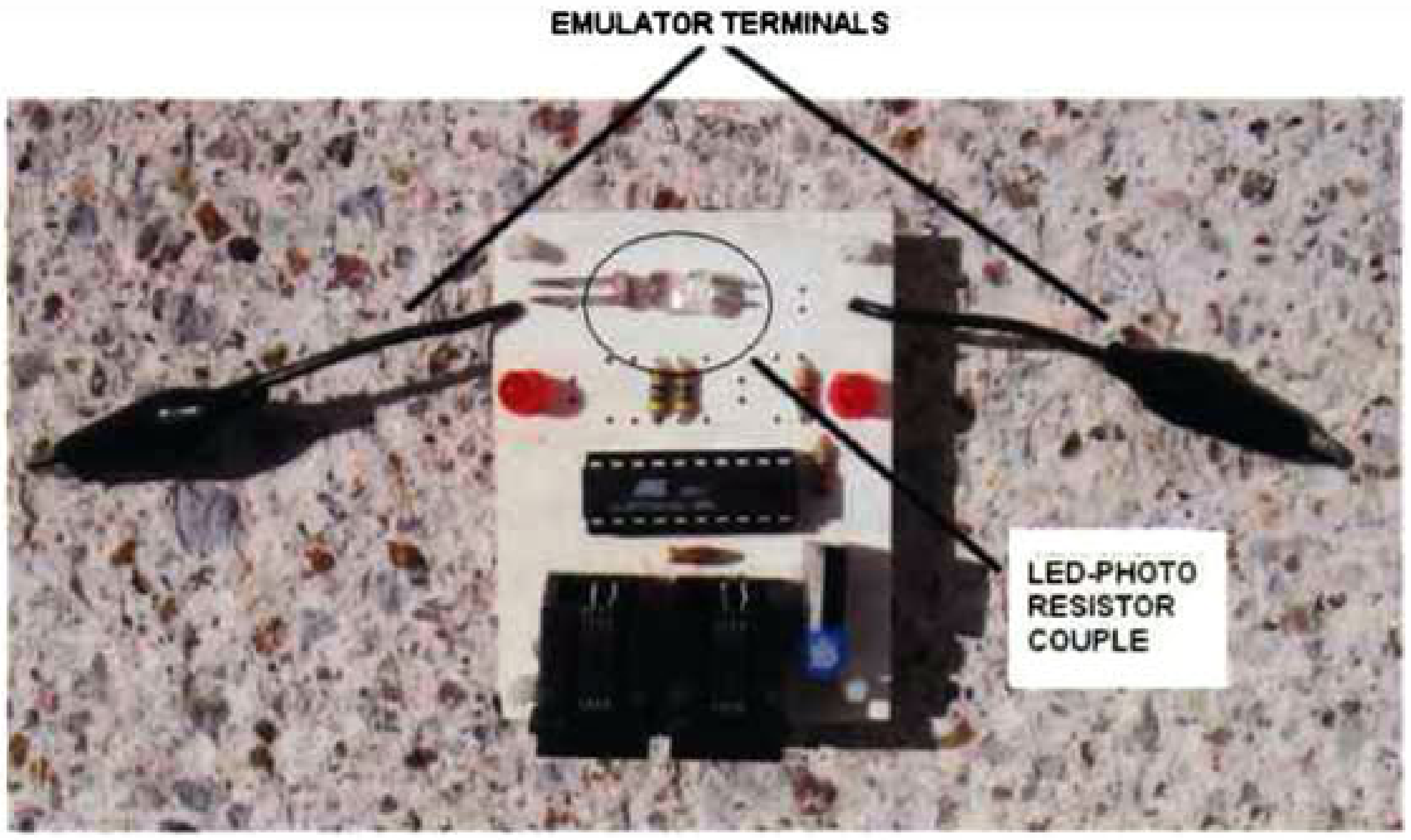


Figure 9, Photograph of the Non-linear emulator device, terminals and the photo-resistor couple are pointed, it also can be seen the microcontroller integrated circuit.

More detailed information about the hardware of this Non-linear Emulator circuit can be found at Annex 1 at the end of this thesis.

The emulator is programmed to continuously measure the voltage and adjust its variable photo-resistance. The microcontroller can be programmed to follow any I-V signature and it is constrained only by the photo-resistor limits. The devices are programmed to follow an NDR behavior similar to the one in the dinitro-based molecular device analyzed in the theoretical demonstration [46]. The microcontroller program in Basic language to emulate the behavior of a NDR device can be found at Annex 2.

Two identical devices have been built and soft-programmed to establish a lookup table of resistance versus measured voltage. The I-V curves of the two devices have been traced for each separately and for both in series. The plots were done using an oscilloscope and a function generator at 0.01 Hz frequency in order to assure steady state results.

In the series configuration a 10 KΩ resistor (R_c) is connected between the emulator junctions and to ground or voltage source (V_{in}). The resistor is used to bias the system between two possible stable states. In addition, the series circuit has been used to apply short pulses as perturbations to detect unstable states.

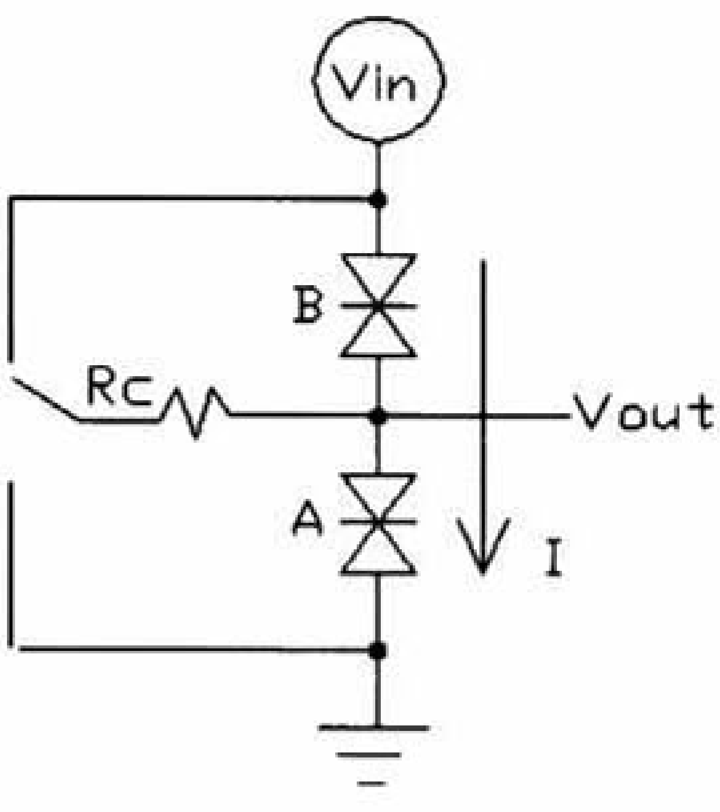


Figure 10, Electronic circuit of two NDR (Device A and Device B). R_c is a 10 kΩ control resistor.

During this thesis work a relevant paper from UCLA and HP researchers has been published, the paper claim the discovery of a new fundamental electronic component existing at nanometric scale, so this component might be of great relevance for molecular electronics use. The discoverers are calling the new component the Memristor [47], this device is basically a resistor which changes of value depending of the charge flowing across it. Accordingly to these researchers this effect may be the cause of several non-linearities measured experimentally at nanometric scales.

The Memristor as a highly non-linear component may require as well special tools to be understood, so we have used the same hardware we have built originally to emulate NDR devices and we have changed its software in order to be able to simulate the behavior of a Memristor device. The mathematical approach followed to achieve this behavior is based in using the same formula Williams et al. use to describe the behavior of a Memristor.

$$M(q) = R_{OFF}\left(1 - \frac{\mu_V R_{ON}}{D^2} q(t)\right)$$

We adapted this equation by using as R_{ON} and R_{OFF} values the maximum and minimum photo resistor values. Charge mobility and the thickness of the devices are replaced by a C constant and the charge flowing through the device is calculated as a sum of current values at specific time increments.

$$M(q) = R_{MAX} - ((R_{MAX} - R_{MIN})C \cdot Abs(q))$$
$$q = \sum (i)\Delta t$$
$$M(q) \geq R_{MIN} \Rightarrow Abs(q) \leq 1/C$$

The Basic software made for the microcontroller to emulate the behavior of a Memristor device can be found at Annex 3.

3.2. - Simulation of Non-linear circuit devices using Computer Software

3.2.1.-Introduction to Molecular circuit simulation

Several approaches have been tried to achieve functional hardware architectures built by self-assembly methods to improve; performance, size, power consumption, cycle speeds, and production processes over the present silicon-based technology. Some of these approaches such as the crossbar [18, 48], nanoFabrics [24], majority logic arrays [25], nano-PLA [26, 27] and the nanoCell [2, 9, 13, 28] propose to use negative differential resistance (NDR) nano-devices interconnected in several ways to build circuits capable to be configured to perform specific tasks of digital electronic hardware.

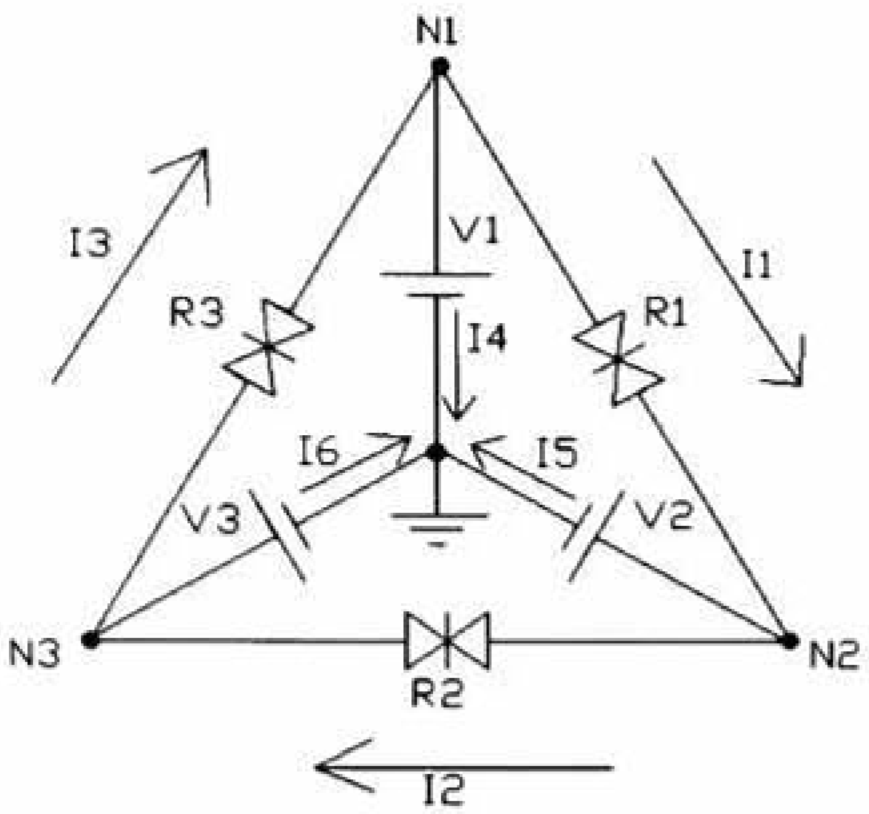
It is well-known that circuits formed by NDR devices have several possible operation states [2, 9, 13, 43]; this implies that a system can yield multi-valued outputs that can be switched by external perturbations, thus performing molecular programmability. In turn this allows the use of the self assembled molecular circuits as minimum configurable logic blocks. Therefore we need to understand the mechanisms involved in the internal behavior of physically non-addressable but programmable molecular circuits by only having accessibility to a reduced number of interface points.

The feature of programmability of molecules pertains to the action of programming arrays of molecules to perform some specific function logical or arithmetical. As molecules cannot be arranged and interconnected in pre-defined distributions.

Programs such as SPICE [28, 43, 49] and ACES [50] among others have been used to simulate NDR behavior; however no multivalued results were reported. In the present work we develop custom software using lookup tables to model NDR behavior, thus making easier to simulate devices having highly nonlinear I-V characteristics obtained from theory or experiments. Our simulation speeds are compatible to simulate the programmability of realistic arrays of molecular devices in a deterministic way but obtaining the possible operation states of a circuit by random methods.

3.2.2.-Circuit solving approach

To calculate voltages and currents we solve matrix equations using Kirchoff laws [51]. Figure 11 shows an example with the equations needed to build the matrices; however instead of having fixed-value resistors we consider specially proposed molecules with current-voltage characteristics obtained using ab initio methods [2, 9, 13] such as the one in Fig. 12a.



$$I_1 R_1 - V_1 + V_2 = 0$$
$$I_2 R_2 - V_2 + V_3 = 0$$
$$I_3 R_3 - V_3 + V_1 = 0$$
$$I_1 - I_3 - I_4 = 0$$
$$I_2 - I_1 - I_5 = 0$$
$$I_3 - I_2 - I_6 = 0$$

Figure 11, Example of how the equations are written from a circuit containing 3 nodes and 3 molecules. This equation system can be converted to a 6-row 10-comlumn matrix.

We implement the non-linear I-V characteristics through a lookup table in which every voltage value across the NDR devices yields a resistance value as shown in Fig. 12b.

This method allows us to analyze devices showing any type of non-linear behavior. Using this approach we can simulate any nonlinear device or any other one that depends for instance on its charge. Such as the so-called memristor [47], a device having a charge dependent resistance. This behavior was already found in atoms and molecules [52, 53]; their resistance depends on the charge in the molecule (or atom) as unambiguously shown by ab initio methods [2, 9, 15, 46, 54].

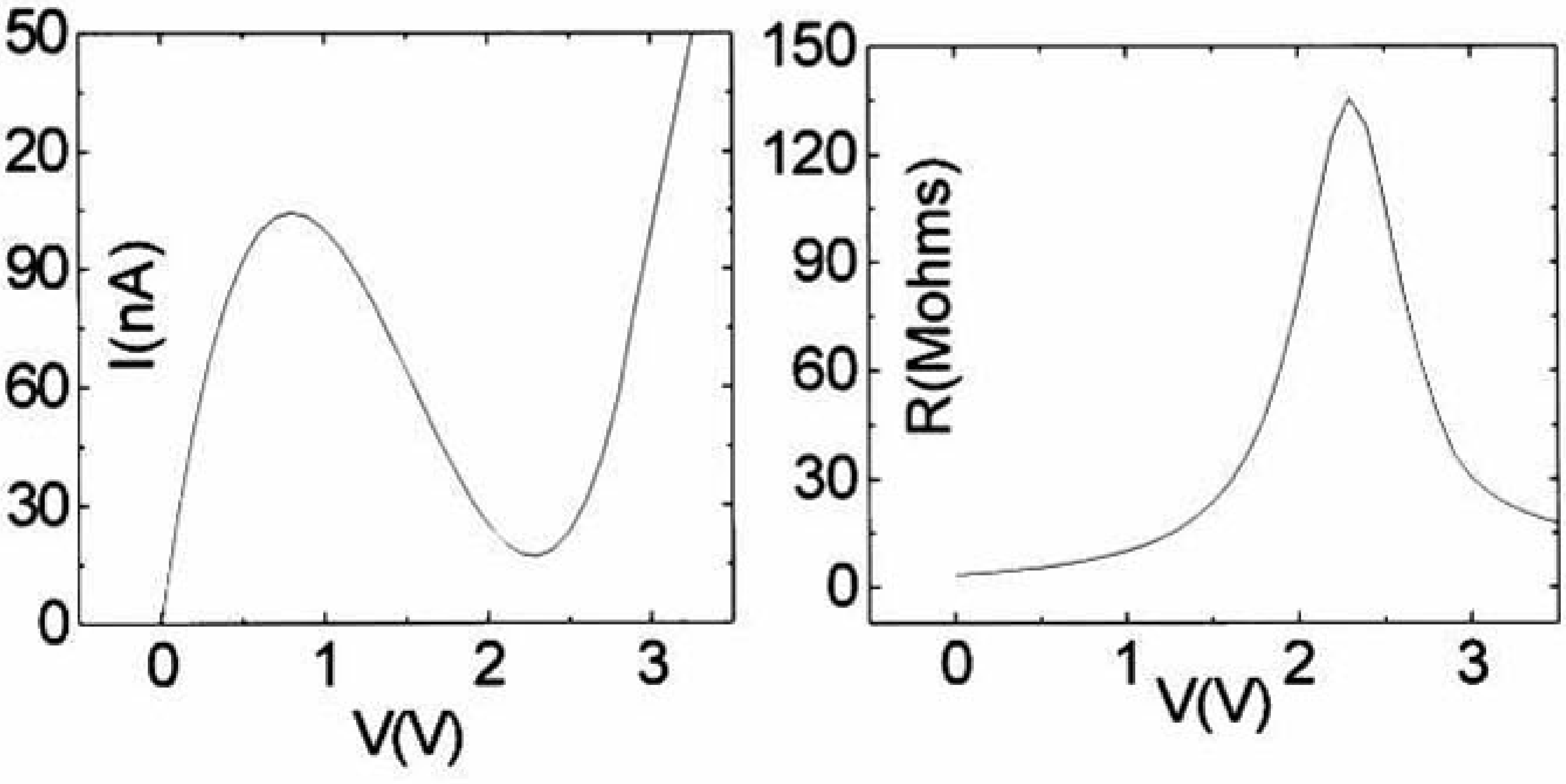


Figure 12, (a) Current-Voltage characteristics of NDR devices obtained by ab inito methods [2, 9, 13]. (b) Resistance table values for NDR devices.

3.2.3.-Simulation redundancy problem

Simulating a non-linear electrical component as a resistor changing its resistance as a voltage function involves a redundancy problem when calculations are made, for example if we are simulating a series circuit like the one in Figure 13, we will calculate the current in this circuit using the next equation:

$$I = \frac{V}{R_A + R_B}$$

And the resistance values R_A and R_B are obtained as a function using the voltage across the component,

$$R_A = f(V_A)$$
$$R_B = f(V_B)$$

But the only way we can calculate the voltages V_A and V_B is by multiplying the resistance values by the current of the circuit.

$$V_A = I \times R_A$$
$$V_B = I \times R_B$$

So it results that we require the same current we are looking to calculate from the beginning here is where it is the redundancy lies, then in order to solve these kind of system we need to use some initial values for the voltages or resistance values.

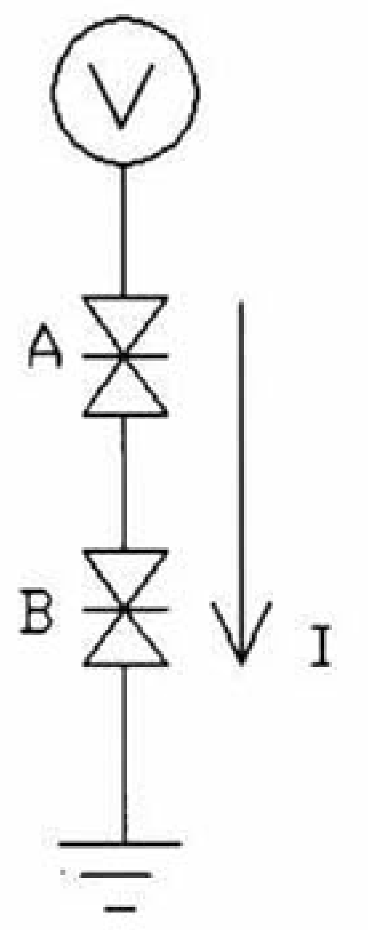


Figure 13, two in series circuit example.

3.2.4.-Deterministic method to solve molecular circuits

As we mention in the last point this kind of circuit simulation is sensitive to its initial conditions, thus we propose two methods to solve this circuit the first is to solve through a step by step simulation departing from zero volts at every input and output. Inputs are the nodes connected to external voltages and outputs are the ones unconnected to external voltages. We apply successive small increments to the inputs, solving the system matrix at every step, using the resistances corresponding to their voltages in the last step.

The small increment steps yield errors small enough to be practical. The algorithm repeats this cycle until reaching a desired input voltage. As result, we obtain the node voltages and device currents at every step, in Figure 14 is shown a block diagram of this algorithm used to solve a two in series circuit like the depicted in Figure 13.

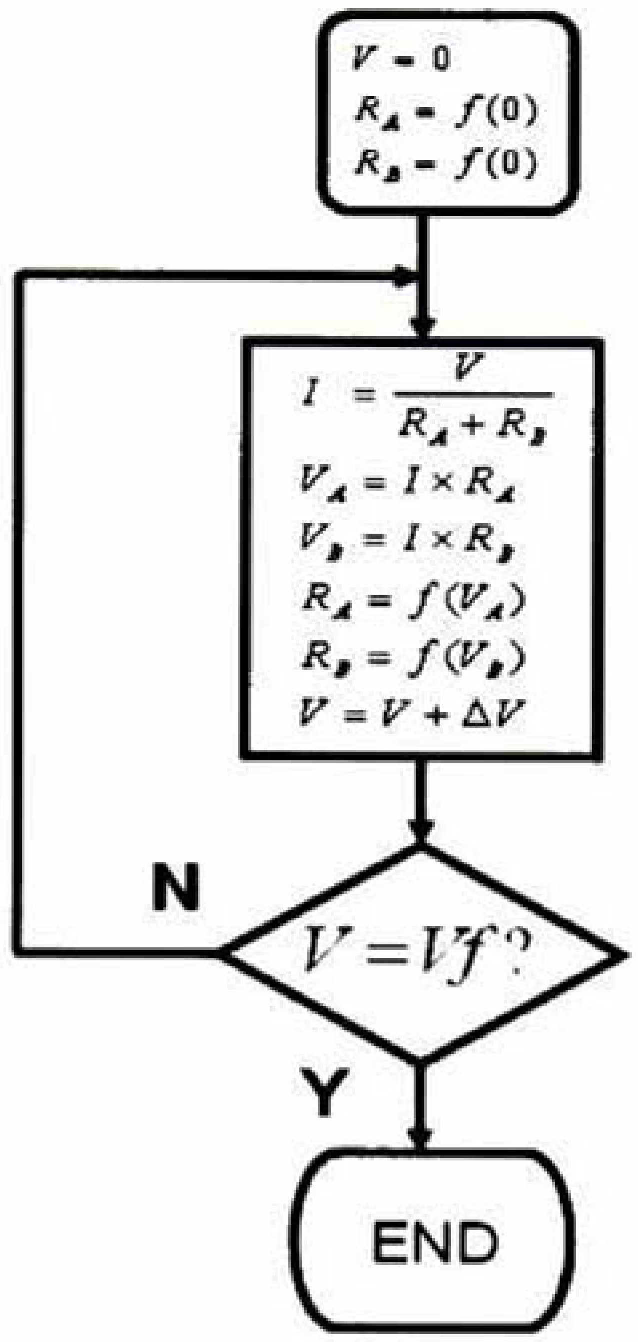


Figure 14, Deterministic algorithm block diagram to solve molecular circuits.

3.2.5.-Random method to solve molecular circuits

We also implement another algorithm using Montecarlo [55] methods, in which the circuit inputs are fixed at desired values and the outputs vary using randomly generated states. In an operational state, the output nodes do not source or sink any current because these nodes are not connected to external voltages; therefore, we apply external currents to the output nodes, and the algorithm modifies the nodes voltages in self-consistent cycles to reduce the external currents applied to the nodes until the currents vanish indicating that we get an allowed operational state for the molecular circuit. This procedure is repeated until the highest amount possible of allowed states is obtained.

This analysis yields a spectrum of allowed operational values; those could be useful to determine important properties of the molecular circuits such as the amount of molecules and configuration inputs necessary to perform a task and the optimal operation voltages for the input values.

For example, for an specific input set, we obtain a set of values in which the outputs operate, thus we have to configure the inputs in a specific way to have well-localized stable outputs otherwise we risk to have outputs easily perturbed by noise, in Figure 15 is shown a block diagram of this algorithm used to solve a two in series circuit like the depicted in Figure 13.

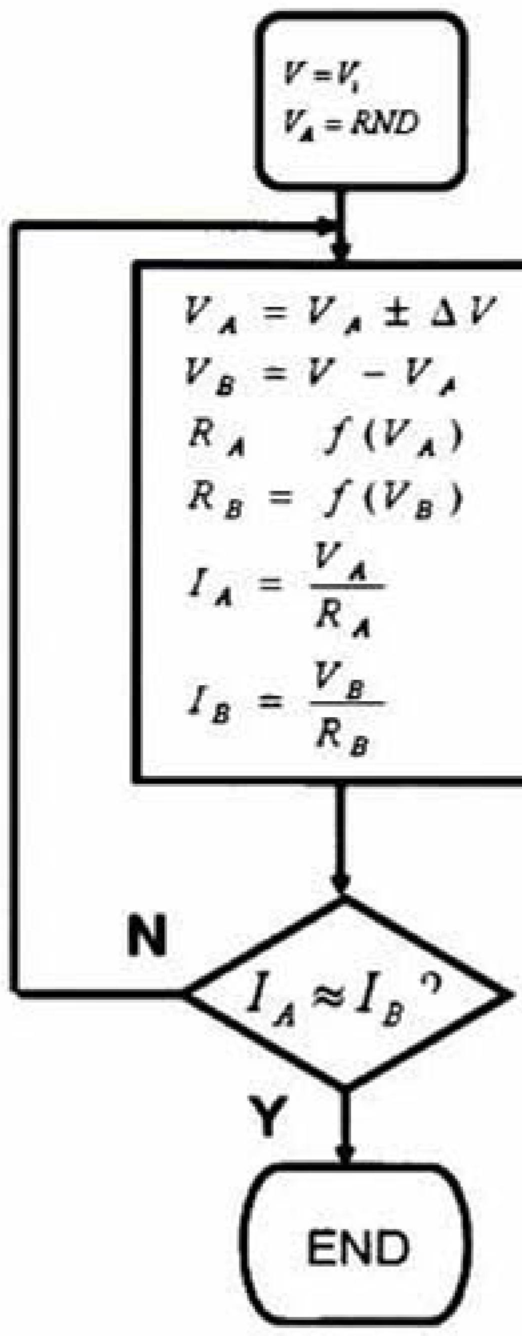


Figure 15, Random algorithm to solve molecular circuits.

3.2.6.-Stability Analysis for molecular circuits

Simulations and other work in this thesis about circuits of NDR devices have pointed the fact that some of the theoretical expected operation states for NDR circuits are unstable and only are present in a transitory manner, if we are going to use in a practical way the NDR circuits we must know how to identify a unstable state to have it in mind when designing a working device.

The approach we have followed to evaluate the stability of an operation state is simple, we just apply in the simulation small perturbation at each node, we evaluate the outcome of the perturbation, if the result oppose the perturbation we can said the system is self stabilizing and then is stable, if at contrary the result of the perturbation is additive to the perturbation the perturbation effect will increase so the that operation state will change meaning instability.

We can compare this system with the classical example of the stability of a ball over a curved surface as shown in Figure 16, a ball in a valley of a curved surface will keep its position if we apply an small force upon it, but a ball in a peak will move from its position when we apply any small force upon it.

