The simulations were performed using a Coulomb-Boltzmann distribution for the energy of particles [10], introducing a plasma temperature of 30 eV and a plasma potential of 50 V (with energy ranging from 100 to 700 eV). The magnetic field is fixed with dimensions of 25x25x10 mm; it has a value of 0.18 Tesla, in the centre of system. This study would be fine if we use the 32 faraday cups of this device. However, due to the low number of ions that out of the two pinholes and their subsequent separation due to magnetic field, the spectrometer resolution is very low. A solution designed for this device could be to work with a Windowless