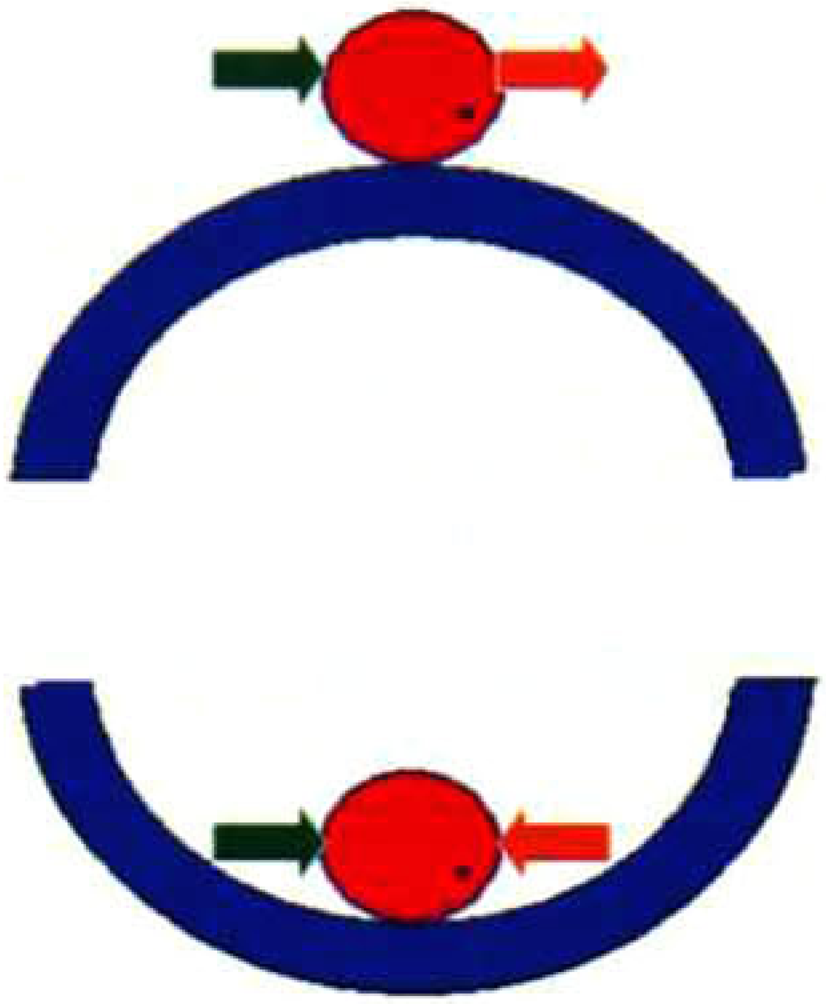
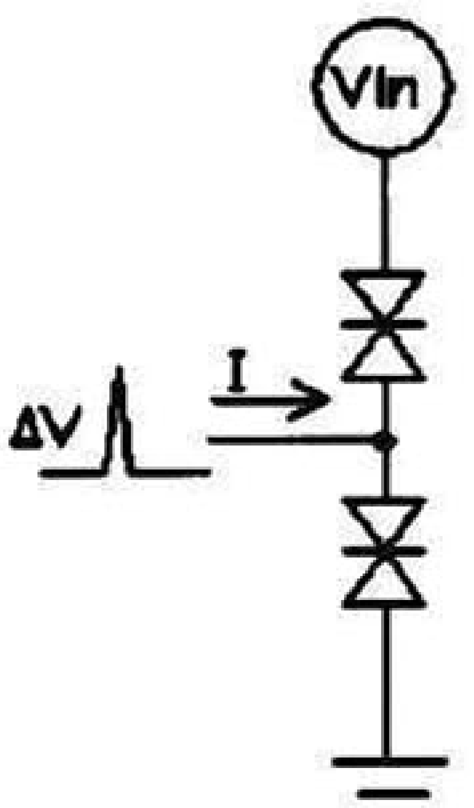


Figure 16, Classical example for stability definition: green arrows represent small forces applied to the ball, orange arrows represents the system response for these forces, when the two forces oppose the systems self stabilizes, when the forces over the ball sums the system is unstable.

In Figure 17 it can be seen an example of how to calculate stability in a two NDR in series circuit, this is a simplified version because larger circuits require the stability to be evaluated in many directions, a node can belong to many nets and it could be evaluated as stable in one net and unstable in other net, so every node must be evaluated at every net and has to be tested as stable in every node to be considered stable.



$$V_A = V_A + \Delta V$$
$$V_B = V_{in} - V_A$$
$$R_A = f(V_A)$$
$$R_B = f(V_B)$$
$$I_A = \frac{V_A}{R_A}$$
$$I_B = \frac{V_B}{R_B}$$
$$I = I_A - I_B$$

Figure 17, Example of stability calculation for a two in series NDR circuit, if I>0 then the circuit is considered unstable if I<0 then we know this circuit is stable.

3.2.7.-Software description

The procedure to perform and simulate nonlinear molecular-like behavior is programmed using Visual Basic 2008 [56].

The software development is divided in modules involving the circuit simulation. The first module builds the matrix to solve the circuit, the program panel shown in Fig. 18 requires from the user the schematic information relating the nodes with the components of the circuit.

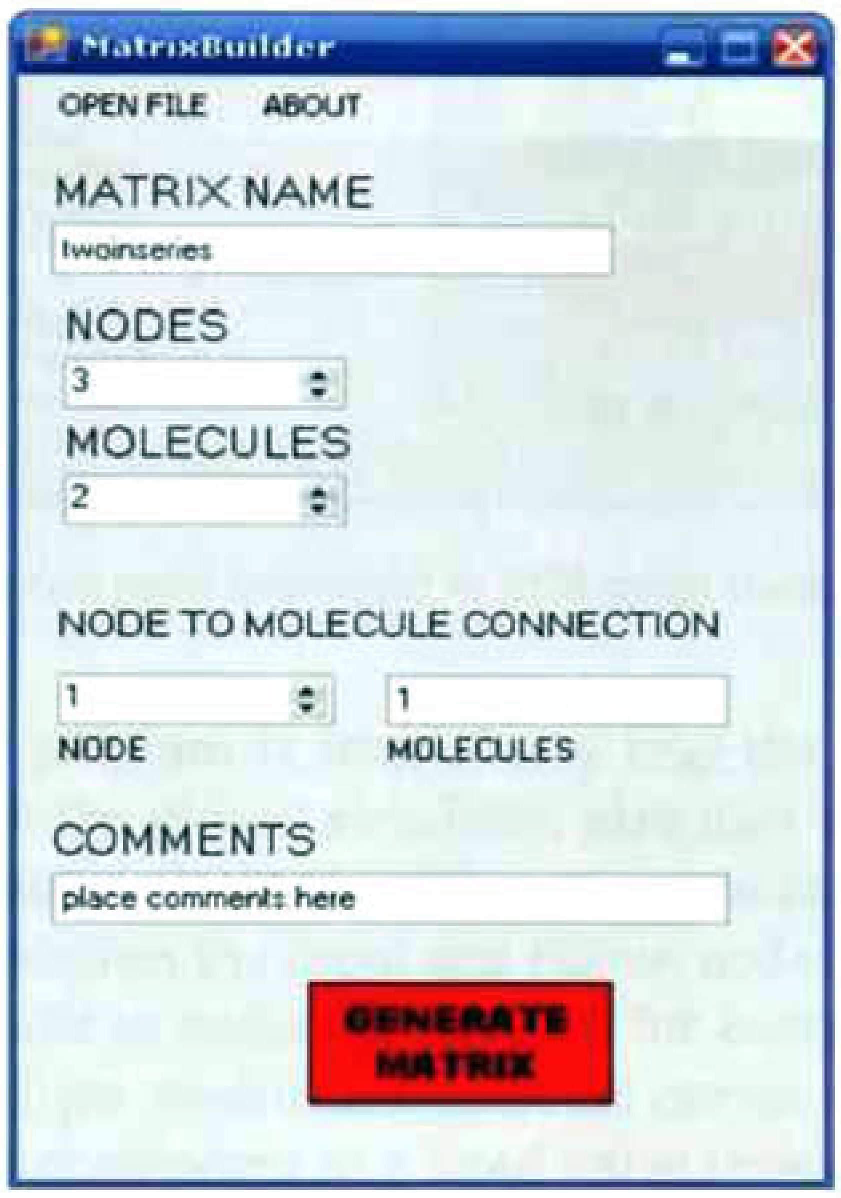


Figure 18, Program panel used to create matrix files for circuit simulation and analysis.

The second module is a circuit simulator that reads the matrix generated by the first module; the simulation parameters and steps are defined by instructions written by the user in a text window as shown in Figure 19. The results of the simulation are shown as text files created in a folder containing the outputs for every node configured to be watched. This module is able to make changes in the I-V signature of individual components and also can modify thermal noise amplitude of the circuit.

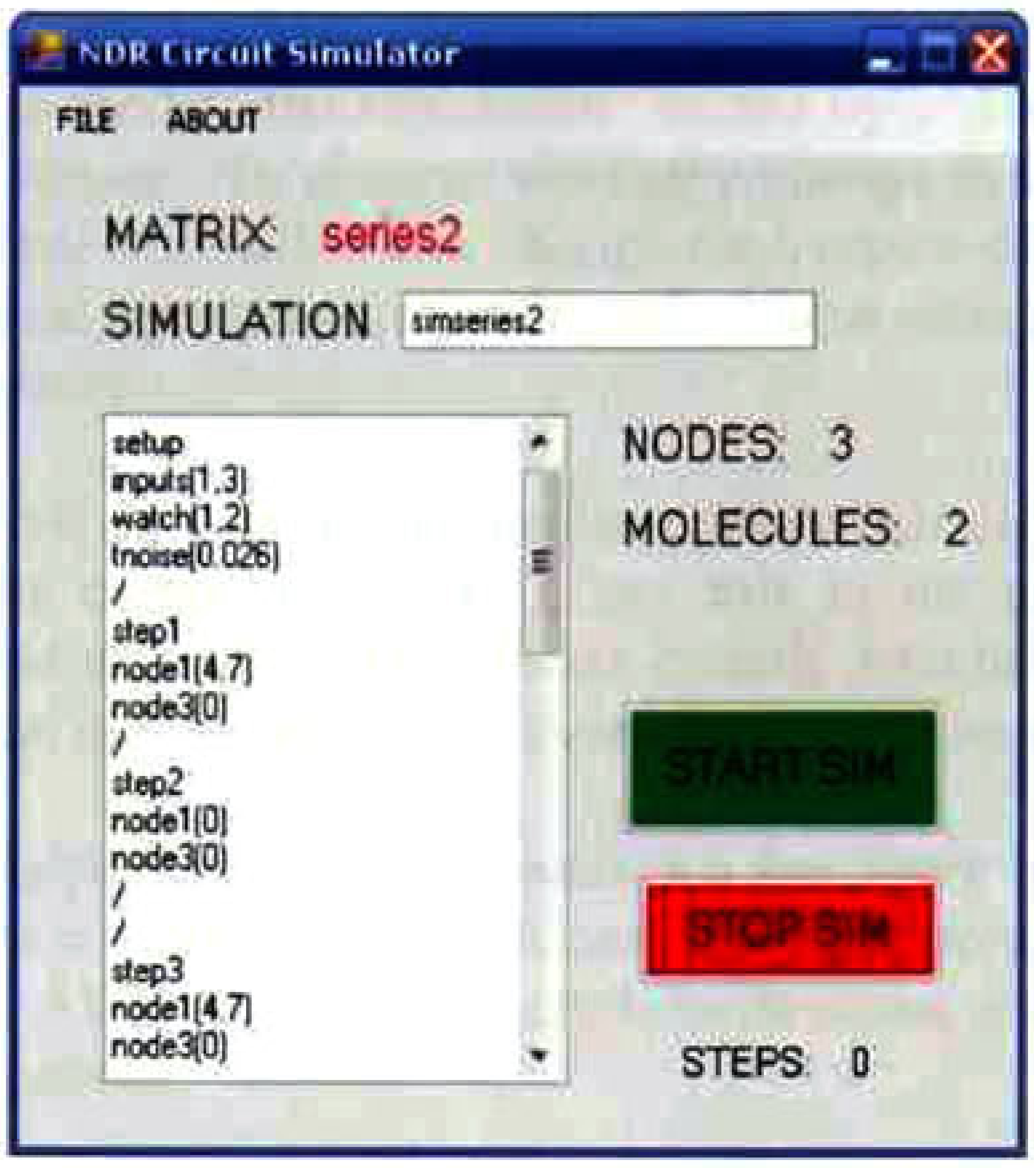


Figure 19, Program panel specialized for NDR circuit simulation.

The third module of the program is intended to find the operational states of the circuit. This module, similarly to the circuit simulator, also uses a matrix generated by the first module and implements a Monte Carlo algorithm to create random inputs to find valid operational states. The user determines the input and output nodes and the voltages applied at each input. Also, the user is able to make adjustments for every component as shown in Fig. 20. These changes can be slight modifications to the curves or changes in component behavior such to change an NDR component to a fixed value resistor for example.

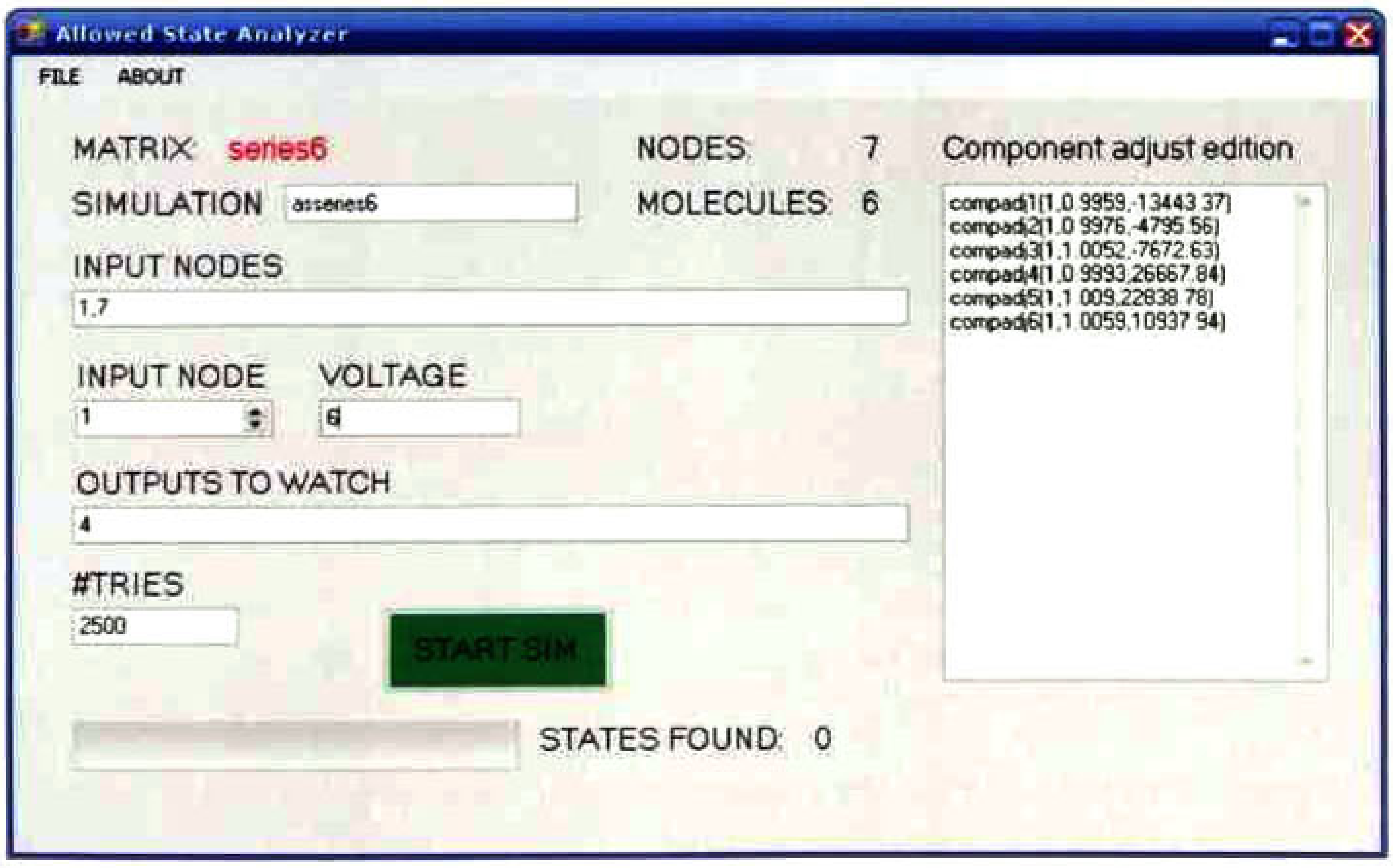


Figure 20, Program panel for finding multiple operational states for NDR circuits.

The software is able to modify the simulation "on the fly". This is very convenient when simulating a nanoCell sensor. To observe whether a change in the current-voltage of a device caused by an external interaction can change the outputs of the sensor, thus the detection of a specific chemical agent can be performed. These simulations can be used to estimate the sensibility of sensors.

Further simulation work done in this thesis has pointed that differences between the electrical properties from the components play a key role in the performance of NDR circuits, so it has been created an additional software module intended to generate files to modify randomly the electrical characteristics for every component in a circuit.

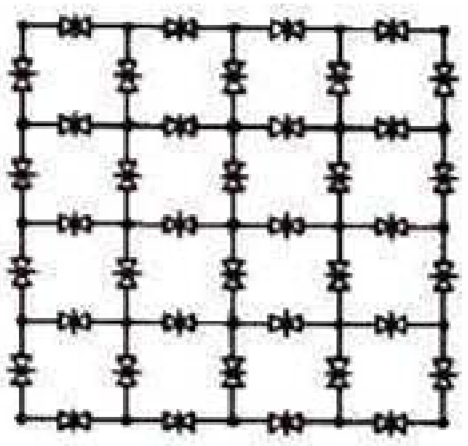
The program can be easily modified, just adding a few lines; we can place routines to extract specific information from the simulations, detect patterns, display variables, generate random inputs, etc. All these features help to understand arrays of NDR devices and also to design new applications.

3.2.8.-Software User Guide

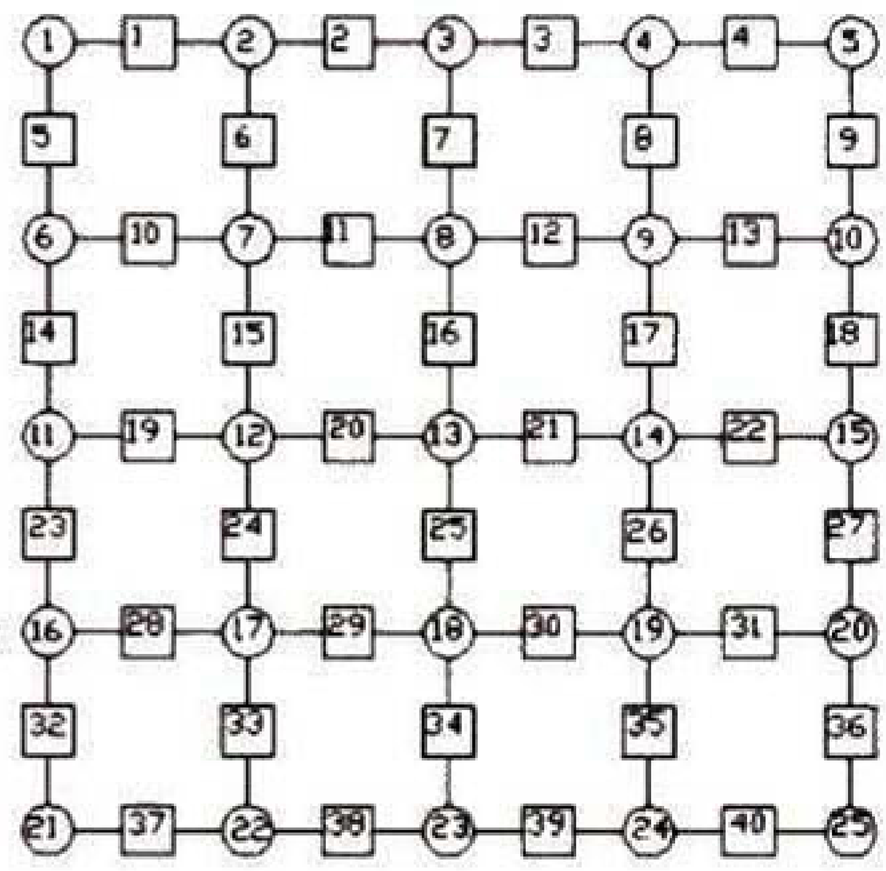
Use of Simulation Software for NDR circuits

STEP 1:

Define circuit schematics in a drawing numbering every node and every component.



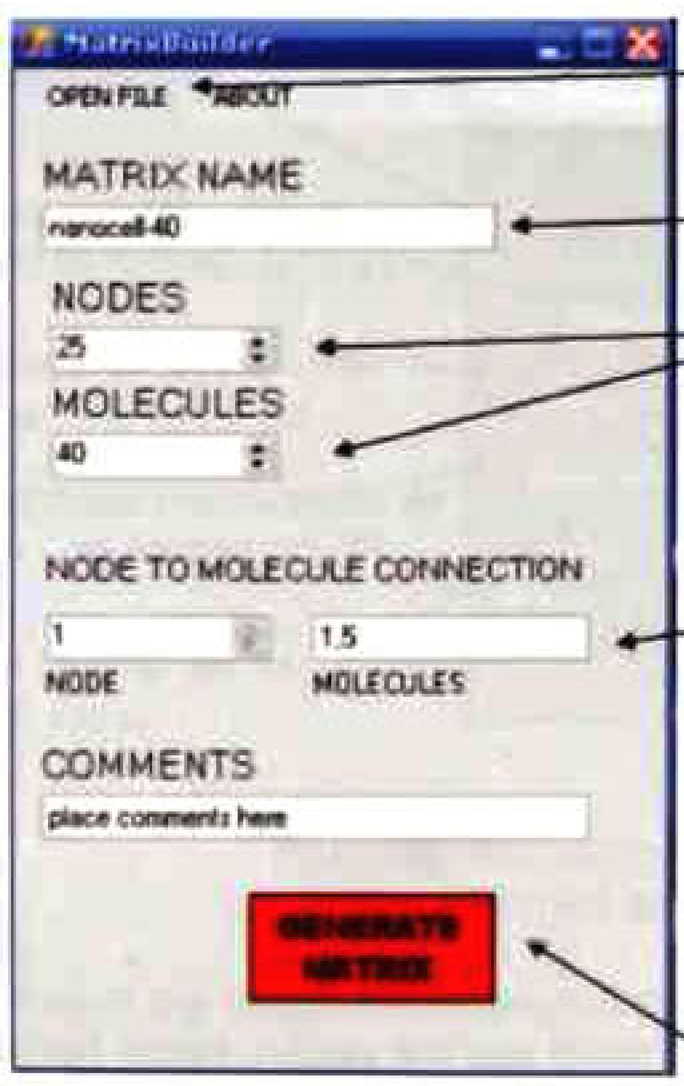
NDR Schematic circuit



In this example the circles represents the nodes and the squares the Components.

STEP 2:

Capture schematics data using the MatrixBuilder program.



The Matrix can be saved and opened later

Name the Matrix

Specify the amount of Nodes and Molecules

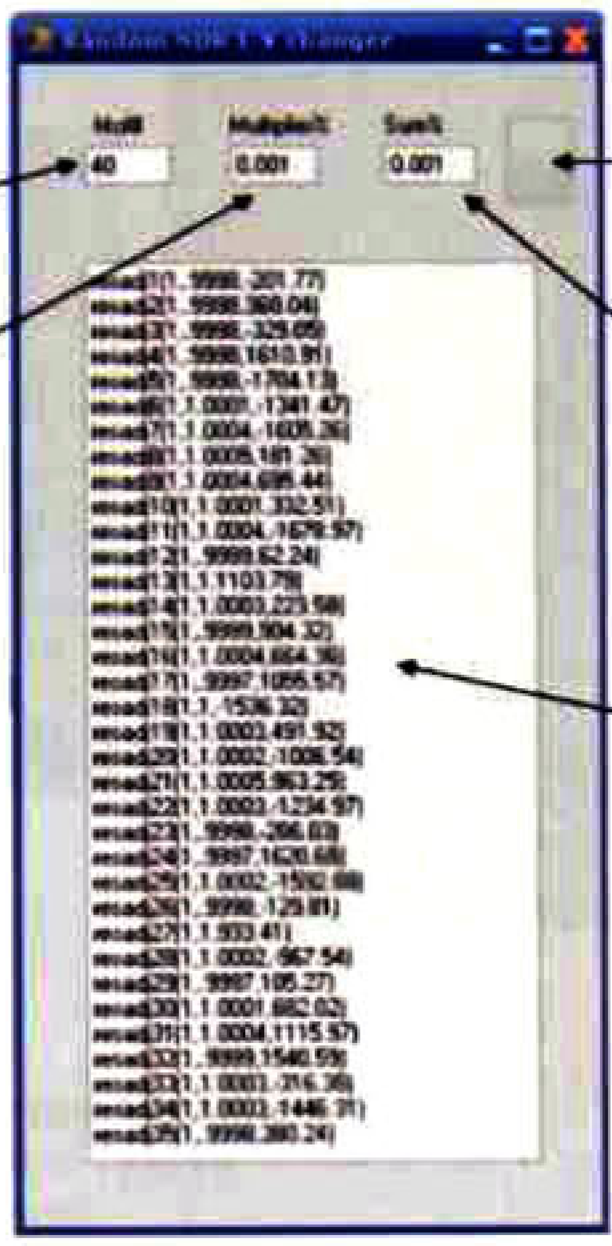
Capture how the Nodes are connected to the molecules in this case Node 1 is connected to Molecules 1 and 5.
You have to use this format: 1,5
Do the same for every node.

When all data captured press to generate Matrix, the program will ask for a folder destination

*File generated included in User Manual folder as nanocell-40.txt

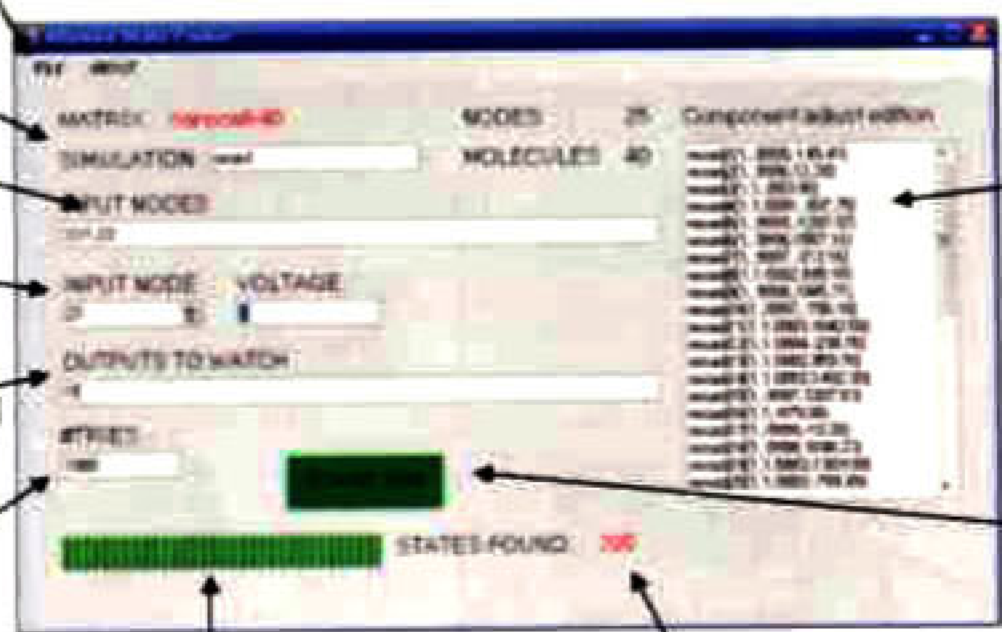
STEP 3:

Create a Text of changes in the I-V signatures for the 40 NDRs of the circuit



STEP 4:

Find operational States for a specific input to the circuit



*The files of the results if this simulation are found in the folder ncas1 in User Manual folder

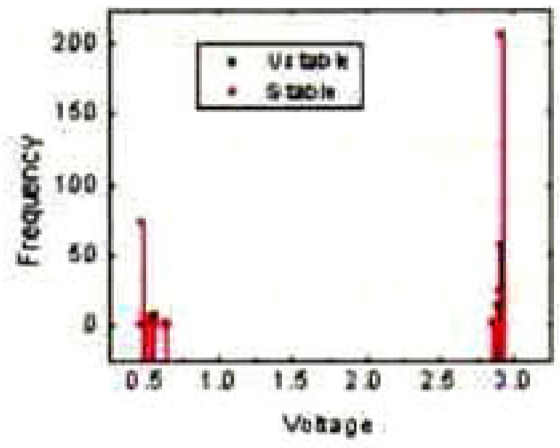
ALLOWED STATES FOUND IN EXAMPLE SIMULATION

siminfo.txt:

ncas1,
Creation date: 30/05/2008 09:28:11 p.m.
Simulation time(min): 107.23
Input nodes:3,11,23 /
Output nodes:15 /
#Tries:1000,
States found: 395,
Input voltages:
3:3,
11:0,
23:3,

node15.txt

Voltage	#unstable states	#stable states
.48	0	72
.49	0	7
.5	0	1
.53	0	2
.55	0	1
.56	6	0
.64	1	0
2.86	1	1
2.88	2	0
2.89	0	1
2.9	14	0
2.91	57	23
2.92	0	206



*The Allowed States Finder Software also generates a Matrix Text file as backup

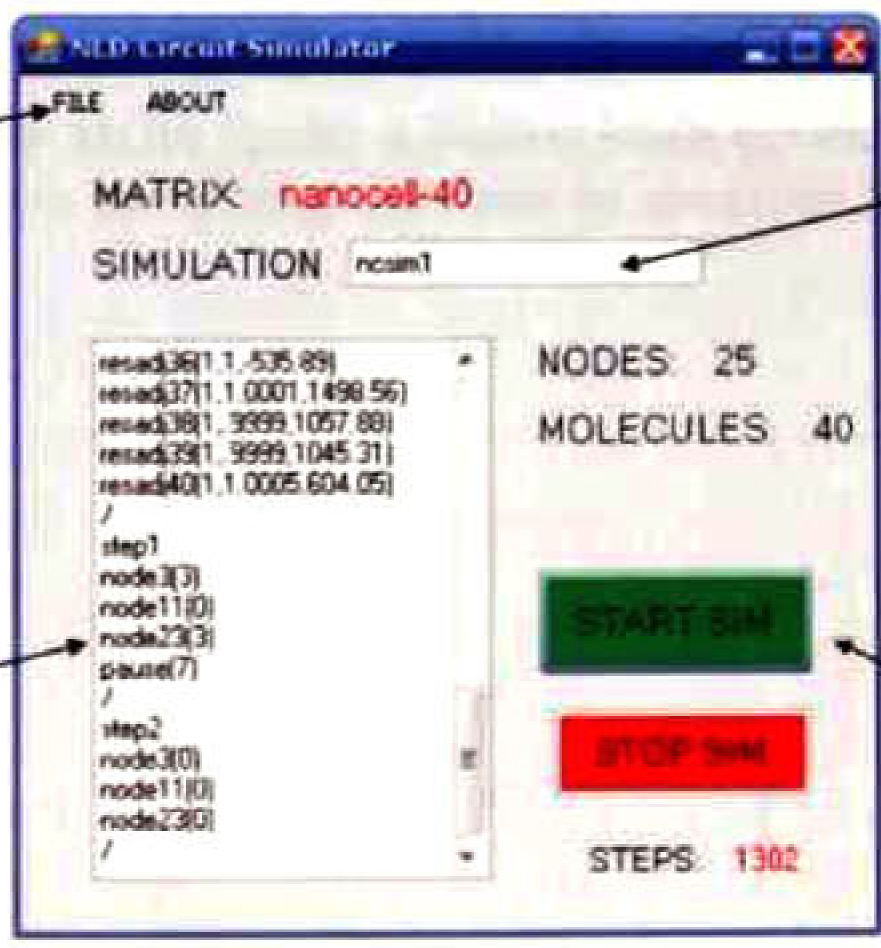
Plot of Allowed States of node15

STEP 5:

RUNING SIMULATIONS OF NDR CIRCUITS

To open Matrix files and past simulations

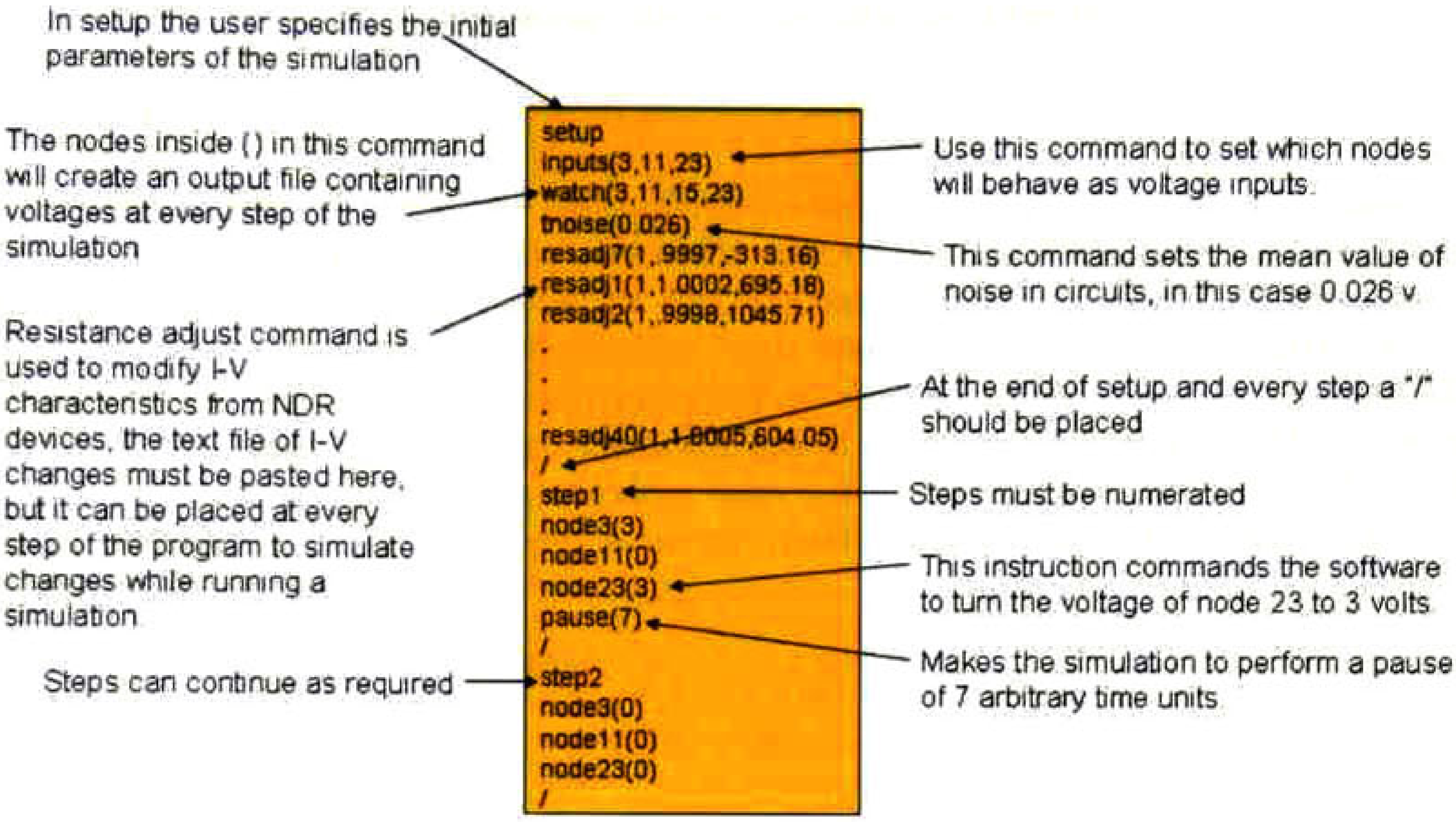
Name the simulation



The simulation parameters all steps are typed here as in a programming language

Press when simulation program ready to run simulation

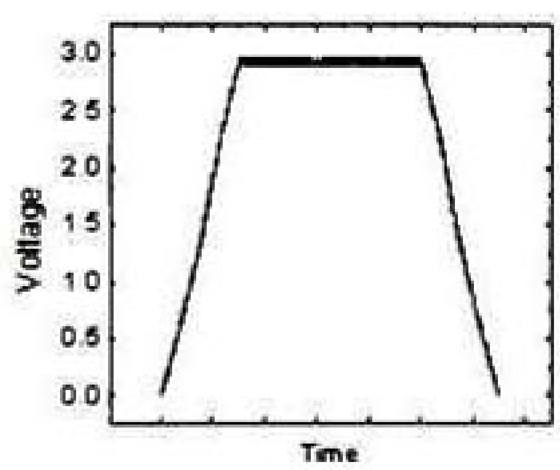
SIMULATION PROGRAMMING



All simulations always start at step1 from 0 volts at every node of the circuit

SIMULATION RESULTS

Files containing all the data about voltage and current of every watched node are created in a folder with the name of the simulation in a user selected location, besides in this same folder a Matrix back up file is created and a file containing info about the simulation as date of creation and time elapsed during simulation.



Plot of node 15 output from the example simulation

4.-Results and discussion

4.1.-Non-linear device emulator tests results

4.1.1.-Negative Differential Resistance Emulator results

Once having the emulator devices built, these were tested on a test bench using only an Oscilloscope and a Function Generator, Figure 21 shows the I-V signatures from the two molecular emulator devices. Despite that the two circuits are built and programmed identically; the curves are not identical to each other. This is due to the differences in characteristics from the photo-resistors and from their matching with the control LEDs. However, the slight difference in characteristics is not a major problem. The important point here is the fact that the two devices show NDR in the region between 0.75 and 1.5 Volts, from now we will call Device A to the highest resistance device and Device B to the lowest resistance device.

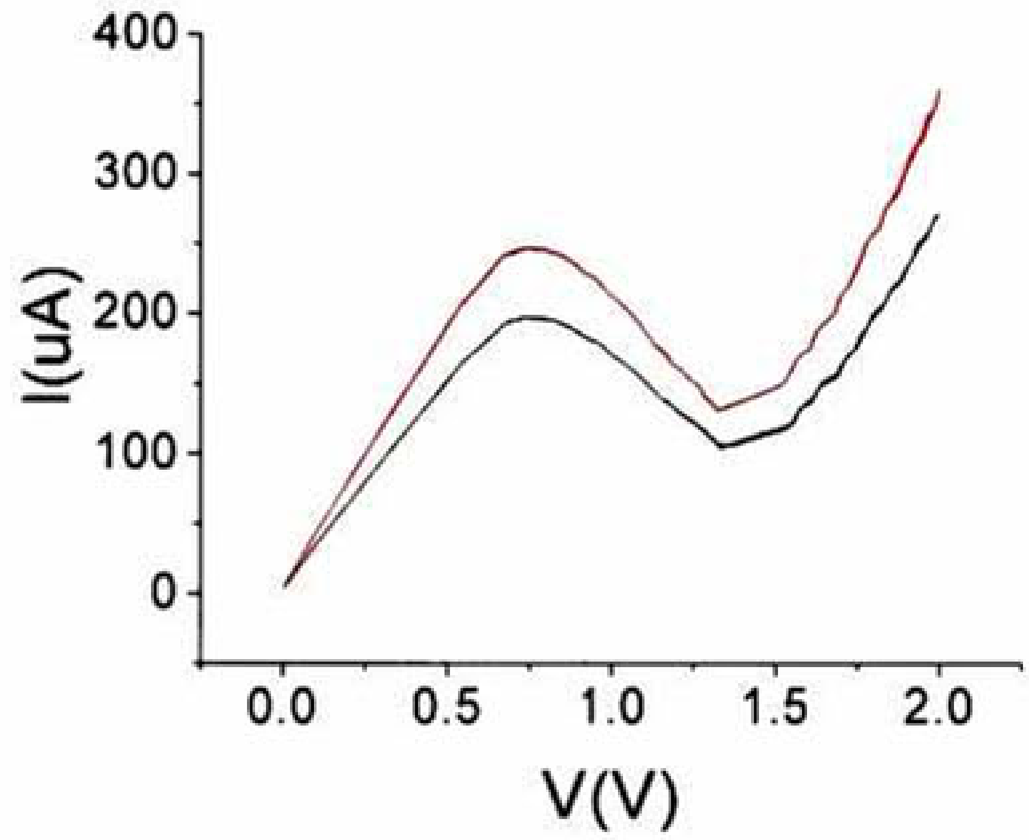


Figure 21, I-V Signature for two emulator devices, Device A (black) and Device B (red)

It have been analyzed a circuit of two devices in series configuration shown in Figure 13. The current vs. voltage curve for this series configuration in Figure 22 shows two peaks corresponding to the peaks of each device: The first peak belongs to device A which is the first to reach NDR region due to its higher resistance and the second peak belongs to device B.

We can compare the obtained curves from the ones expected from theory, looking at Figure 23 [2] the curves plotted from the measurements on the emulator devices and in Figure 22 the curve expected from theory. In this case, the curve we are emulating is the one marked in red and is the stable one. The curves from theory are similar but not identical to the curve measured; differences are caused by the different signatures from devices A and B.

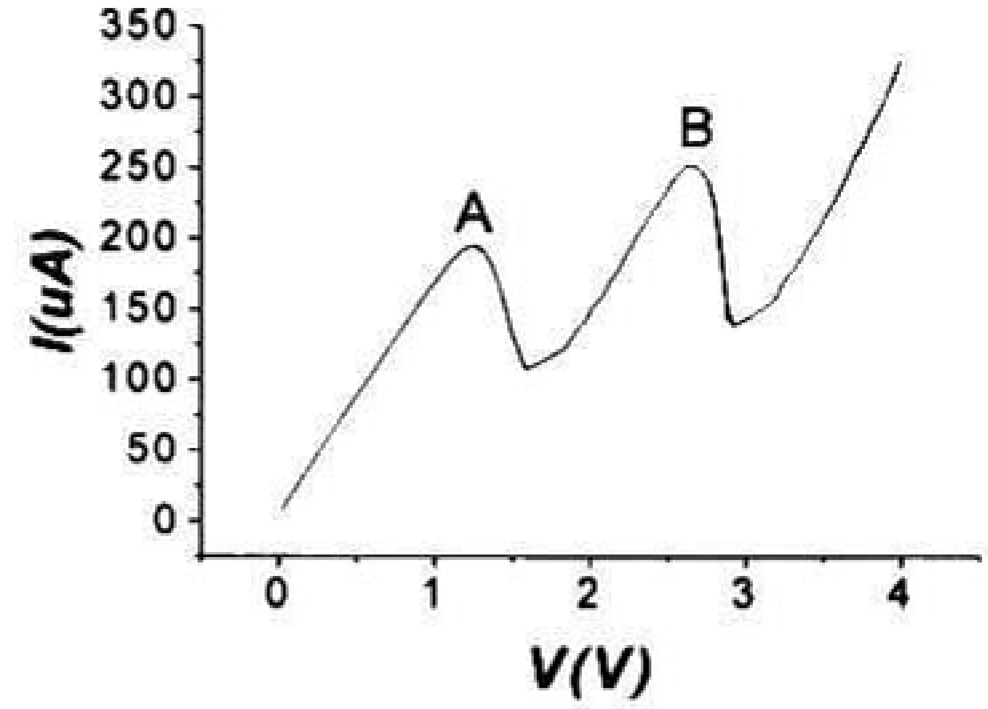


Figure 22, Current vs. voltage curve measured from two emulator devices in series

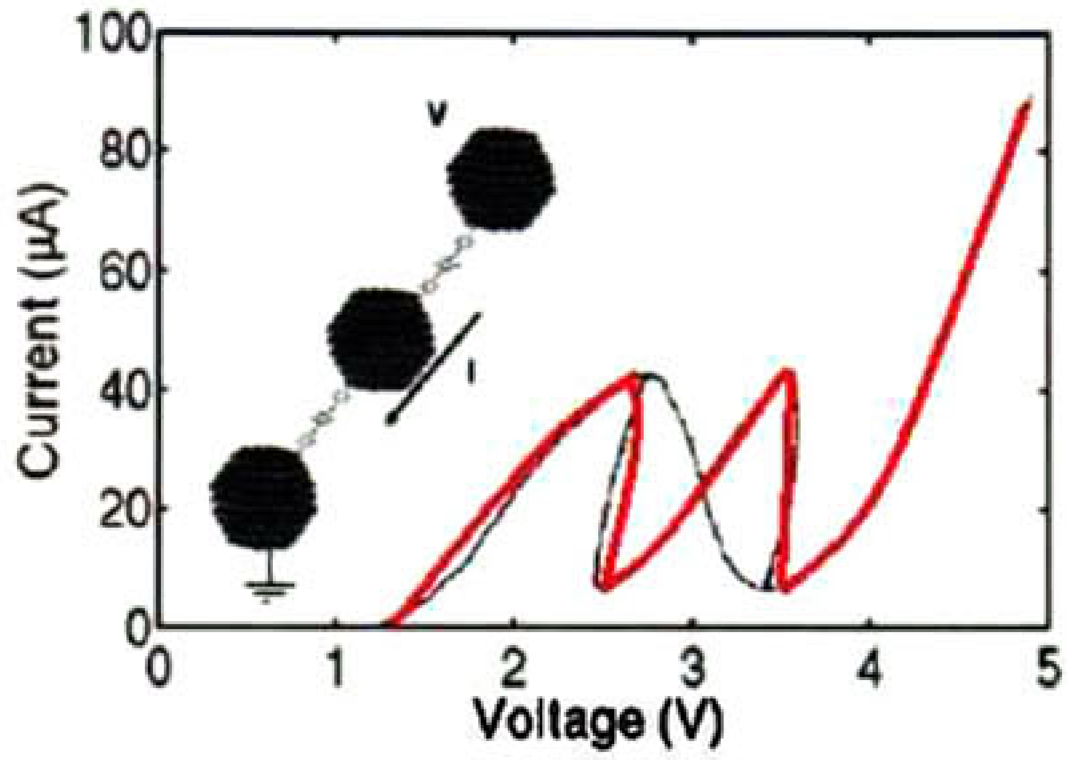


Figure 23, Current vs Voltage curve expected from theory, red part is the part obtained by measurements on two in series NDR emulator devices.

A unique situation is presented inside the region between the two peaks A and B in Figure 22. One device is operating in the NDR region (relatively higher in resistance) while the other is not (lower resistance). With such asymmetric structure, it is expected to have two well-defined voltage outputs either high or low voltage, depending on which device is operating in the NDR region. These two outputs can be observed using the circuit depicted in Figure 13. In this circuit, the relative resistance decides which device goes through NDR first. Figure 24, depending on the resistor configuration, shows the different type of outputs.

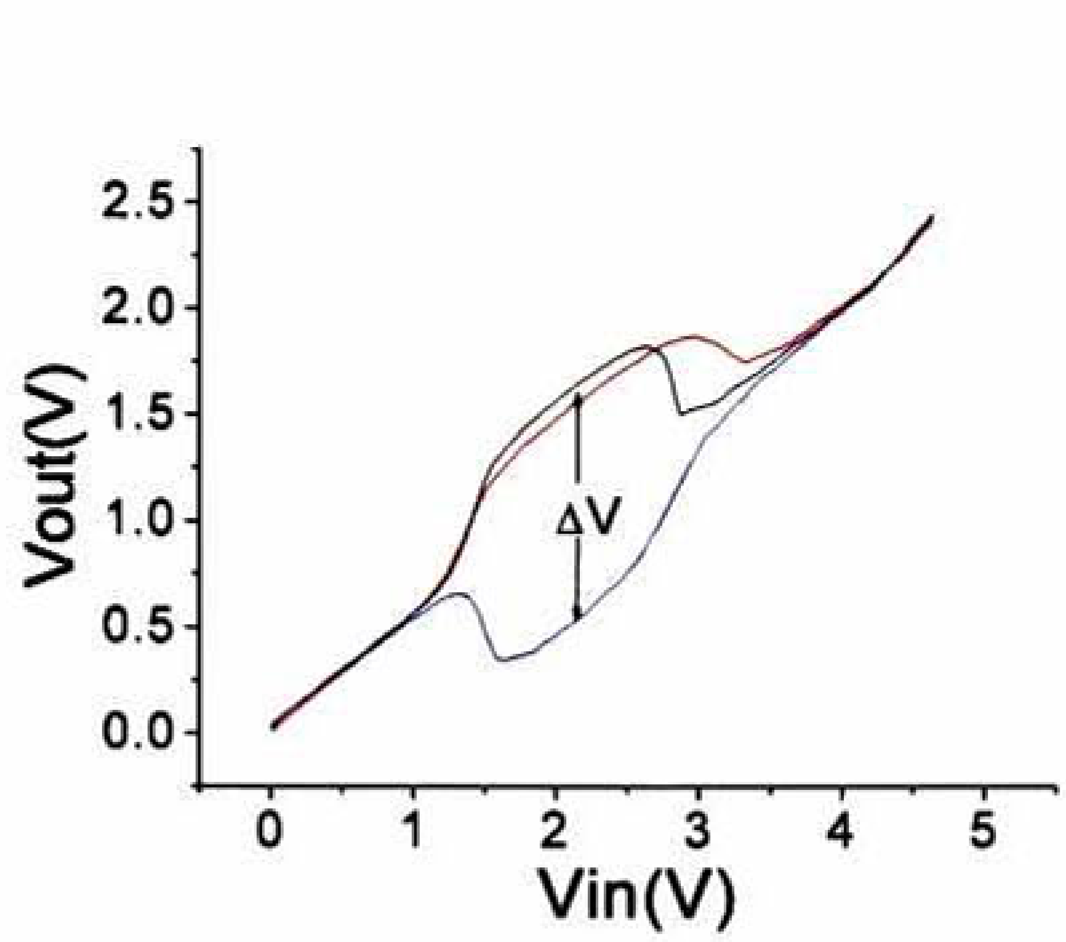


Figure 24, Curves for V_{out} depending on resistor configuration. Using no resistor(black), resistor connected to V+(red), resistor connected to ground(blue), From 1.5 Volts to 3 Volts, there are two possible V_{out} states having a ΔV difference between them. These two states could be latched applying pulses through the resistor and source voltage or ground.

When no resistor is used, the first emulator device to work in the NDR region is the one with higher resistance; that is why this behavior is similar to the one using the resistor attached to the voltage source.

The unstable state currents are present for a short time (Figure 25), when the circuit is latched from different stable points by applying pulses using the circuit shown in Figure 13. The pulse current is measured at different values of V_{in} when V_{out} latching is possible.

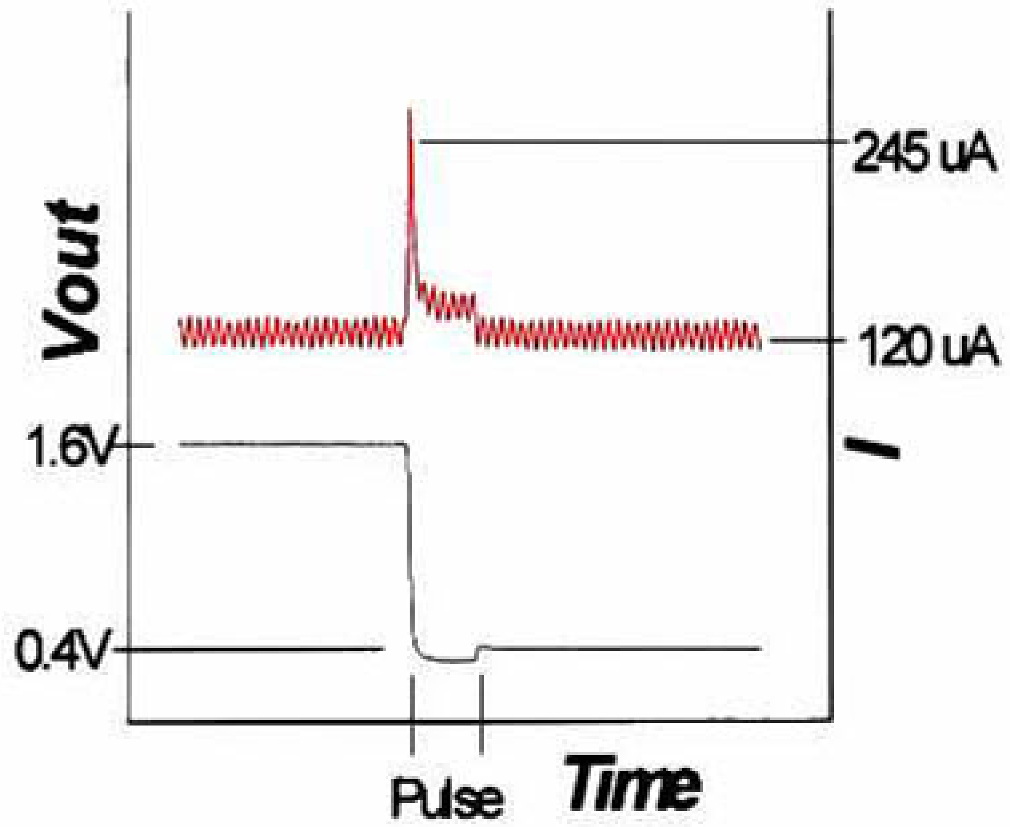


Figure 25, Transient current pulse at V_{in}=1.9V when V_{out} latches from 1.6 to 0.4 Volts.

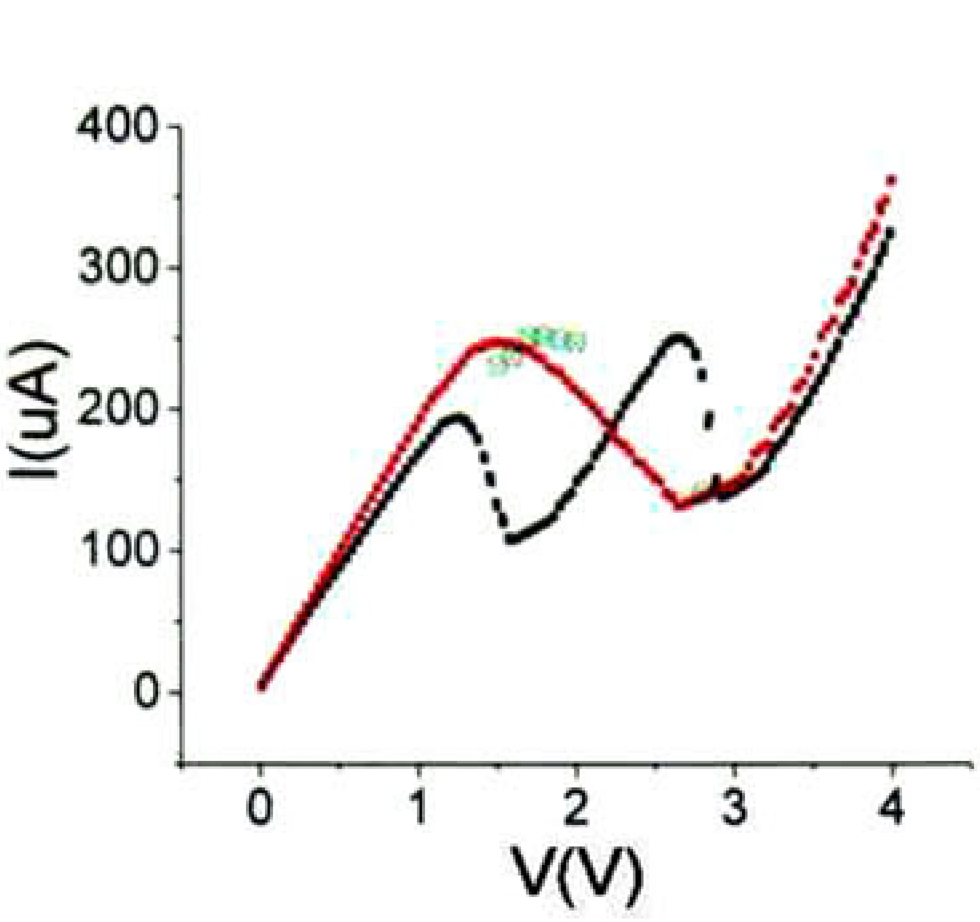


Figure 26, unstable state measurements at different voltages (green points). These measurements can be compared to stable state current (black) and unstable state approximation (red) obtained by multiplying by two, one device I-V.

The curve in red shown in Figure 4b labeled as "Double Voltage One-device curve" is only an approximation of the expected values. It is plotted on a double scale in the abscissa, thus the value of 4 V in the abscissa corresponds to a value of 2 V. The real unstable states are more complex due to the differences between devices A and B. Unstable state currents can be measured in the regions where the current difference among stable and unstable states is large. When these currents are similar, the unstable state pulses are not clearly observed nor measured.

4.1.2.-Memristor Emulator results

Using the same electronic programmable devices we have used to emulate NDR devices, we also have emulated Memristor[47] devices, in Figure 27 we can observe the signature plot for a Memristor emulator device applying 2 volts alternating voltage at 0.2 hertz, in this plot it can be seen a non-linear behavior, red arrows show the path of how this curve is plotted, this plot is very similar to the experimental data obtained by Williams et al. from real Memristor nano devices shown in Figure 28.

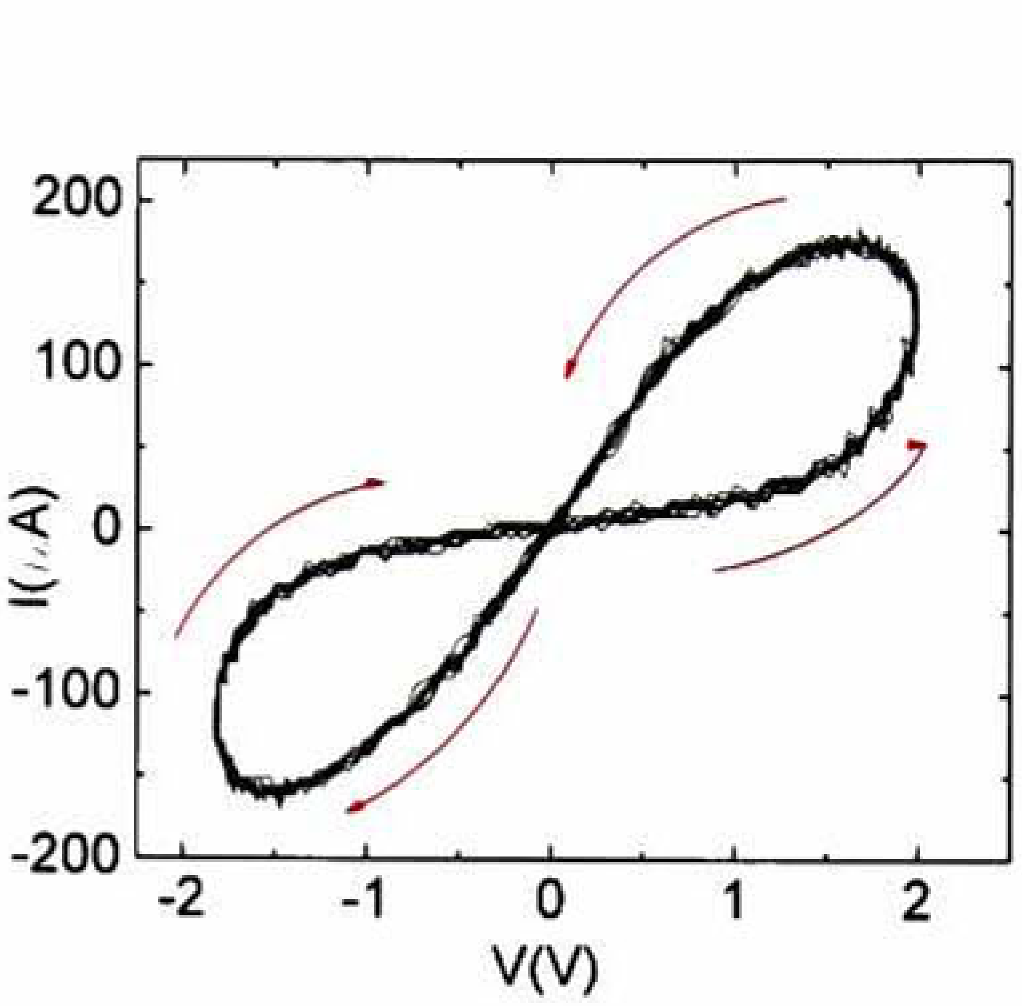


Figure 27, Current vs. Voltage plot for a Memristor emulator device, using 2 volts ac at 0.2 Hz, red arrows show the direction of the plotting.

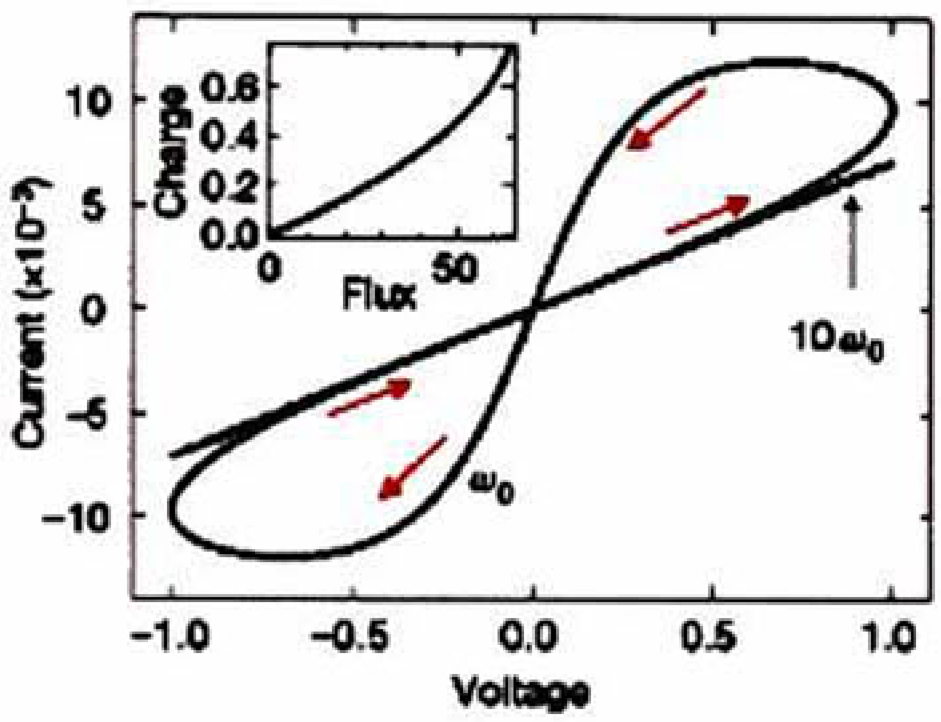


Figure 28, Current vs. Voltage Plot obtained by Williams et al. of a Memristor device[47].

To test frequency response we have plotted curves at different frequencies, at Figure 29 it can be seen a current vs. voltage curve plotted at lower frequency (0.01 Hz), this can be compared to the measurements done by Williams at Figure 30.

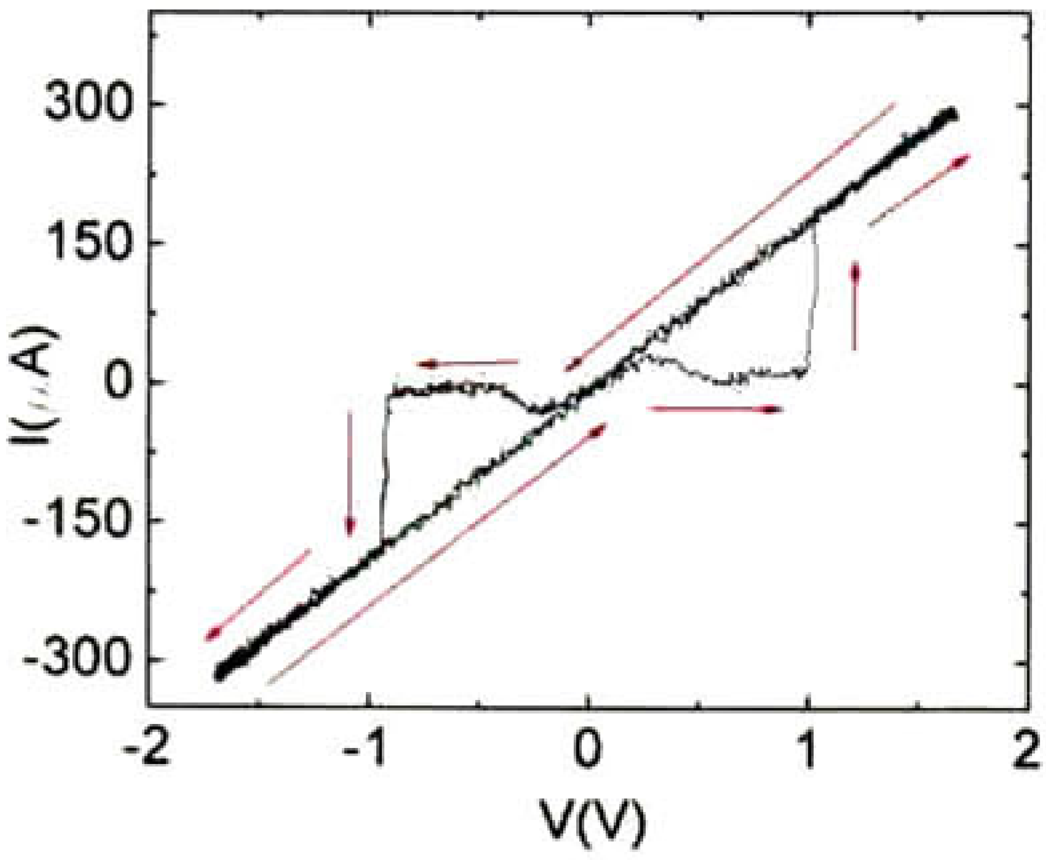


Figure 29, Current vs. Voltage plot for a Memristor emulator device, using 2 volts ac at 0.01 Hz.

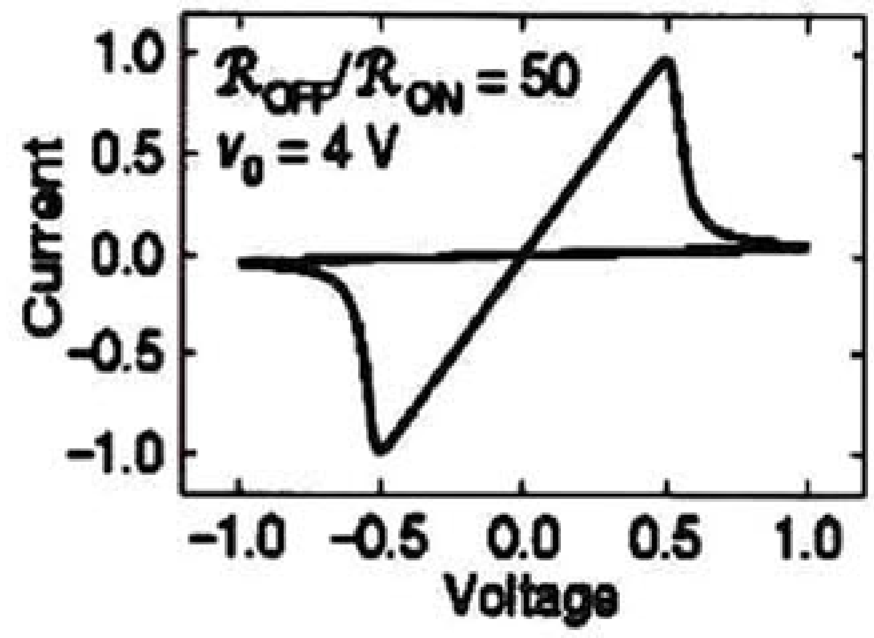


Figure 30, Current vs. Voltage Plot obtained by Williams et al. of a Memristor device[47].

4.2.-Computer software simulation results

4.2.1.-Deterministic simulations of two NDR devices in series

To understand how large NDR circuits work we must start to understand how small circuits work, a circuit of two NDR in series circuits, is known to behave as a bi stable latch circuit and some research groups are proposing this simple circuit to implement architectures like the Majority Logic Arrays[25], then our first simulations were directed to simulate a two in series NDR circuit like the one depicted in Figure 31.

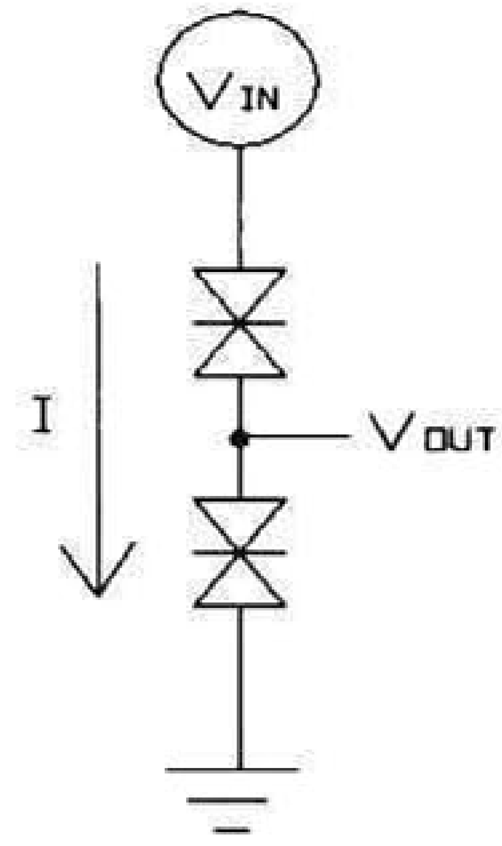


Figure 31, Two NDR devices in series simulated circuit.

First we have simulated this circuit using the deterministic algorithm assuming the two NDR devices to be identical, and we obtained a circuit behaving as a half voltage divider as it can be seen in the V_{OUT} vs. V_{IN} plot shown in Figure 32, it also can be seen in Figure 33 that the I vs. V_{IN} shows the same signature of one single NDR device but multiplied by two.

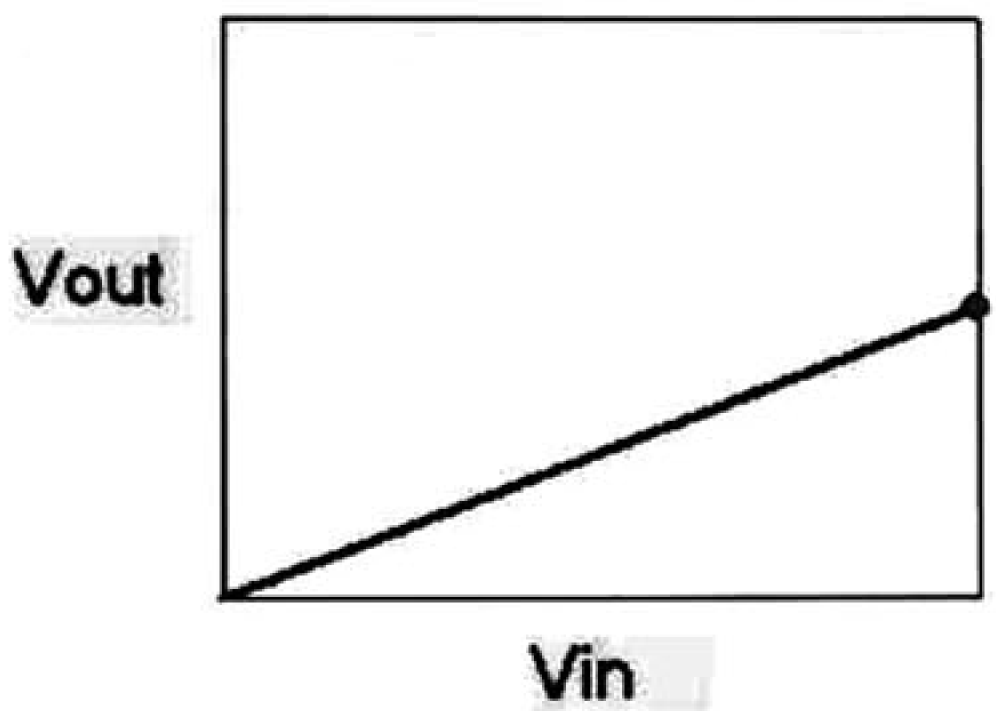


Figure 32, Vout vs. Vin plot for a two equal NDR series circuit.

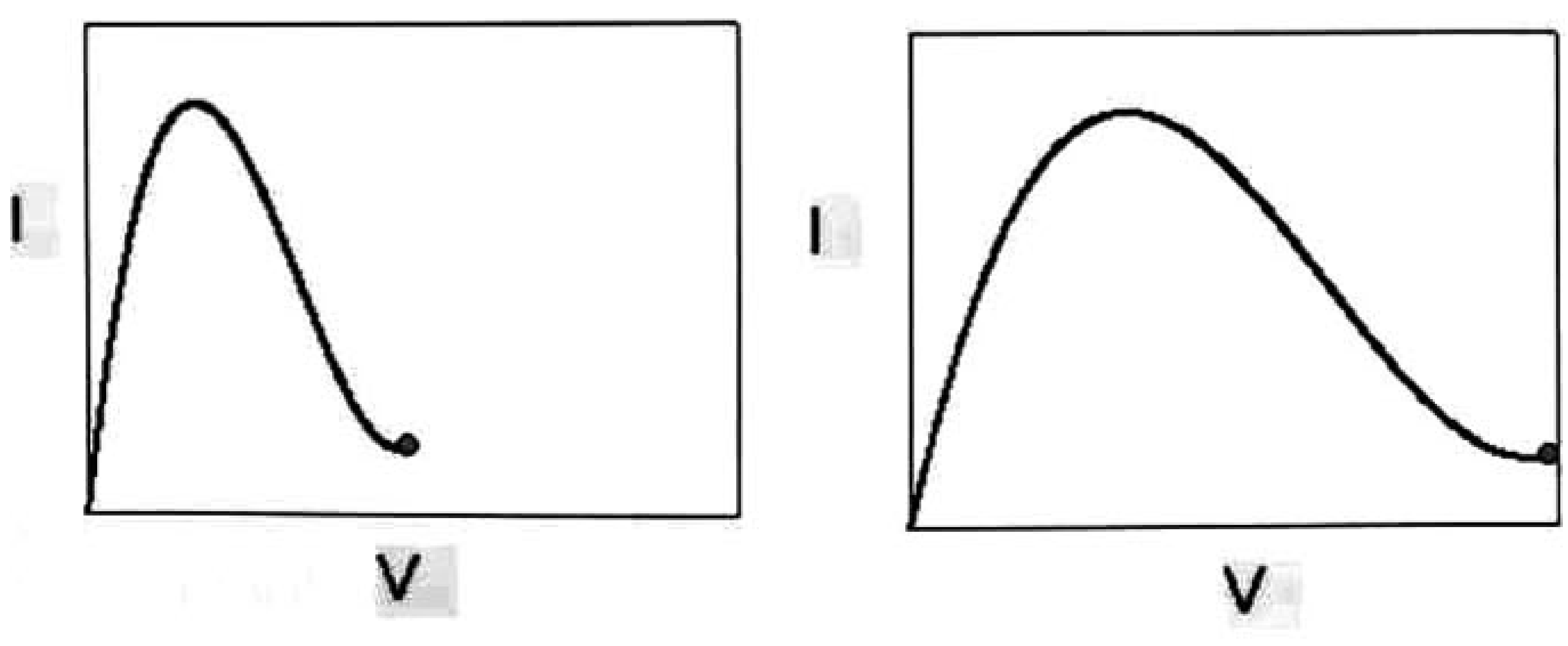


Figure 33, Left: One device I-V plot, Right: Two device I-V plot for a two equal NDR series circuit.

This simulation makes sense because this circuit obeys the laws of series circuits, but at the other hand we are not observing the multiple operation states expected from this circuit, and we are neither observing the behavior from the emulation of a two in series circuit of NDR devices, this point led us to test small perturbations in the form of noise to find new operation states, we have applied a random voltage distortion of 1 microvolt in magnitude at the node where the two NDR devices are connected, and we have observed a non-linear signature at the Vout vs. Vin curve which changed randomly yielding a high or low voltage output as show in Figure 34, it also has been observed how the I-V signature of the device has a two peak shape (Figure 35) similar to the one obtained from the emulation of two NDR series circuit.

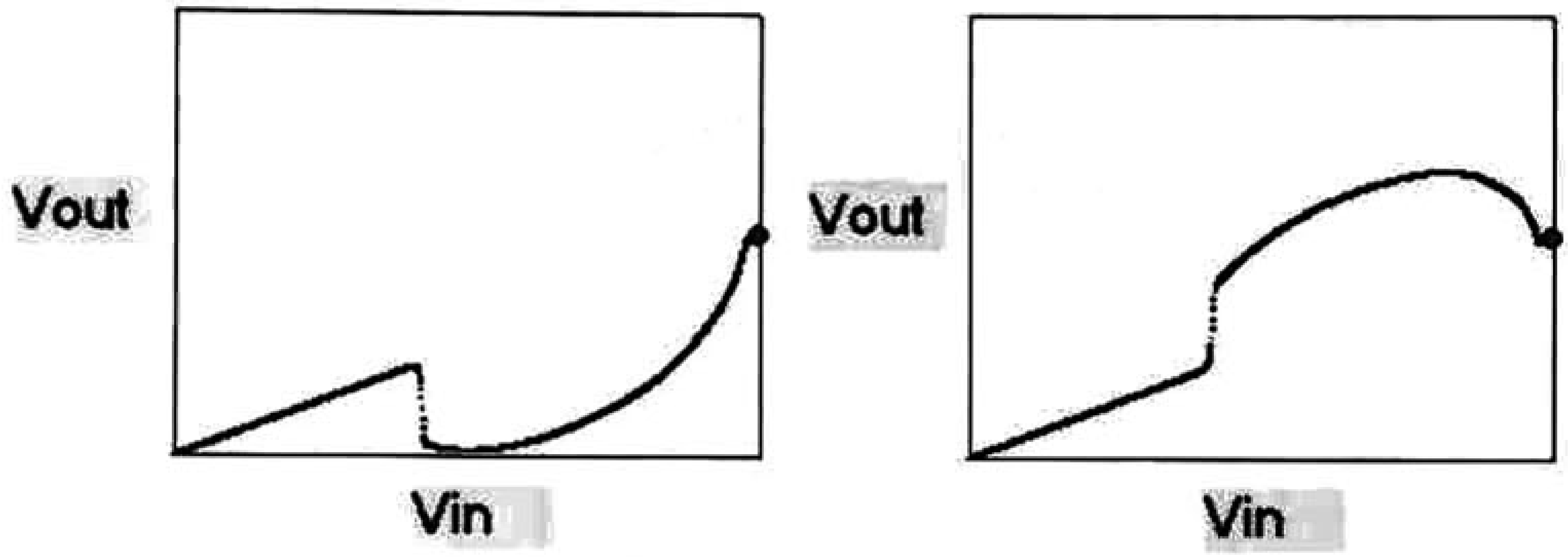


Figure 34. two possible voltage output operation modes for a two in series NDR circuit simulated including a small noise in the simulation.

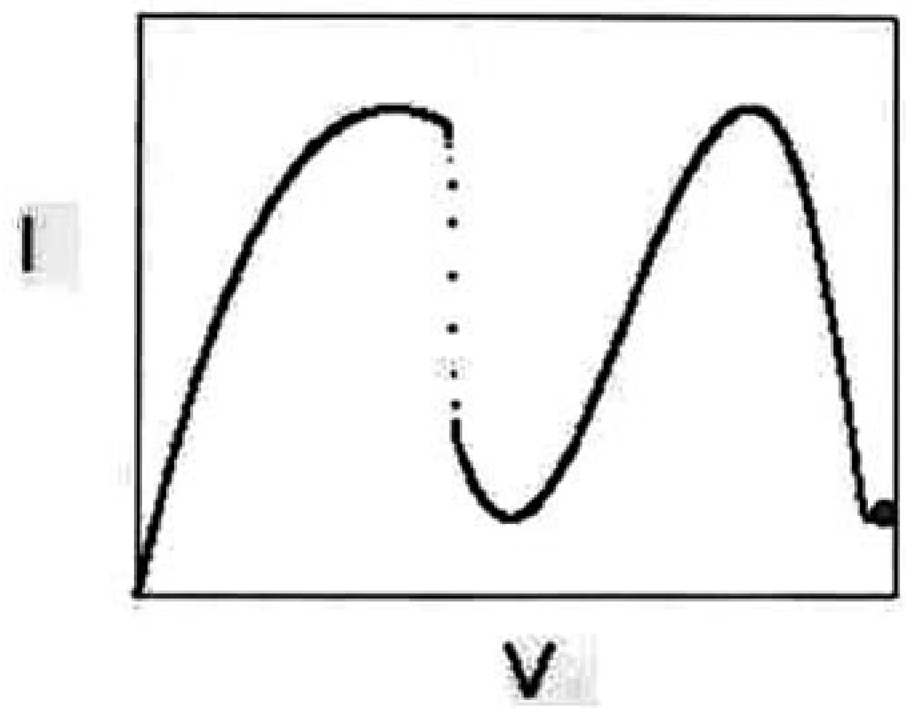


Figure 35, I-V signature plot for a Two in series NDR devices circuit including a small noise in the simulation.

This important difference between the results from the simulation, when adding and not adding noise in the calculations, points that the some operation states might not be stable so in our deterministic algorithm noise have to be included in the calculations, however we know that in real circuits noise is always present so to include a noise in the calculation makes this kind of simulation closer to reality.

In these simulations so far we have assuming also identical NDR behavior from both of the simulated devices, but this is an idealization because in the real word we expect differences due to many reasons like different contacts between molecules, substrate effects, interconnection cluster size differences, etc. So we have tested the effect of having small differences between the two NDR devices in the series circuit, for this test we applied a 0.1% change to one of the NDR devices by multiplying its resistance value by 1.001, to isolate this effect we have not assumed noise in the calculation, simulating using these parameters we obtained a Voltage output yielding always a low voltage level as shown in Figure 36 without random behavior, and the I-V signature has a two peak shape (Figure 37) similar to the one from the simulation adding noise.

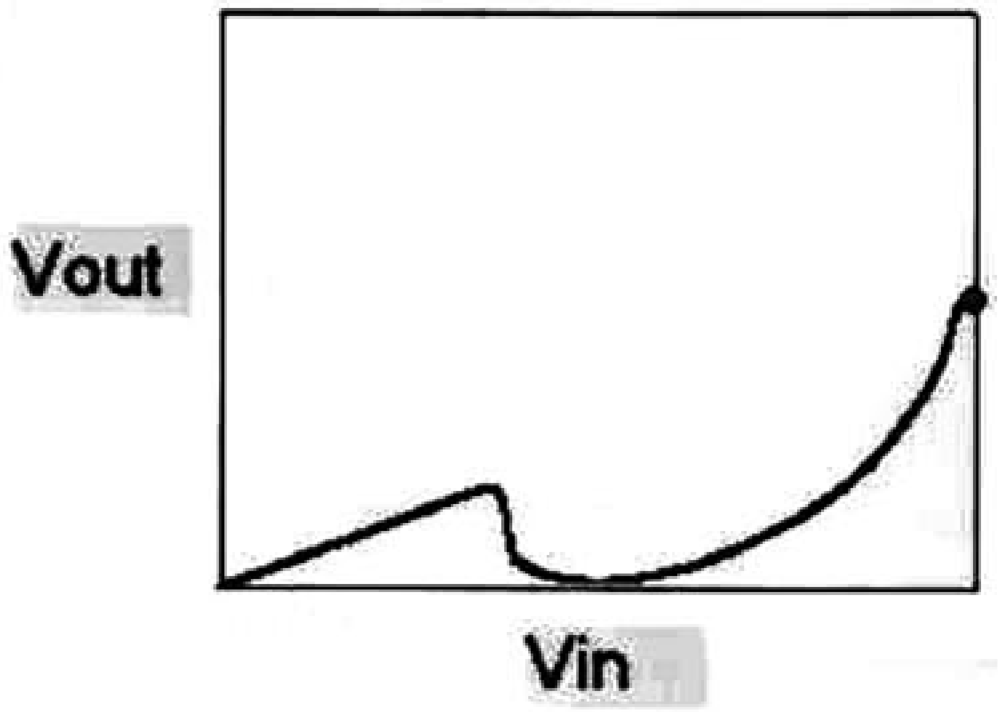


Figure 36, two slightly different NDR series circuit voltage output.

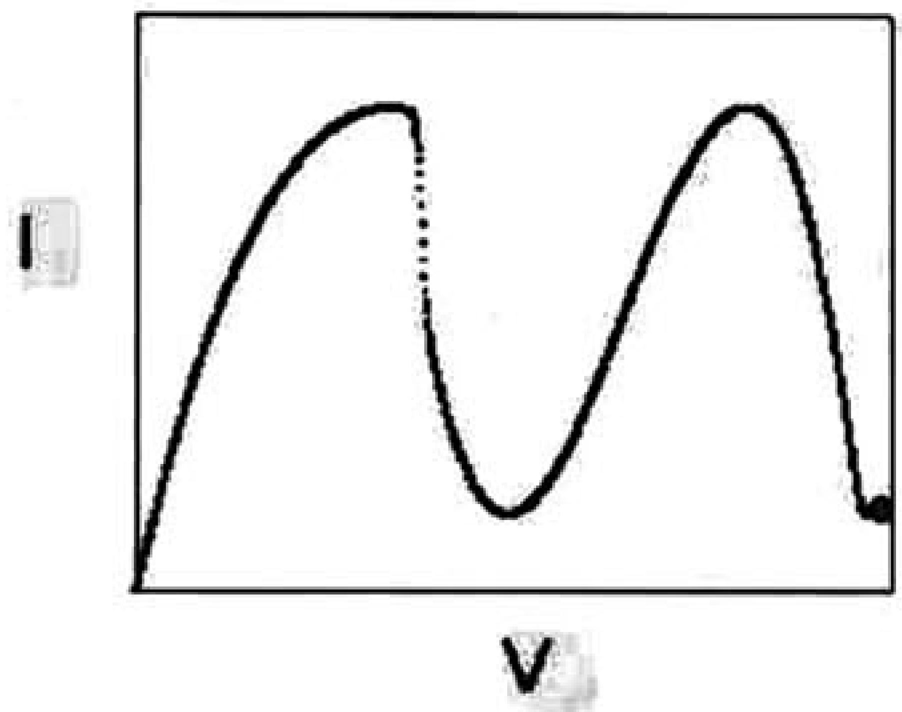


Figure 37, two slightly different NDR devices series circuit I-V signature.

This result about series circuits having small differences in the electrical properties from its components shows the importance of having in mind also these effects, so in further deterministic simulations we always include noise as well as differences from the components forming the NDR circuits.

4.2.2.-Montecarlo simulations of two NDR devices in series

We also have used the random Monte Carlo method to analyze a two in series NDR circuit, like the one from Figure 31, the Allowed state finder software module applies this algorithm and also performs an extra calculation to evaluate the stability for every operation state, in Figure 38 it can be observed a plot of the I-V signature and in Figure 39 it can be seen a plot of Vout vs Vin including all the operation states possible from a two in series circuit of two equal NDR devices, the different colors on the plot specify the stability of each state.

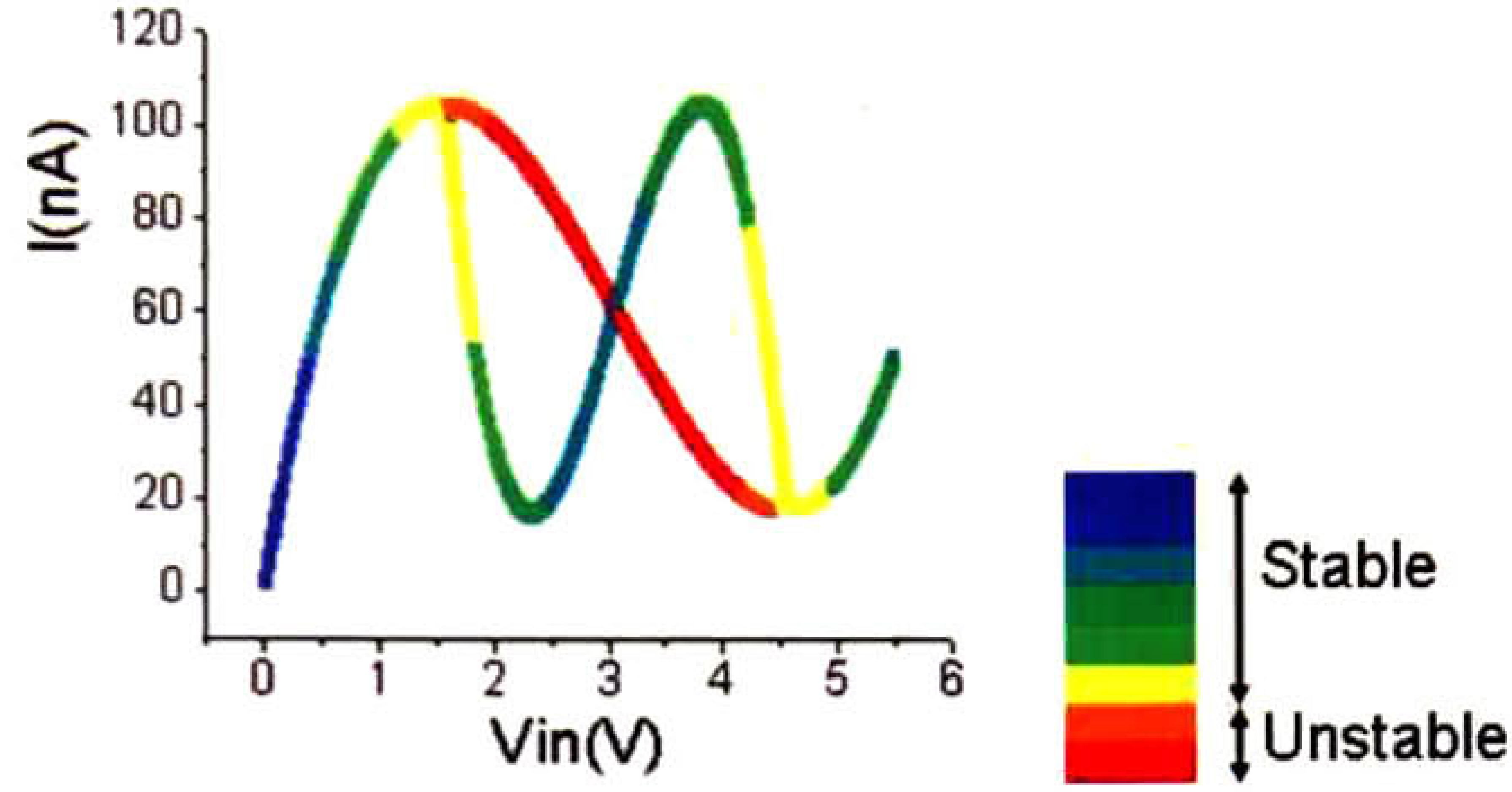


Figure 38, I-V curve including all the operation state of a two in series circuit for two equal NDR devices.

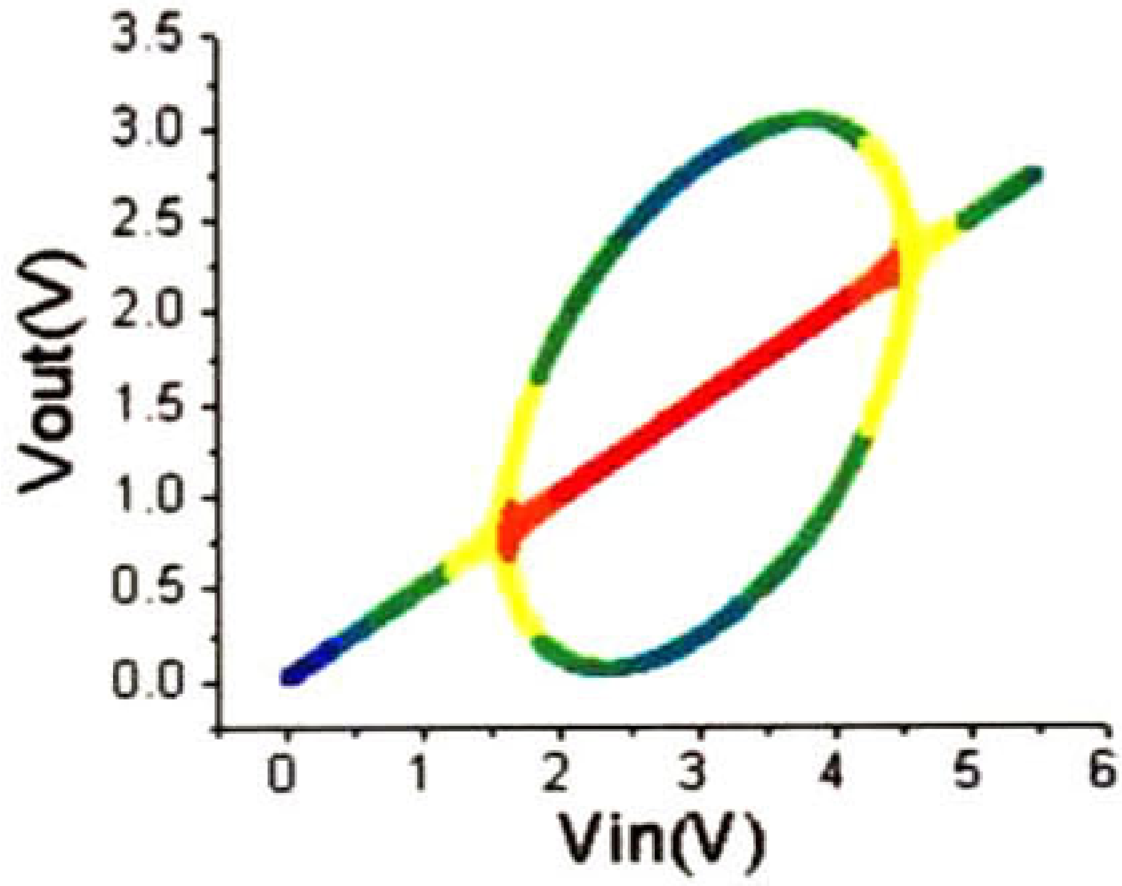


Figure 39, Vout vs. Vin plot of all operation states of a two in series circuit for two equal NDR devices.

If we analyze these plots we will see that the two peak shape is the most stable trace for the I-V signature, we will also notice an unstable state in red color, in the Vout vs. Vin plot we can see the existence of two possible stable states and a third unstable mid voltage state.

We have used this same tool to plot the operation states of two different NDR devices, then it is obtained a much more complex I-V signature (Figure 40), and a Vout vs Vin plot (Figure 41) in which the Vout is forced to leap abruptly depending on the Vin value. The behavior shown by this circuit might look like a Hysteresis effect.

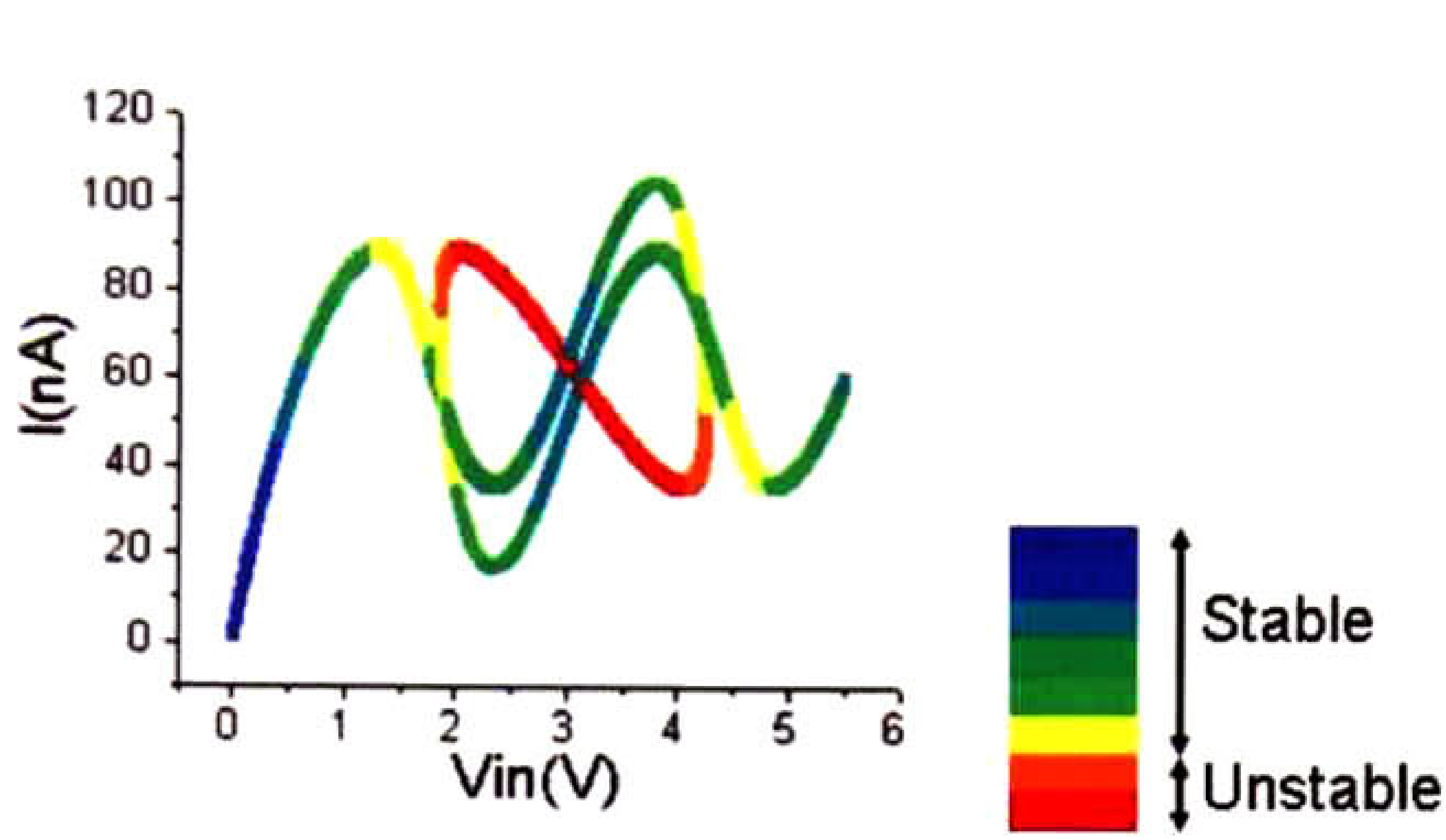


Figure 40, I-V curve including all the operation state of a two in series circuit for two different NDR devices.

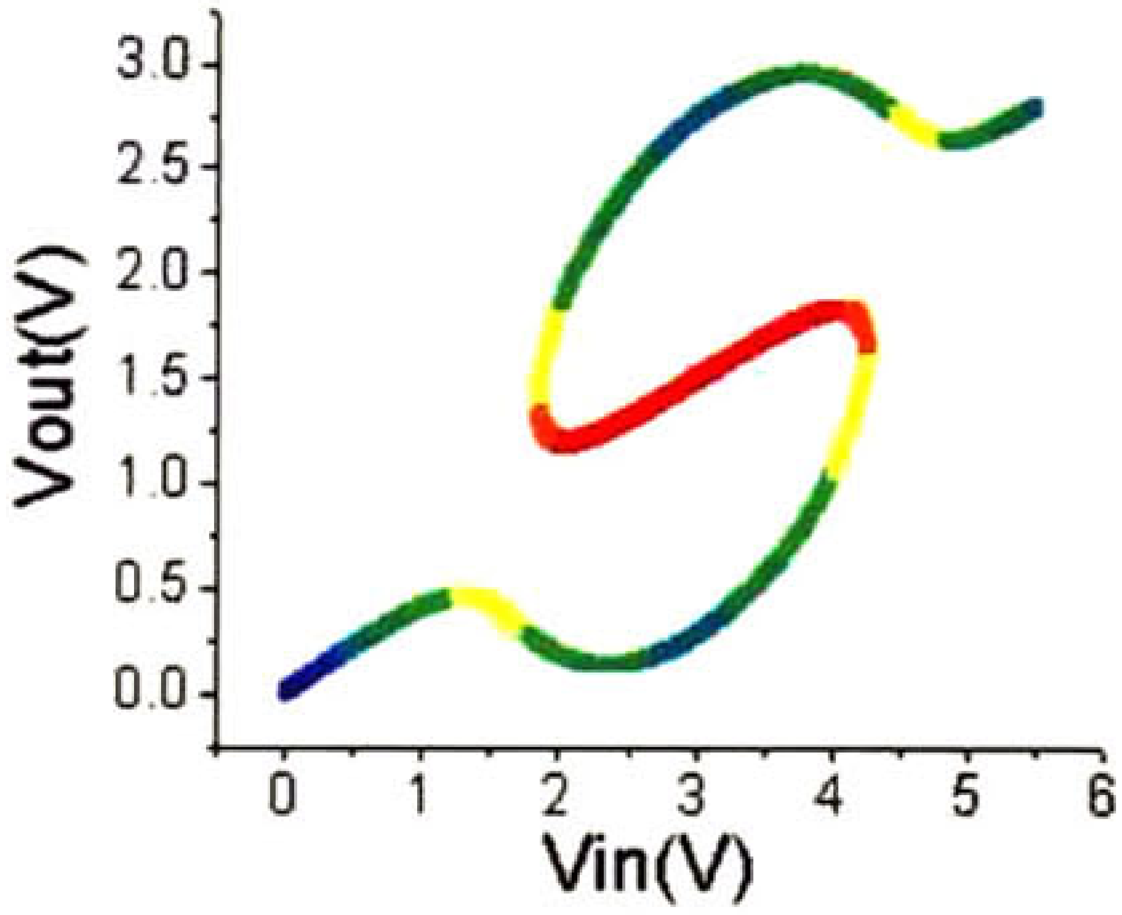


Figure 41, Vout vs. Vin plot of all operation states of a two in series circuit for two different NDR devices.

4.2.3.-Deterministic simulations of Memristor devices

Our software was programmed to be able to simulate Memristor devices; we ran simulations of one device to test if our simulation results are similar to the ones published by Williams et al., due to the charge dependency of a Memristor device these components change its behavior in frequency, to be able to observe the saturation effects shown in the Williams paper we have to adjust the frequency and voltage values of the input applied to plot the Current vs. Voltage signatures.

In Figure 41 it can be seen the Memristance effect without reaching the saturation level in which the device cannot increase any more its conductivity, when the device is operated like this the I-V signature has an 8 like shape, this shape is also presented in the Williams paper [47] in Figure 42.

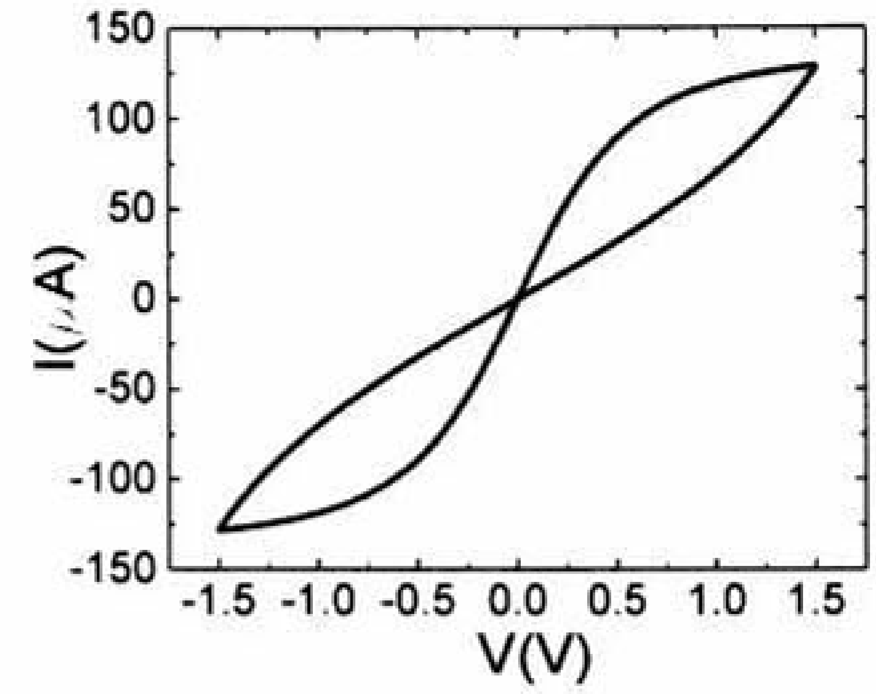


Figure 42, Simulation of the Memristor effect without reaching saturation limits

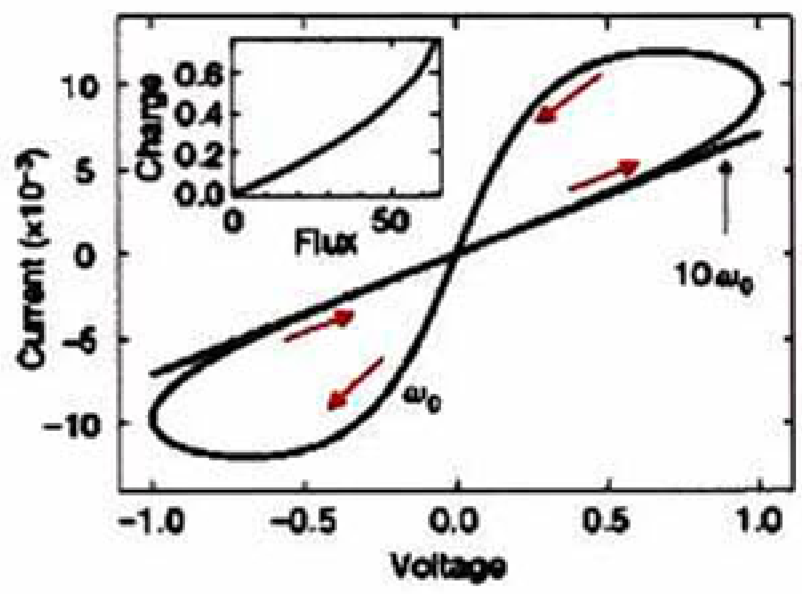


Figure 43, I-V from Williams et al. [47]

We have modified the simulation parameters to make the Memristor device operate into its saturation region Figure 44, doing this we plot similar curves to the ones obtained by Williams [47] Figure 45.

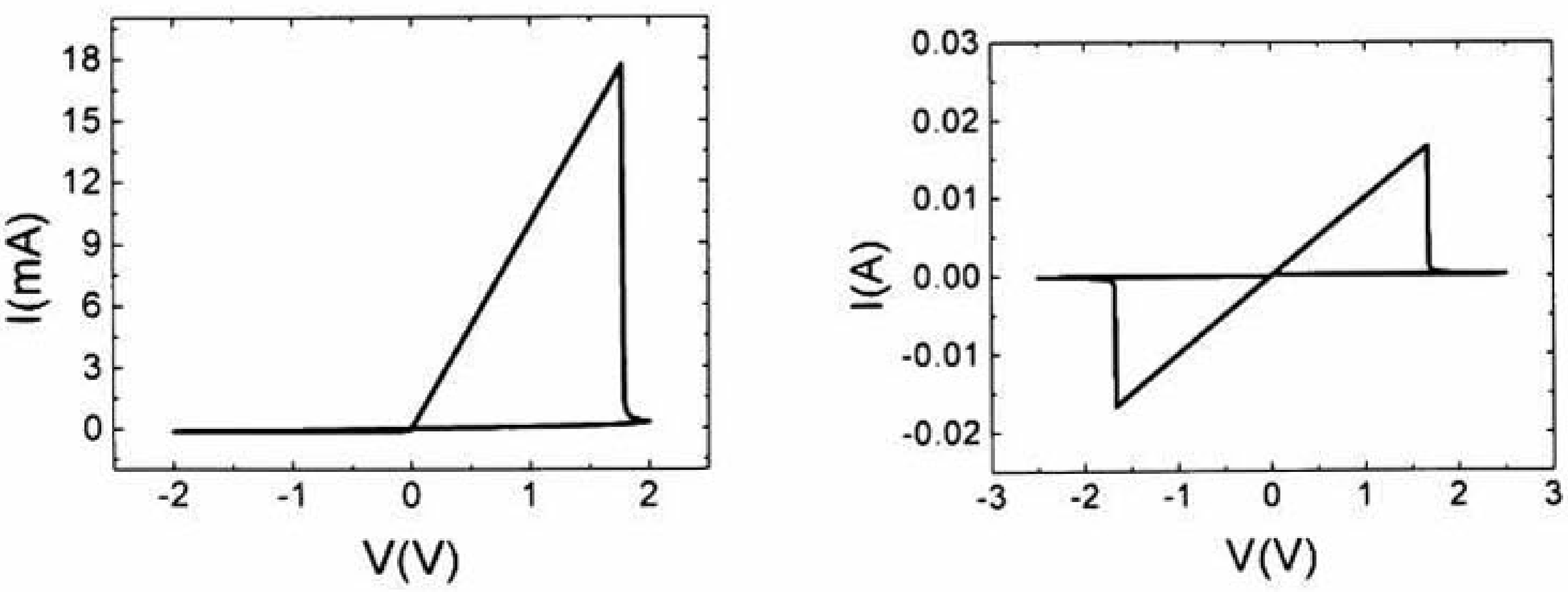


Figure 44, Simulation of Memristors operating at saturation.

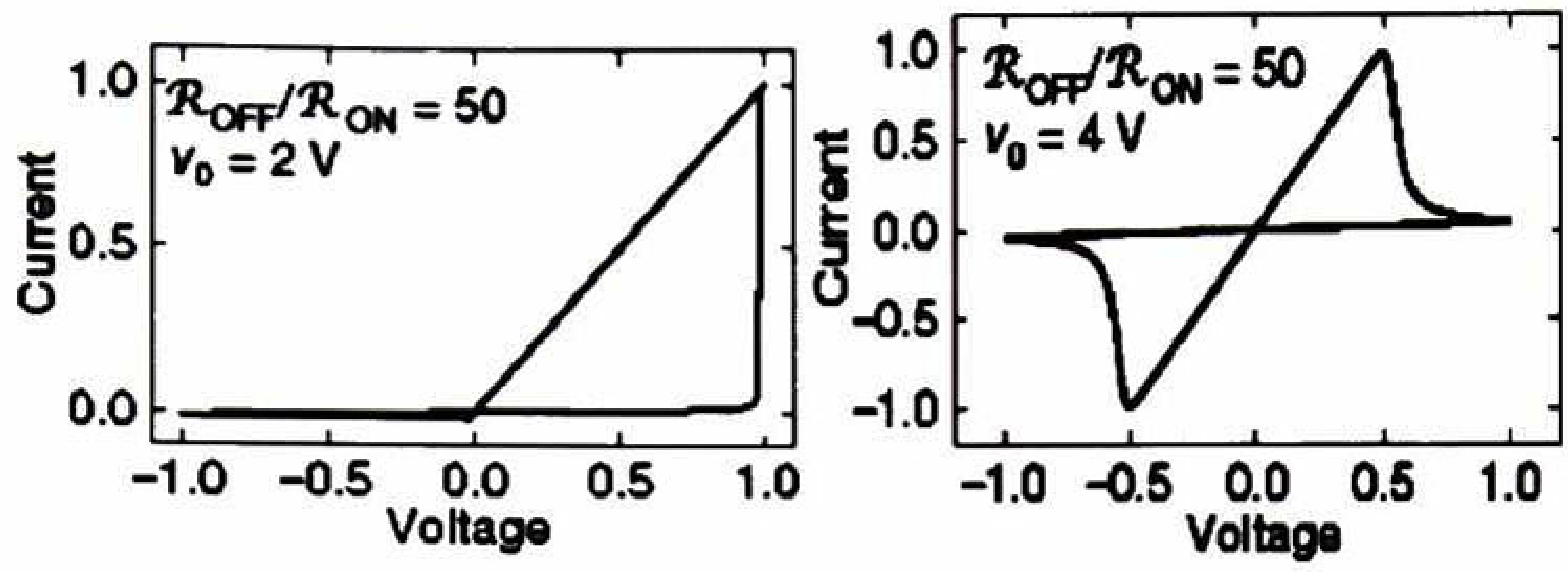


Figure 45, Saturation effects from Williams research[47].

There is a good agreement between our simulations and the results obtained from Williams at the HP labs, it can be noticed that our simulation have sharper edges this is more easier to see in the 8 shape, this sharper edges come from our software because we use ramp signals to trace this curves instead sinusoidal signals used by Williams.

4.2.4.-nanoCell Simulation

To test the software and to start to understand how larger circuits of NDR devices behave, we have performed simulations of circuits resembling nanoCells like the one in Figure 46, this nanoCell is formed by 40 NDR components, this nanoCell has a square configuration and we are applying three inputs and one output evenly distributed at the sides of the square.

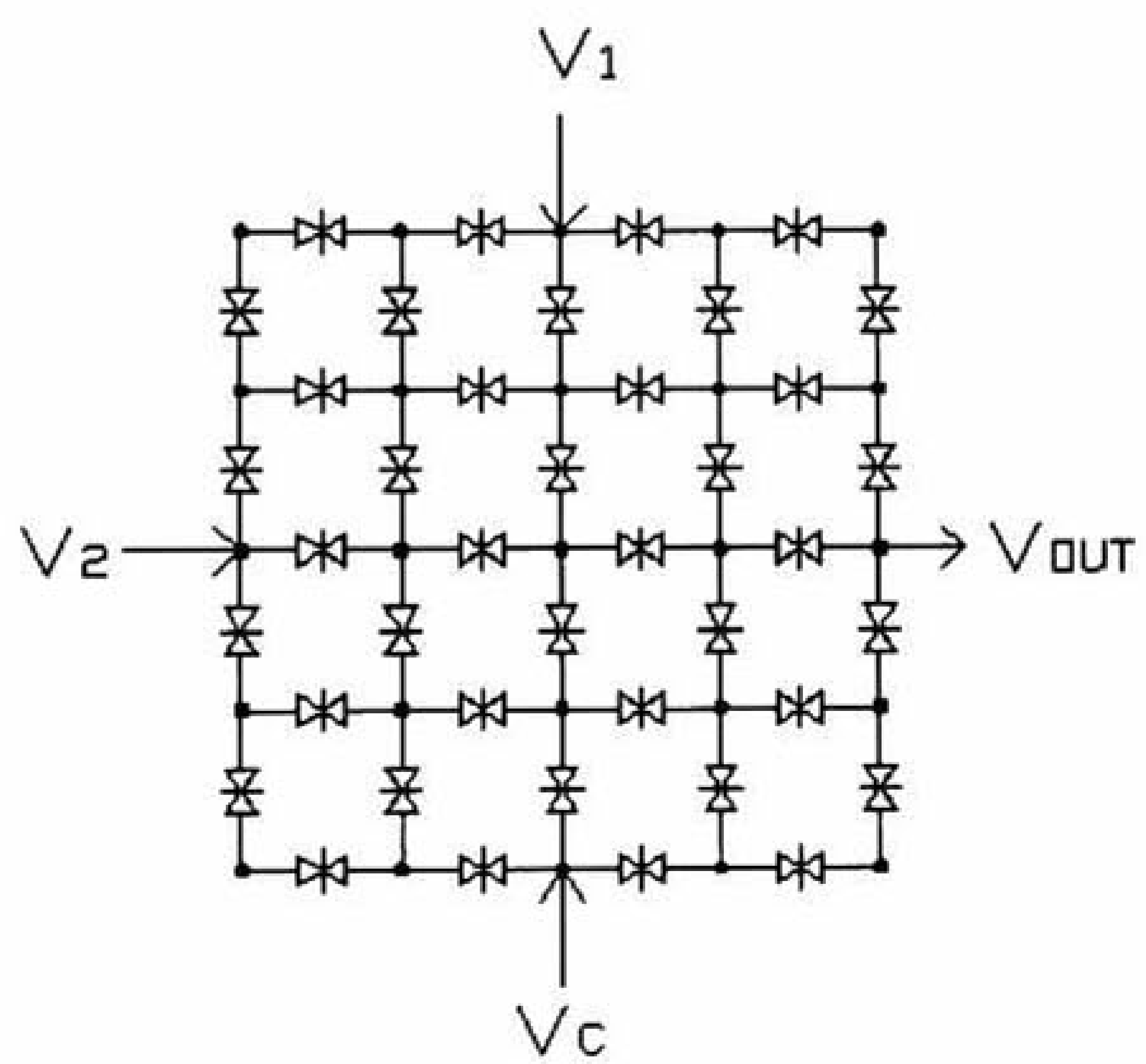


Figure 46, 40 NDR nanoCell Simulated.

To simulate this circuit we used the deterministic algorithm implemented in the NDR simulator software, we assumed random differences from the components in a range of 5% of its resistance and we also applied a noise of 26 mV of magnitude, at the inputs we applied a binary count by using 3 volt pulses as "1" and absence of pulses as "0" in the way it can be seen in Figure 47, using a binary count from zero to seven we input all possible permutations, we use 3 volts because at this voltage we have higher chances to get a low or high voltage output instead of a mid voltage output.

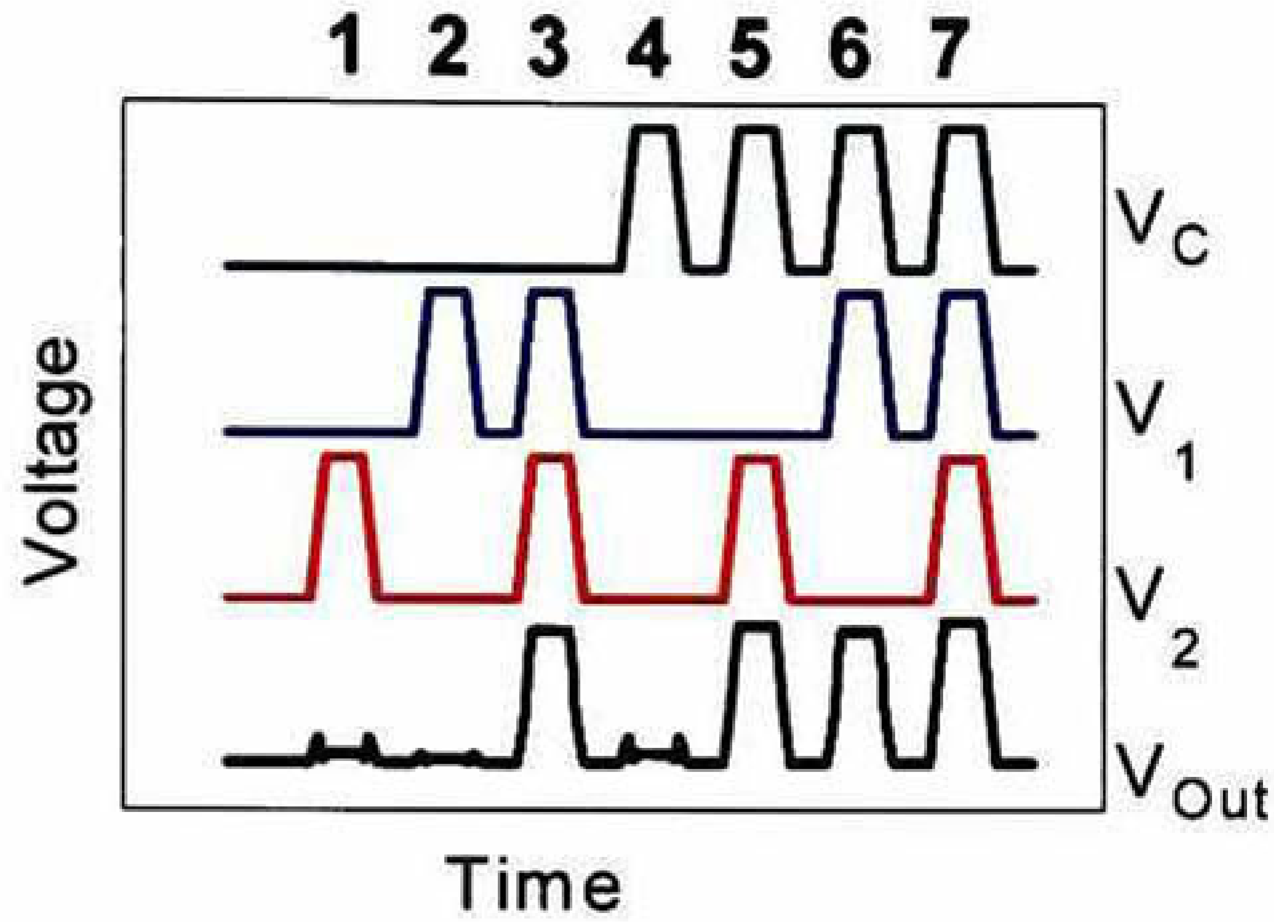


Figure 47, Inputs and output from a nanoCell simulation.

From Figure 47 we can see some interesting points in this simulation, the first point is that at the outputs we have well defined low or high voltage levels, it is a low level at the output at step 1,2 and 4 and a high voltage level at the output at step 3,5,6 and 7. This fact confirms that NDR circuits when properly operated yield low or high voltage outputs, a useful feature to implement binary digital logic, the second point is that this circuit is behaving as a programmable digital gate which can be implemented as a logical AND or a logical OR, just depending on a Voltage control applied at one input the truth table is in Figure 48, It may look unlikely to obtain a usable circuit so easily but actually the way this circuit works is simple, this circuit is working as a Majority Logic Circuit [25], which means that the output will be zero if the majority of the inputs are zero, and the output will be one if the majority of inputs are one, we can build a circuit with this same behavior using resistances and only two NDR devices, but in this large circuit it seems that a predominant NDR pair is biasing the output to behave like this.

V_1	V_2	V_C	V_{Out}	Gate
0	[illegible]	0	0	AND
1	[illegible]	0	0	
0	1	0	0	
1	1	0	1	
0	[illegible]	1	0	OR
1	[illegible]	1	1	
0	1	1	1	
1	1	1	1	

Figure 48, nanoCell truth table

4.2.5.-NDR circuits as sensing devices

A potential application for molecular circuits is to be used as sensor, departing from the fact that a molecule can be a very efficient sensor to detect other molecules, the easier way to implement a sensor this way is to build a molecular circuit and if we have an adequate architecture when a molecule of this circuit interact with an external molecule or stimulus, the outcome of the circuit will change, as a proof of concept we ran a simulation of a two NDR devices in series circuit, and we simulate the effect of having the electrical properties of one molecule modified by en external agent, we assume the molecule to change its electrical I-V behavior from the NDR signature in blue in Figure 49 to the linear behavior in red in the same Figure.

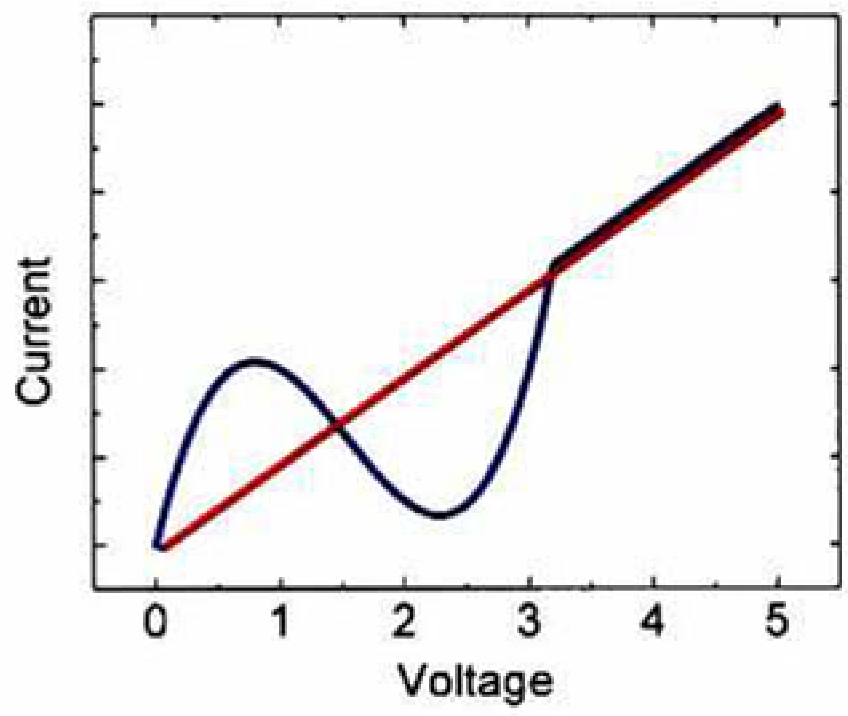


Figure 49, two different behaviors for a molecule, blue is for a clean molecule and red for a molecule interacting with an external agent.

We plotted the I-V characteristics of the two in series circuit when modifying one component, in this way in Figure 50 and we observe a large change in its shape.

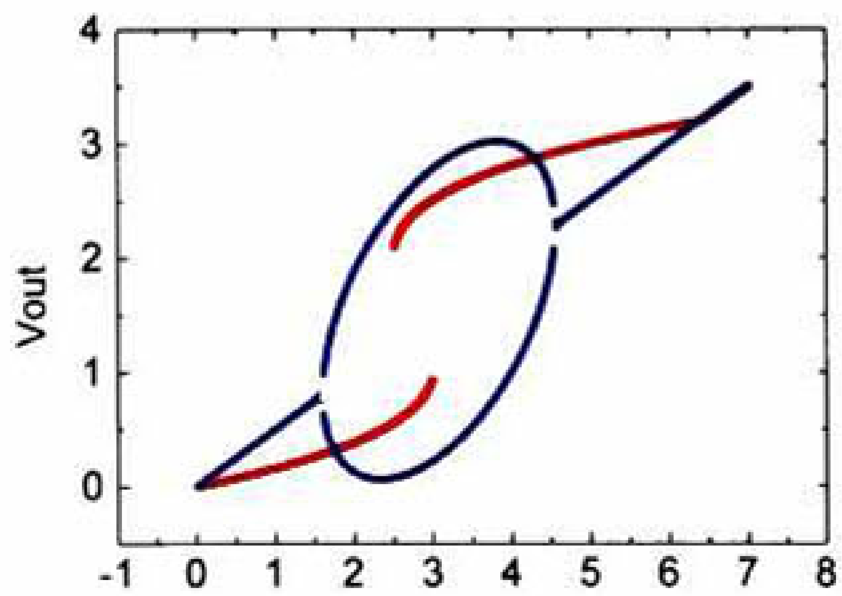


Figure 50, Vout vs Vin signature of two NDR devices, in blue without modifications, in red with modifications due to external agents.

The large changes in these signatures can be translated in large changes at the output voltages of the circuit, which can be easily detected by electronic means this way we prove that a sensor circuit can be implemented by molecular circuits, but the approach we are using would not be practical because it involves direct addressing to molecules which is very complicated, then we need to use other kind of approaches to solve this problem, so we have used the nanoCell approach.

To test a nanoCell sensor circuit we have simulated a 40 NDR circuit establishing four inputs and four outputs (Figure 51), we applied a voltage pattern at the inputs and observe the outputs, and then we have modified one by one the components using a change of the same nature shown in Figure 49.

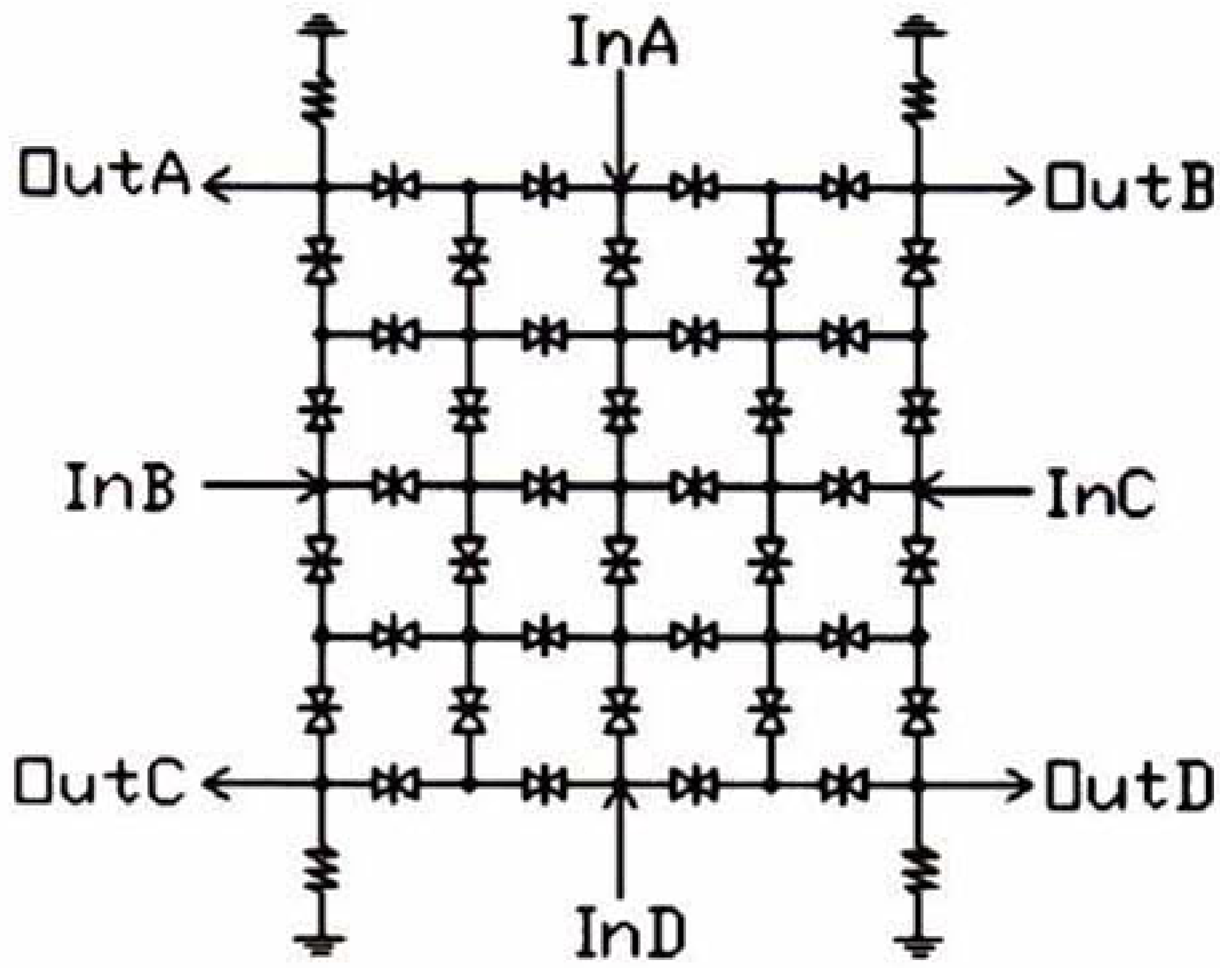


Figure 51, 40 NDR nanoCell sensor circuit.

When we ran simulations applying changes, we were able to detect large changes at the outputs of the circuit, this circuit yield noticeable changes when the properties of single NDR components are changed for 75% of the components, in Figure 52 it can be seen this voltage changes for different components being modified.

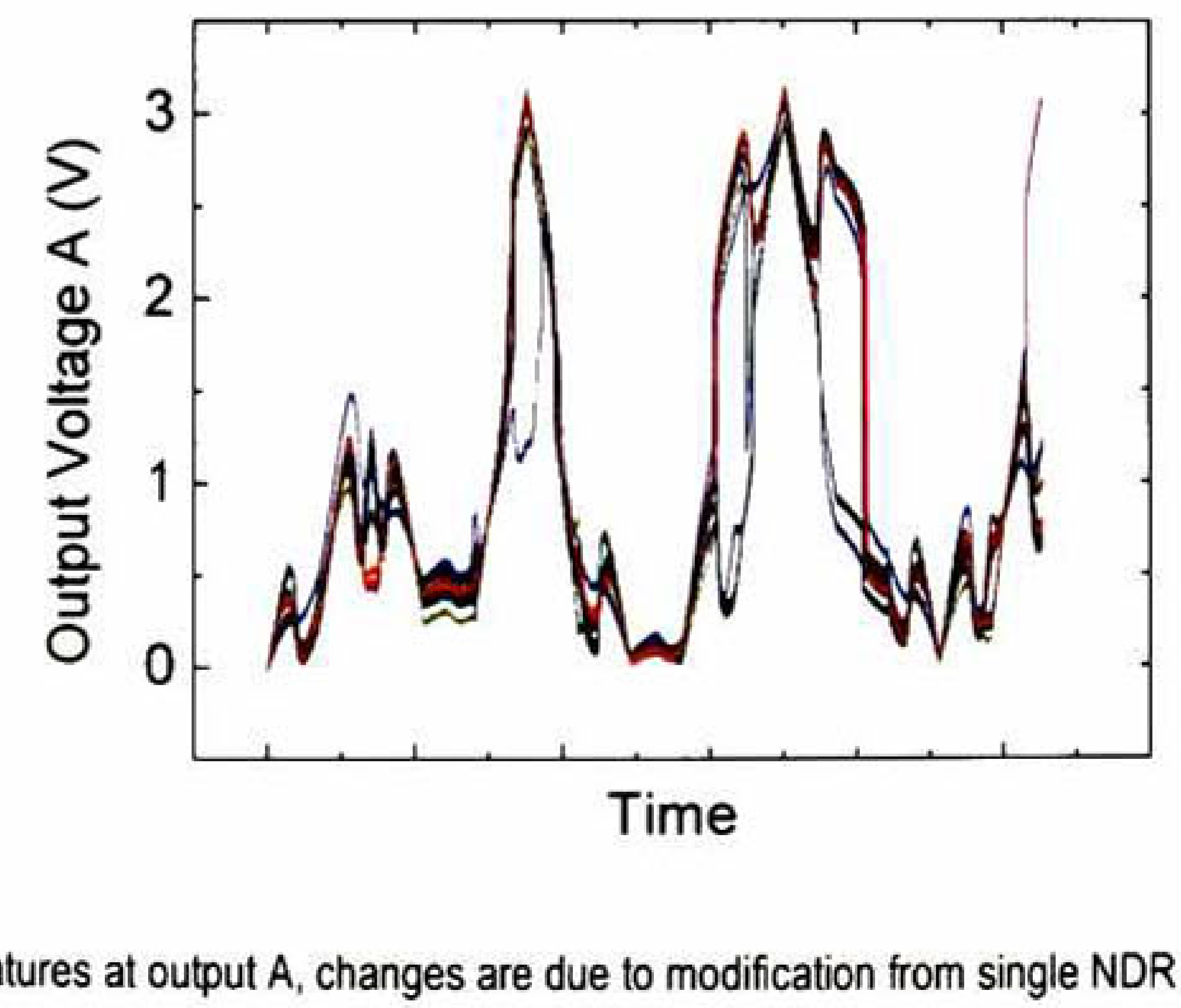


Figure 52, Different signatures at output A, changes are due to modification from single NDR devices properties.

We have growth the circuit to make this same test on an 84 NDR devices nanoCell as seen in Figure 53, but the changes result to be smaller (Figure 54), just 11% of NDR were modified and the sensitive devices are the only ones connected to the inputs.

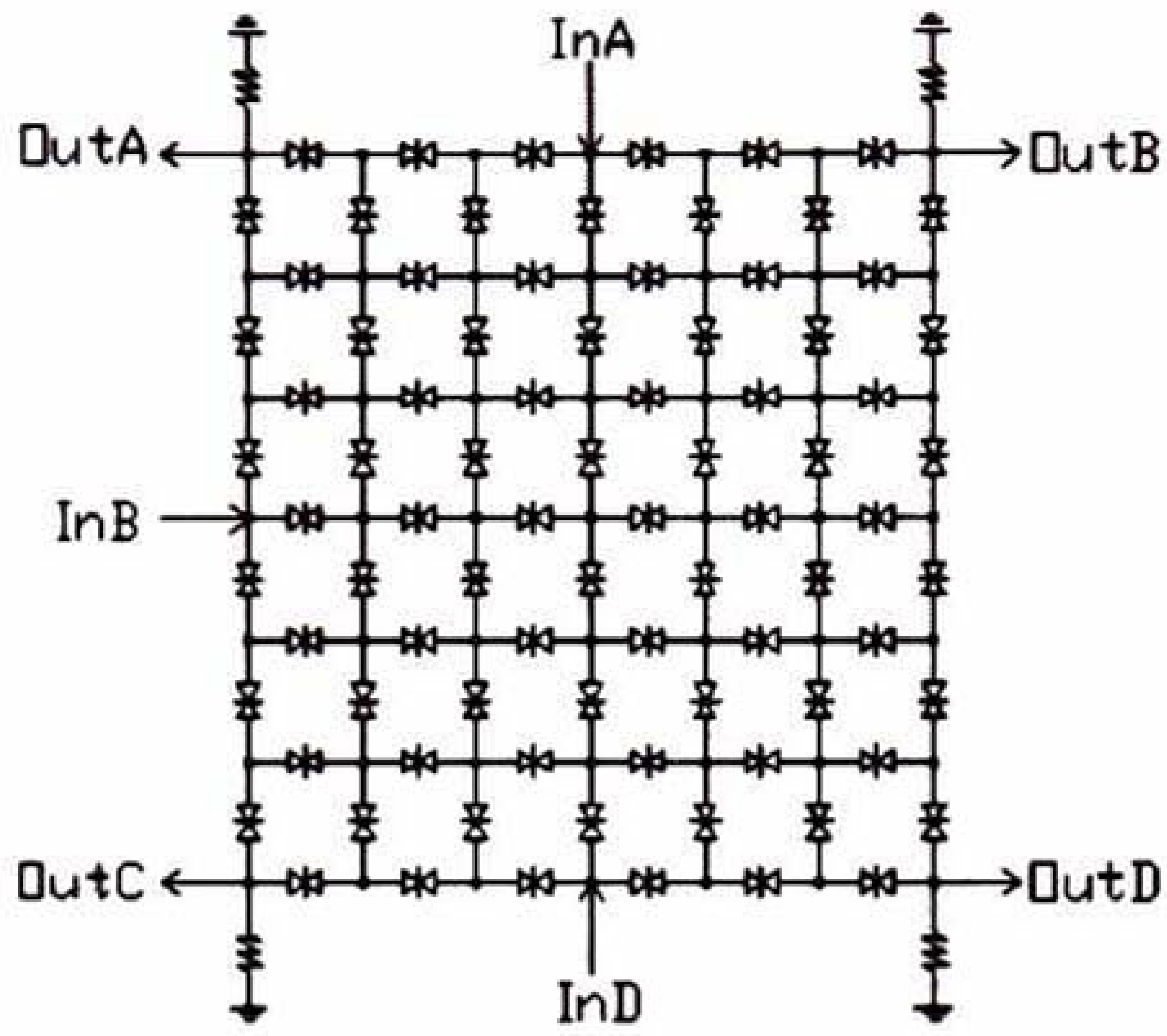


Figure 53, 84 NDR nanoCell sensor circuit.

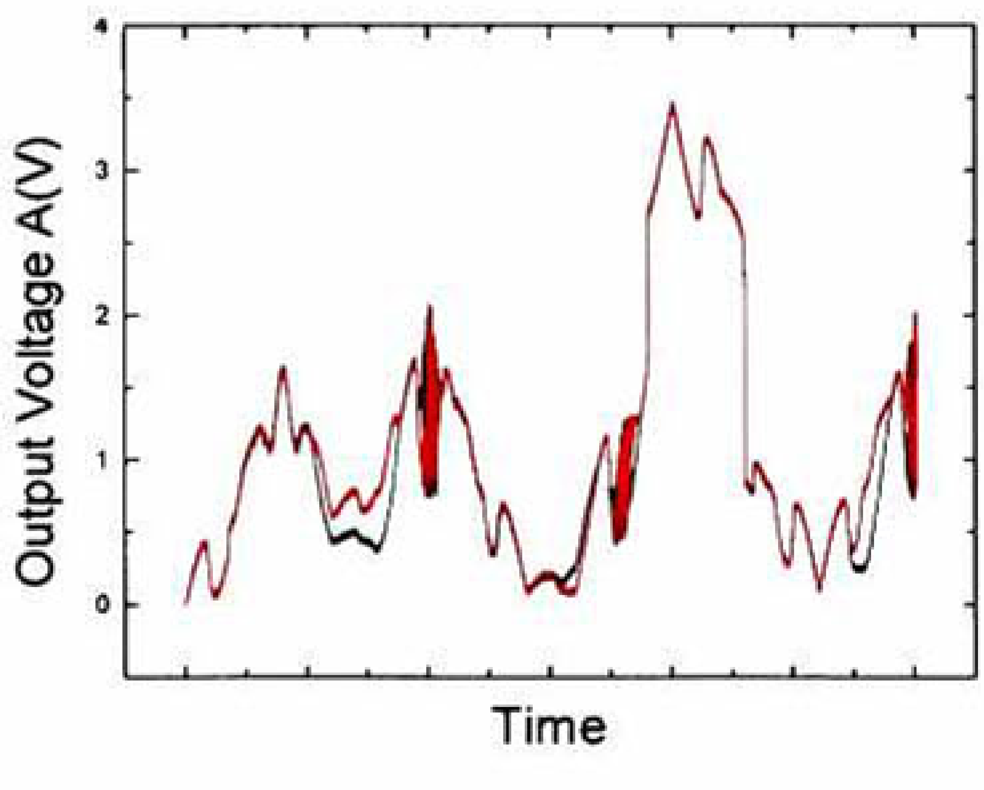


Figure 54, Small changes at Output A due to modifications from single NDR devices.

The poor results of a larger nanoCell sensor circuit, led us to take a different approach to implement sensors from this type of configurations, then we have simulated a nanoCell circuit and we applied a voltage through two terminals as depicted in Figure 55, and we observed the Current vs. Voltage signatures.

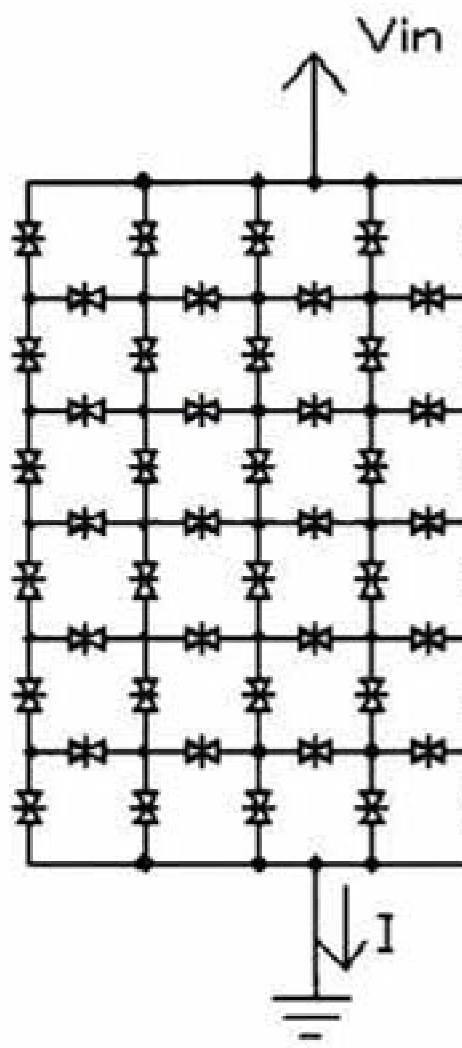


Figure 55, nanoCell sensor circuit using two electrodes to plot its I-V signature.

Analyzing the I-V signature of this kind of circuit we observe it has many peaks, these peaks are result of having many NDR devices in this circuit, to test the sensitivity to changes we have modified the electrical properties of one NDR component and we observe a noticeable displacement in the position of some peaks as can be seen in Figure 56, this displacement can be detected and processed as a detection of an external agent, besides all the NDR components parallel to current flow reflect this kind of peak displacements which involves that near 50% of the components of the molecular circuit work as sensors.

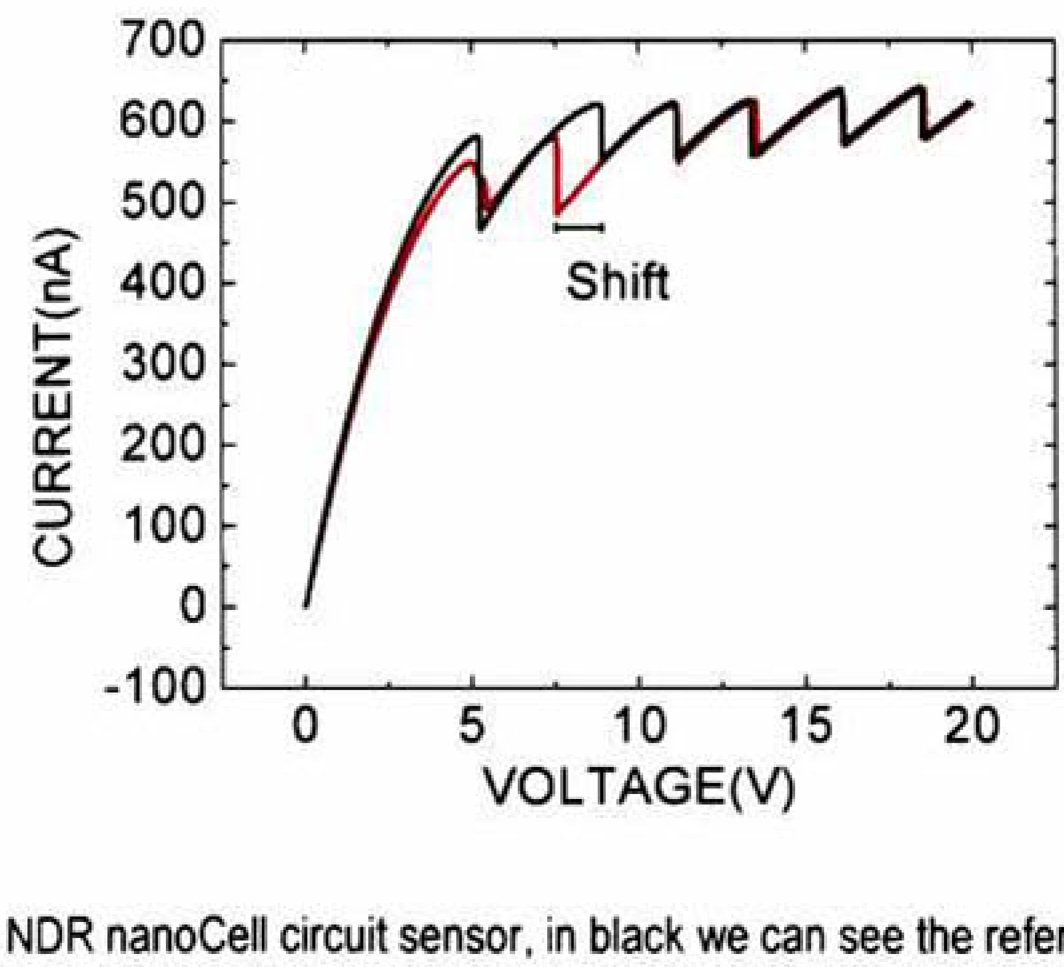


Figure 56, I-V signature of an NDR nanoCell circuit sensor, in black we can see the reference signature and in red we can see the signature when modifying one NDR component.

We have grown up this system to verify if this effect still present in larger nanoCells, and we have simulated a 128 NDR nanoCell circuit shown in Figure 57, the dimensions of this circuit are closer to the size theoretically reachable by lithography methods, approximately this circuit would measure 20 nm x 30 nm, electrodes having gaps of these dimensions can be implemented by lithography methods so we can say this simulation is close to the molecular circuits that can be possible built, it is also relevant to mention that a 128 NDR circuit is large enough to say our simulator is useful to simulate real case circuits.

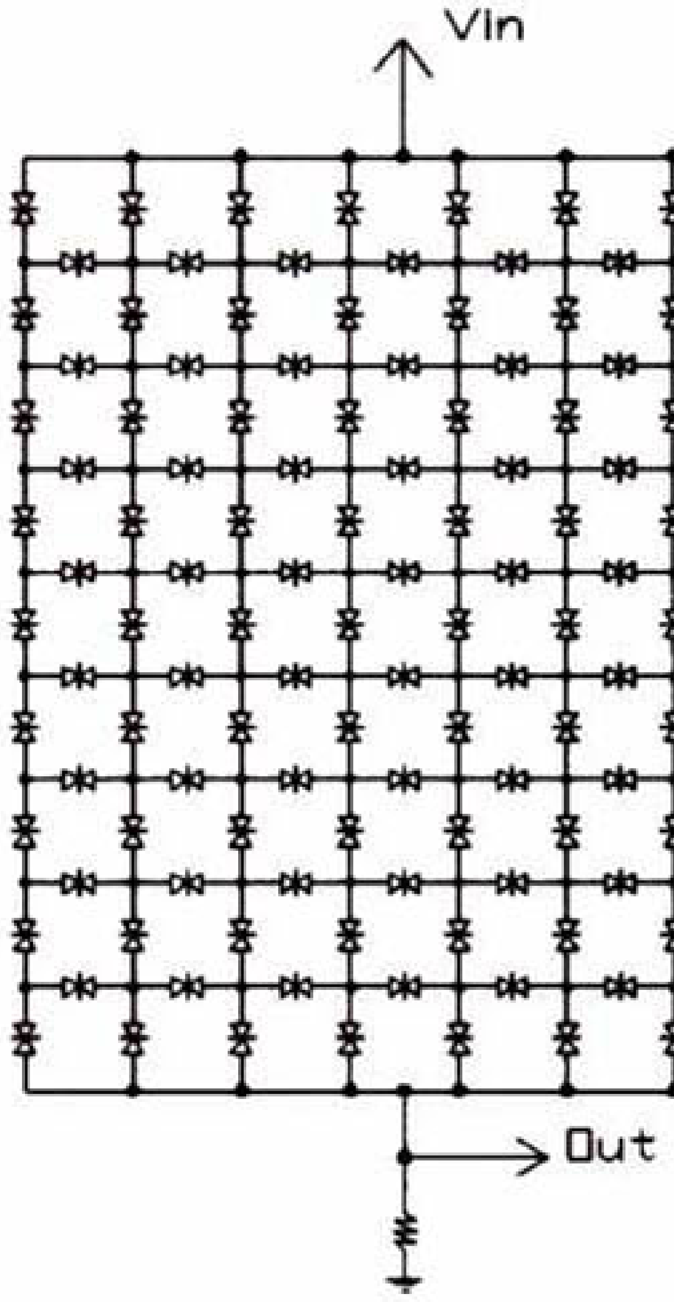


Figure 57, 128 NDR nanoCell sensor circuit.

We ran simulations of this 128 NDR circuit, in order to plot its I-V signature, analyzing this signature in Figure 58 we found peaks but we also see that many of these peaks are smaller, and tend to undistinguishable between the noise of the signal, but for these kind of situations we are able to implement electrical filters to get rid of noise and then enhance the information over this signal, in Figure 59 we can see the signal being processed and how it is much easier to identify the peaks.

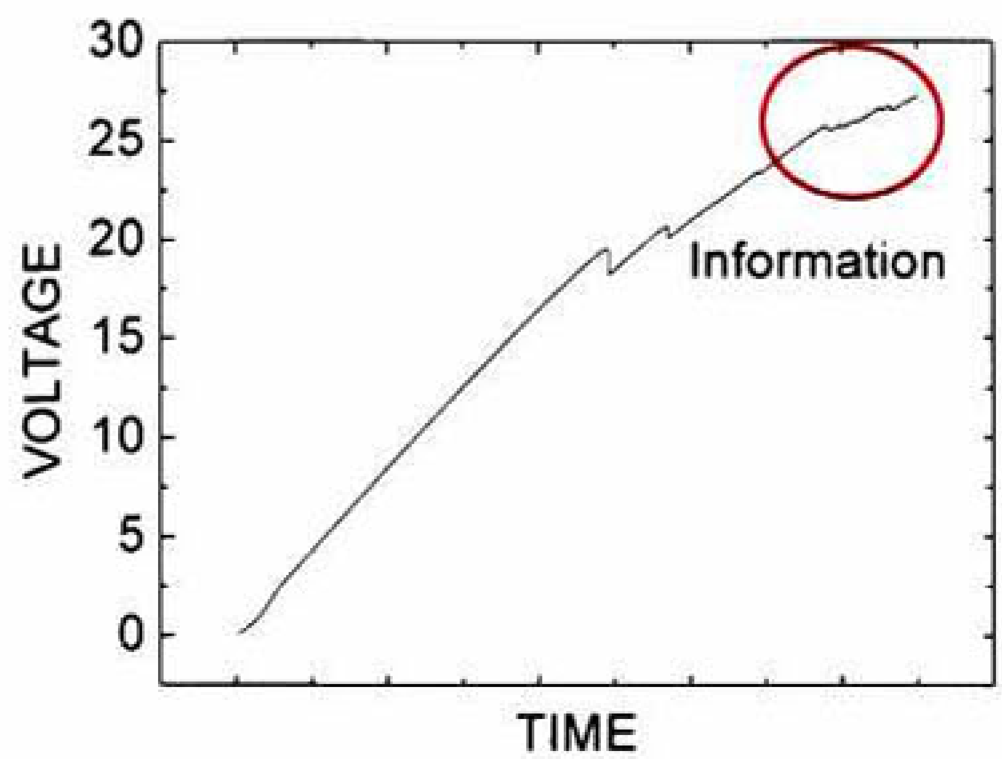


Figure 58, I-V signature of a 128 NDR circuit.

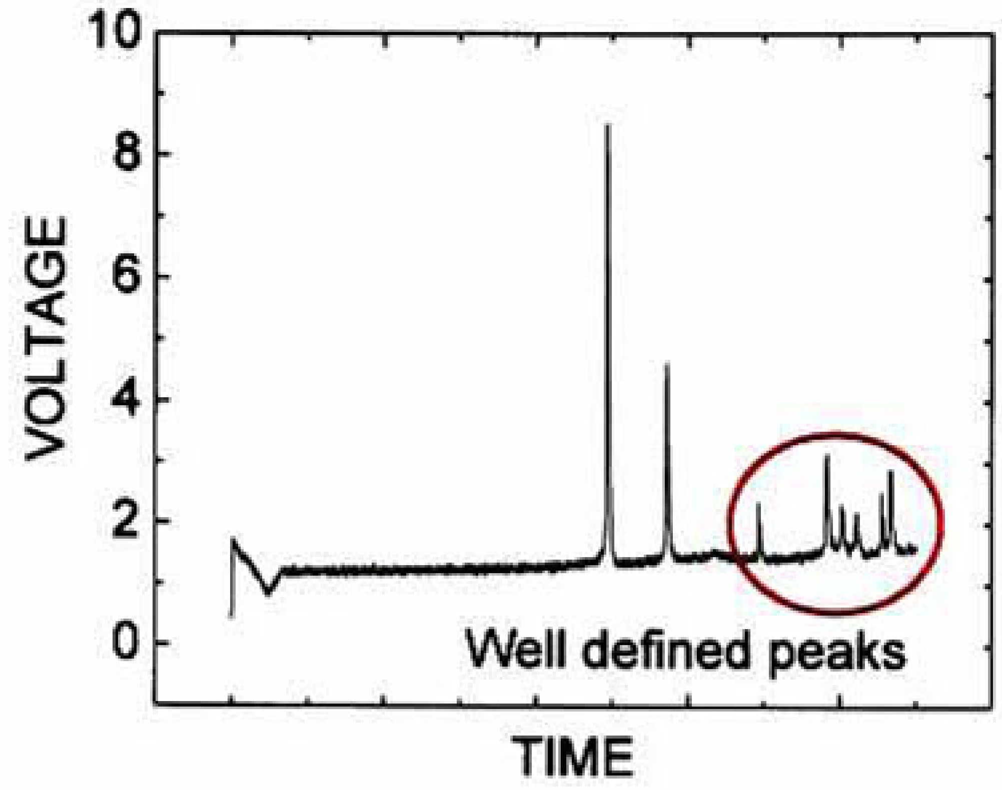


Figure 59, I-V signature of a 128 NDR circuit after enhancement by filters.

This enhancement process only require amplifiers, resistors and capacitors so it can be easily implemented in a real circuit, having this enhanced signal we proceed to test the sensitivity to changes of the circuit applying changes to individual NDR devices, and we still observe noticeable displacements in these peaks as it can be seen in Figure 60.

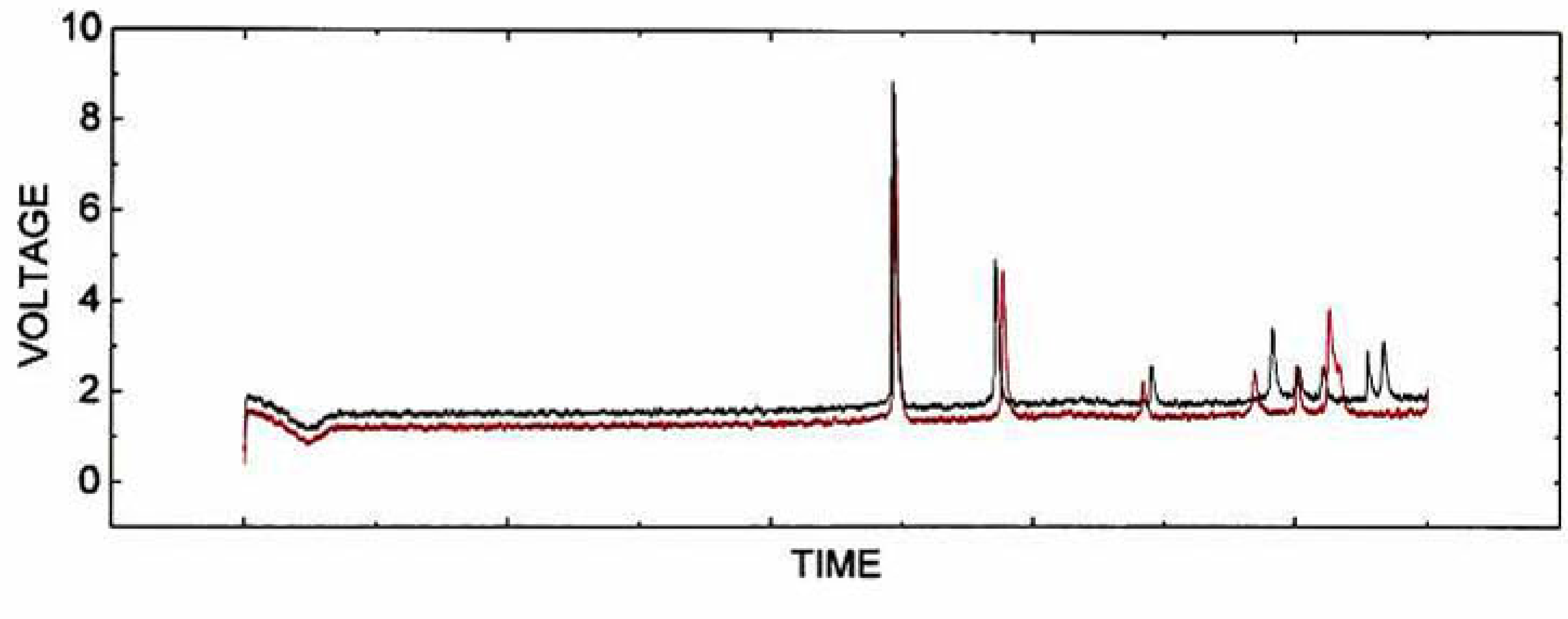


Figure 60, I-V enhanced signature of a 128 NDR circuit, reference plot in black, in red we can see the signature when modifying one NDR device.

These displacements are present when the devices parallel to the current flow are modified; this yields a sensitivity of approximately a 50%.

5.-Conclusions

5.1. - Conclusions on Emulation of non-linear devices

We have built devices capable to emulate non-linear behavior, in the case of this thesis work we have emulated Negative Differential Resistance behavior as well as Memristor behavior, using NDR emulators we have measured how this devices really followed a well defined configurable NDR behavior. This proved to be useful to understand in a didactical way how basic circuits of NDR devices work.

Using these circuits we have built on the test bench a simple bi stable latch circuit, using two NDR emulators connected in series we have been able to switch between two operational states of this circuit by applying momentary pulses. By measuring with an oscilloscope we have confirmed the existence of a third unstable operation state which only exists during a short period. In this way the main use of these devices was as a proof of concept about how Negative Differential Resistances are useful to implement circuits having many operation states.

Taking advantage of already having these emulator devices we have emulated Memristor devices, performing this emulations we also have shown how the emulator devices properly programmed are capable to follow different types non-linear current vs. voltage behaviors. The emulators built are also capable to emulate charge vs. time non-linearities which is the case of the Memristor, probably many other non-linear cases can be implemented with this scheme of emulation.

The principal problem on this approach is the time response of the devices, as we are using photo resistor devices to adjust the resistance of the device we are limited by the time response of the photo resistors which is slow, we have overcome this problem to emulate properly small circuits by using very slow frequencies when plotting current vs. voltage signatures. But the issue lies in the fact that NDR circuits trend to output abrupt fast changing voltages, so if we built a large circuit using emulator devices it would not be able to react in real time, this is because some components will be feed by fast changing signals created from other parts of the same circuit. This problem led us to use software emulation instead to understand larger circuits.

5.2. - Conclusions on Simulation of non-linear devices

In this thesis work software modules were programmed to simulate and analyze the behavior of circuits formed by non-linear components, principally Negative Differential Resistance devices, the main issue regarding developing software for this purposes is that it already exists software to simulate electronic circuits which can be adapted to simulate circuits of NDR devices. In this way it has already been used by other research groups.

In our experience to develop custom made software for these applications has been a good choice mainly for two reasons; first, because programming our own software gave us freedom to change it to fit very specific needs for molecular electronics; second, because by implementing the Monte Carlo allowed state analyzer we have created a tool to know all the states at which a circuit of NDR devices can operate. This software also tells us if these states are stable or not, both of these features are not possible in Spice software; but they can help to understand NDR circuits and to point to circuit designers how to operate a circuit to obtain a desired operation.

Among other advantages of developing this software, we are able to modify during a simulation all the parameters of the circuits to be simulated, as for example: the degree of non-linearity of one component, the amount of noise, the electrical properties, etc. This is very useful to implement tests of circuit sensor devices.

As another benefit we obtain the results from our simulations in text files that we can open using many software tools, like: excel, origin, matlab, etc. This is also a good feature because we have not limits to analyze this information. Other advantage inherent to have control over the simulation software is the possibility to make simulations in an automatic way, for example in this thesis work we have performed several automatic simulations changing parameters to test sensitivity of circuit arrays.

Many important conclusions have been draw about the behavior of NDR circuits using this software, when a simple two in series NDR circuit was simulated we have noticed the determinant effect of noise and differences between the components of a circuit in this kind of systems; these results convinced us to have always in mind these two points when we simulate NDR circuits.

The observations made using the software help us to better understand the nature of the NDR circuits. Simulating larger circuits, we have see other important effects, like the fact that we can bias a large circuit to yield well defined low or high voltage outputs, a useful feature to implement digital logic. As a part of this work we also tried some circuit configuration to build sensing circuits; we have found using our software which configurations have better chances to be suitable for this purpose.

As a proof that this software approach can effectively model non-linear behavior we have modified our software to be able to simulate the Memristor device, which is a component having a resistance dependency as a function of the charge flowing through it, our reported results have a very good agreement with the results reported by the researchers who had discovered this Memristor component. We were actually able to reproduce even the rare effects due to the saturation of this device.

5.3. - General Conclusions

During this thesis work, in collaboration between Cinvestav Queretaro and Texas A&M University, we have developed tools to understand, explain and analyze circuits formed by non-linear devices. The importance to explain and understand these circuits, comes from the fact that the circuits of highly non-linear components as shown in this work behave in a complex way, in this thesis we have simplified fundamental points of how this circuits work. The knowledge generated can be useful for researchers or engineers trying to use NDR devices in practical applications.

There are many improvements yet to be done about the software, for example, this software can not model capacitive or inductive behavior, because of this the software is not able to simulate frequency dependency, this improvement theoretically can be made adding imaginary number calculations. Other important possible improvements could potentially make this software to run faster; which can be done depurating the code and also creating external modules programmed in a faster language like C++ or Fortran.

The simulations done about nanoCell sensors besides exemplifying the use and potential of our software, they open a new possibility to implement molecular sensors with great advantages, as requiring only two electrodes over a self assembled circuit to test several maybe hundreds of molecule sensing devices, this idea seems to be a promising approach to build a useful devices using molecular electronics.

The work generated from this thesis work has produced two papers already submitted to review for publication:

"Emulation of intrinsic molecular programmability using microelectronic programmable devices"

"Analysis of nano and molecular arrays of nonlinear devices"

Both papers have been submitted to IEEE Transactions in nanotechnology,

The work generated in this thesis has been also exposed orally and in a proceedings paper, at the 8th IEEE Conference on Nanotechnology at Arlington Texas USA in August 2008, with the name:

"Program for the Analysis of Molecular Arrays of Highly Nonlinear Devices"

6.-Annexes

ANNEX 1. - Non-linear Emulator Schematics, bill of materials and printed circuit Board information

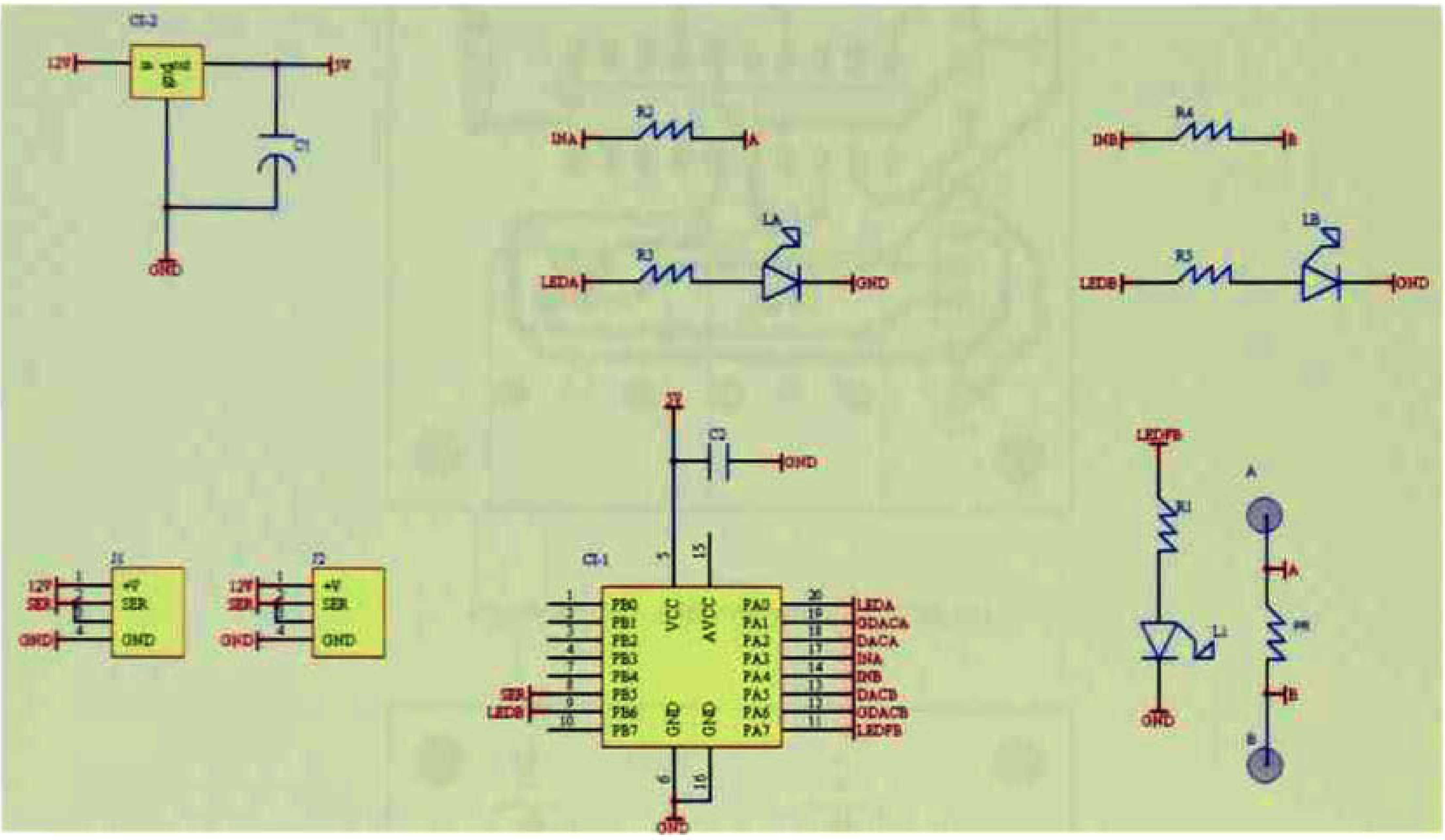


Figure 61, detailed schematics for the non-linear emulator device

Part	Description
R1	1/4 W 470 ohms Resistor
R2	1/4 W 470 ohms Resistor
R3	1/4 W 470 ohms Resistor
R4	1/4 W 470 ohms Resistor
R5	1/4 W 470 ohms Resistor
C1	220 uf electrolytic capacitor
C2	0.1 uf Ceramic capacitor
L1	High intensity blue led
LA	Red led
LB	Red led
PR	Photo Resistor
J1	RJ-11 Circuit board connector
J2	RJ-11 Circuit board connector
CI-1	ATtiny26, microcontroller
CI-2	LM7805, voltage regulator

Table 1. Non-linear circuit emulator Bill of Materials.

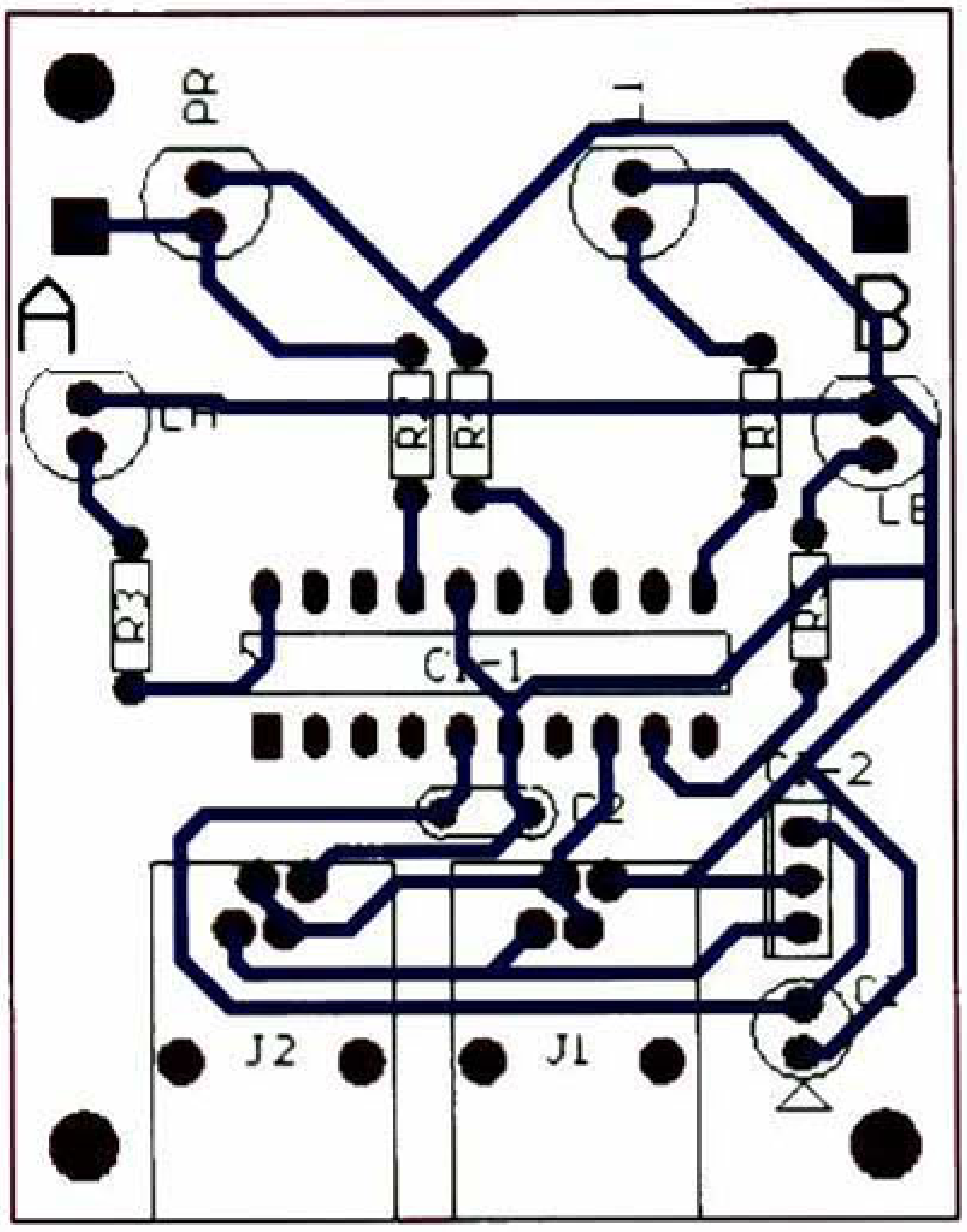


Figure 62, Non-linear emulator board layout.

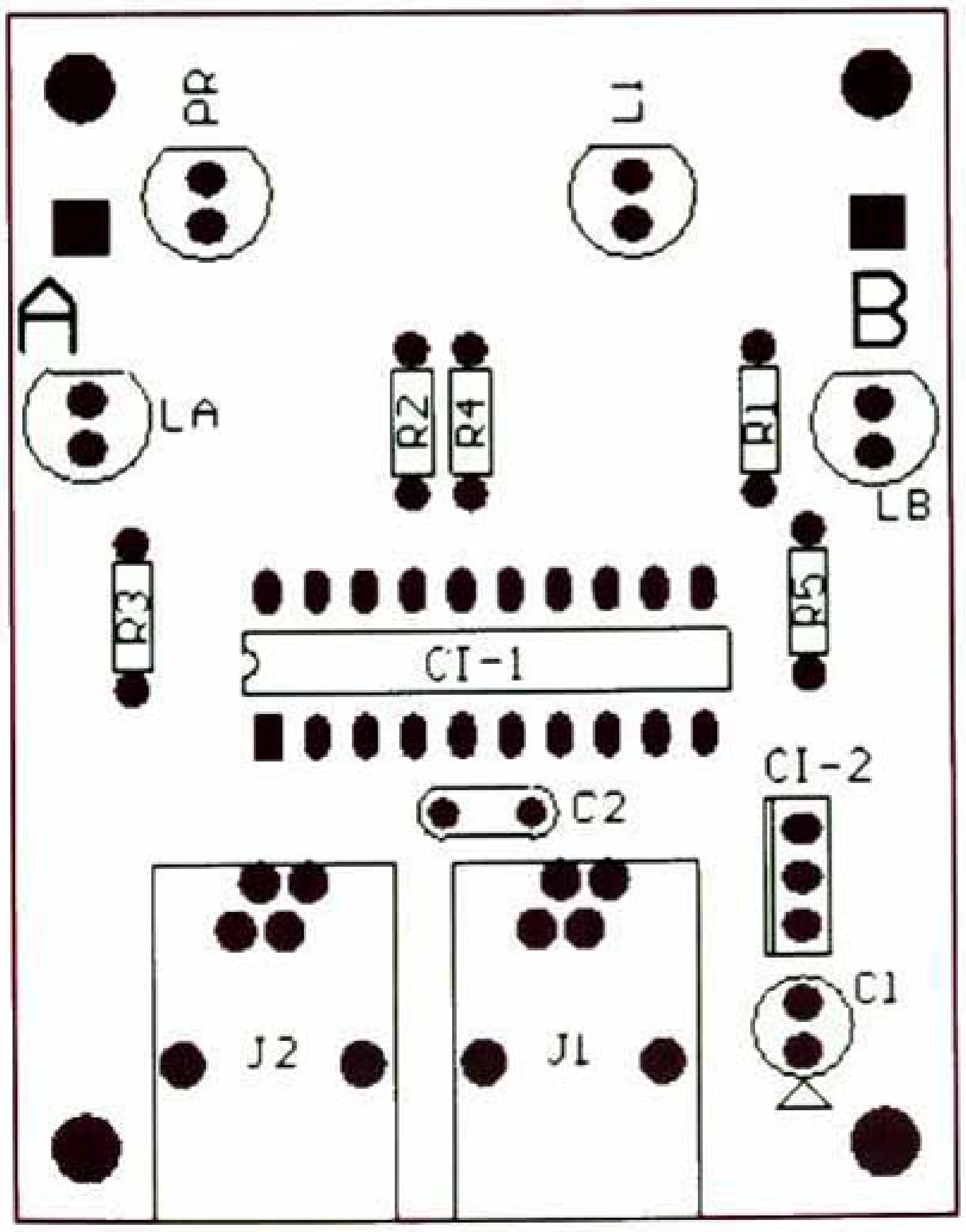


Figure 63, Non-linear emulator component mask.

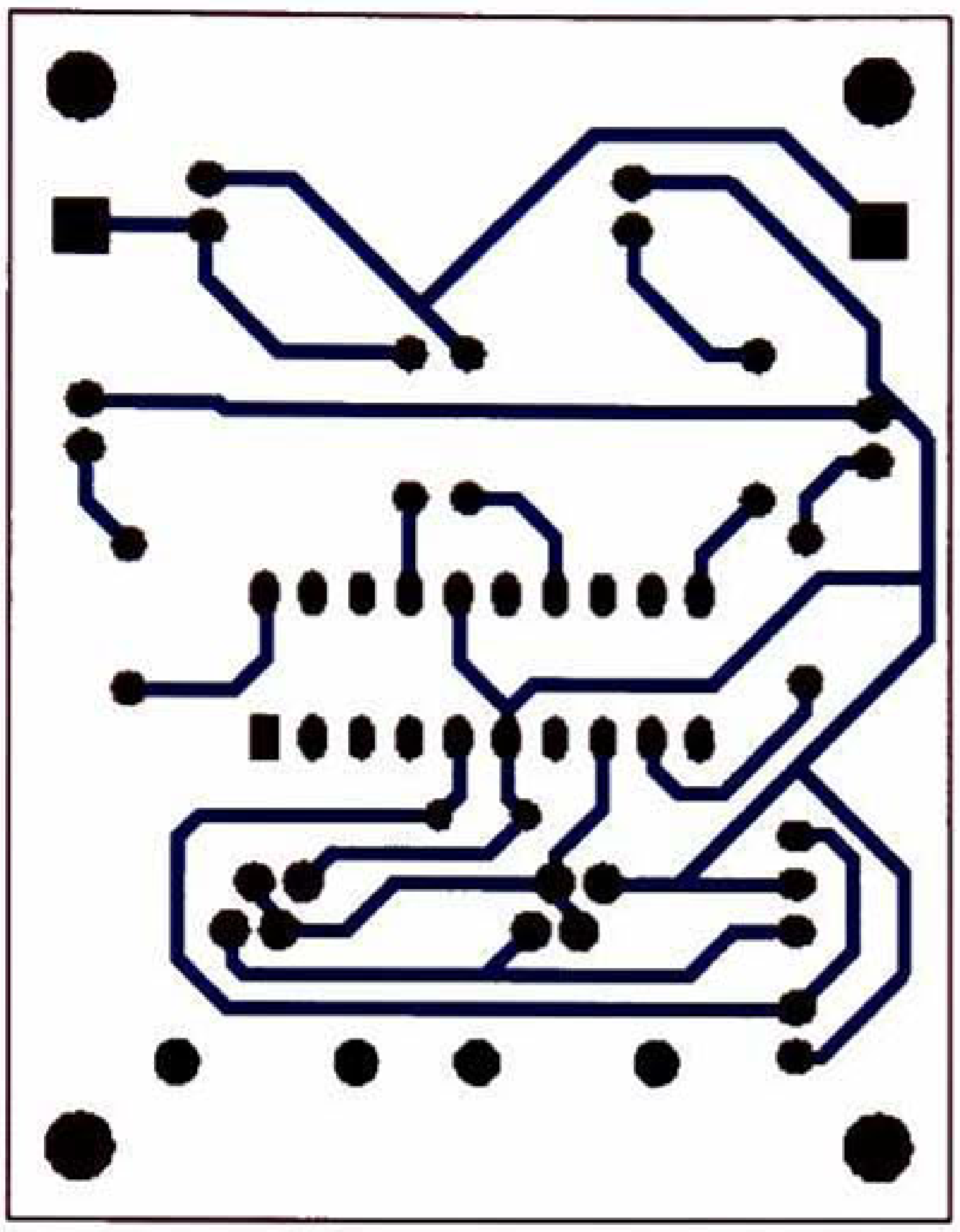


Figure 64, Non-linear emulator bottom layer.

ANNEX 2. - Microcontroller basic program to emulate NDR behavior using the Non-linear emulator circuit.

```
'////////////////////////////////////////////////////////////////////
'///  Program for Molecular-Emulator v-2        //////
'///  First version Sept 11, 2007               //////
'///  Last modified Sept 22,2007                //////
'///  Compiled for V4.1.3                       //////
'////////////////////////////////////////////////////////////////////

$Device= tiny26                    ' used device
$Stack = 30                        ' stack depth
$Clock = 4                         ' adjust for used crystal Int 4 mhz
$Source= On                        ' basic source in Asm

'Define microcontroller's pins

$Def leda=PORTA.0
$Def adcspeed=PORTB.0
$Def sero=PORTB.5
$Def seri=PINB.5
$Def ledb=PORTB.6

$Def resv=ocr1a                    'to change PWM value
$Timer1=PWM,8,PwmA=Normal          'conf PWM mode

'Define Sram

Dim a As Byte
Dim medcount As Byte          'medition counter
'Dim resv As Byte             'resistor value
Dim ina As Word               'analogical input a
Dim inb As Word               'analogical input b
Dim diffvol As Word           'differential voltage
Dim diffvolc As Word          'differential voltage copy
Dim auxdv As Word             'auxiliary diffvol
Dim restab As Flash Byte

'Define Subroutines

Declare Sub init()
Declare Sub selresv()
Declare Sub adcread()

'***Begin program
```

```
init()

Do

adcread()                'Read voltage across device

selresv()                'Change resistor value depending on voltage

Loop

'*****************************************************************
'**Program Subroutines


'*****************************************************************
'***Initialization Subroutine

Sub init()

DDRA=&b10000001    'init porta direction
DDRB=&b01000011    'init portb direction

'Init PWM
tccr1a=&b10000010                'to correct compiler error
tccr1b=&b00000001
ocr1c=255

Start Adc, Vref=Vcc              'Starts Analogical to digital converter

For a=0 To 10  'Leds blink 10 times as init sequence
leda=1
ledb=0
WaitMs 20
leda=0
ledb=1
WaitMs 20
Next a
ledb=0

ina=0
inb=0

End Sub
```

```
'*********************************************

Sub selresv()

If diffvol<66 Then
resv=70
Else
resv=restab(diffvol-66)
End If
If diffvol>506 Then resv=87

End Sub

'***********************************************

Sub adcread()


ina=Adc8(2)     'Reads voltage at input A
inb=Adc8(3)     'Reads voltage at input B


If ina>inb Then          'Check for the larger input
diffvol=ina-inb          'Substracts voltage from both inputs
Else
diffvol=inb-ina
End If

diffvol=diffvol*2

Toggle adcspeed
End Sub


'***************************************
'Resistance Look-up table values

restab=69,68,68,68,68,68,67,67,67,67,66,66,66,65,65,64,63,63,62,62,
61,60,59,59,58,57,56,56,55,54,53,53,52,51,50,49,49,48,47,47,
46,45,44,44,43,42,42,41,41,40,39,39,38,38,37,36,36,35,35,34,
34,33,33,32,32,32,31,31,30,30,29,29,29,28,28,28,27,27,27,26,
26,26,26,25,25,25,25,24,24,24,24,24,23,23,23,23,23,23,23,23,
23,23,23,23,23,23,23,23,23,23,23,23,23,23,23,23,23,23,23,23,
23,23,24,24,24,24,24,24,24,24,25,25,25,25,25,25,25,26,26,26,
26,26,26,27,27,27,27,27,28,28,28,28,28,28,29,29,29,29,29,30,
30,30,30,30,31,31,31,31,31,32,32,32,32,32,33,33,33,33,33,34,
34,34,34,35,35,35,35,35,36,36,36,36,36,37,37,37,37,37,38,38,
```

38,38,38,39,39,39,39,40,40,40,40,40,41,41,41,41,41,42,42,42,
42,42,43,43,43,43,44,44,44,44,44,45,45,45,45,45,46,46,46,46,
46,47,47,47,47,47,48,48,48,48,49,49,49,49,49,50,50,50,50,50,
51,51,51,51,52,52,52,52,52,53,53,53,53,53,54,54,54,54,55,55,
55,55,55,56,56,56,56,56,57,57,57,57,58,58,58,58,58,59,59,59,
59,59,60,60,60,60,60,61,61,61,61,61,62,62,62,62,63,63,63,63,
63,64,64,64,64,64,65,65,65,65,66,66,66,66,66,67,67,67,67,67,
68,68,68,68,69,69,69,69,69,70,70,70,70,70,71,71,71,71,72,72,
72,72,72,73,73,73,73,73,74,74,74,74,74,75,75,75,75,75,76,76,
76,76,77,77,77,77,77,78,78,78,78,78,79,79,79,79,79,80,80,80,
80,80,81,81,81,81,81,82,82,82,82,82,83,83,83,83,83,84,84,84,
84,84,84,84,85,85,85,85,85,85,85,85,85,85,85,85,85,85,86,86

ANNEX 3. - Microcontroller basic program to emulate Memristor behavior using the Non-linear emulator circuit.

```
'////////////////////////////////////////////////////
'///  Program for Memristor-Emulator v-1          /////
'///  First version May 15, 2008                  /////
'///  Last modified May 20, 2008                  /////
'///  Compiled for V4.1.3                         /////
'////////////////////////////////////////////////////

$Device= tiny26                 ' used device
$Stack = 30                     ' stack depth
$Clock = 4                      ' adjust for used crystal Int 4 mhz
$Source= On                     ' basic source in Asm

'Define microcontroller's pins

$Def leda=PORTA.0
$Def adcspeed=PORTB.0
$Def sero=PORTB.5
$Def seri=PINB.5
$Def ledb=PORTB.6

$Def resv=ocr1a                 'to change PWM value
$Timer1=PWM,8,PwmA=Normal       'conf PWM mode

'Define Sram

Dim a As Byte
Dim medcount As Byte            'measurement counter
Dim ina As Word                 'analogical input a
Dim inb As Word                 'analogical input b
Dim diffvol As Word             'differential voltage
Dim diffvolc As Word            'differential voltage copy
Dim auxdv As Word               'auxiliary diffvol
Dim charge As Word              'stores charge value
Dim chaabs As Word              'stores charge absolute value
Dim curdir As Byte              'stores current direction
Dim resvv As Word               'stores resistance value in a word
Dim res As Byte

'Define Subroutines

Declare Sub init()
Declare Sub selresv()
```

```
Declare Sub adcread()

'***Begin program

init()

Do

adcread()                    'Reads voltage across component

selresv()                    'Changes resistance value

Loop

'*****************************************************************
'**Programm Subroutines


'*****************************************************************
'***Initalization Subroutine

Sub init()

DDRA=&b10000001    'init porta direction
DDRB=&b01000011    'init portb direction

'Init PWM
tccr1a=&b10000010                 'to correct compiler error
tccr1b=&b00000001
ocr1c=255

Start Adc, Vref=Vcc

For a=0 To 10              'Starting blinking sequence
leda=1
ledb=0
WaitMs 20
leda=0
'ledb=1
WaitMs 20
Next a
ledb=0

ina=0
inb=0
```

```
diffvol=0
charge=30000

curdir=0
resv=1

End Sub

'*******************************************

Sub selresv()


If curdir=1 Then                               'Calculates depending current direction
charge=charge+(diffvol*10/res)                 'Calculate charge
If charge>55000 Then charge=55000
End If

If curdir=2 Then
charge=charge-(diffvol*10/res)                 'Calculates charge
If charge<5000 Then charge=5000
End If

If charge=30000 Then chaabs=0                  'Charge saturation limit
If charge>30000 Then
chaabs=charge-30000
leda=1
ledb=0
'end if
Else
chaabs=30000-charge
leda=0
ledb=1
End If

resvv=255-(chaabs/100)
res=resvv

resv=255-res


End Sub

'**********************************************

Sub adcread()            'Reads voltage across the device
```

```
ina=Adc8(2)
inb=Adc8(3)

If ina>inb Then
diffvol=ina-inb
curdir=1
Else
diffvol=inb-ina
curdir=2
End If

Toggle adcspeed
End Sub
```

7.-References

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EL JURADO DESIGNADO POR LA UNIDAD QUERÉTARO DEL CENTRO DE INVESTIGACIÓN Y DE ESTUDIOS AVANZADOS DEL INSTITUTO POLITÉCNICO NACIONAL, APROBÓ LA TESIS DE MAESTRÍA DEL C. ALEJANDRO JOSÉ GIMÉNEZ GÓMEZ TITULADA: "EMULACIÓN Y SIMULACIÓN DE CIRCUITOS ELÉCTRICOS FORMADOS POR ARREGLOS DE DISPOSITIVOS MOLECULARES", FIRMAN AL CALCE DE COMÚN ACUERDO LOS INTEGRANTES DE DICHO JURADO, EN LA CIUDAD DE QUERÉTARO, QRO., A LOS TREINTA DIAS DEL MES DE ENERO DEL AÑO DOS MIL NUEVE.

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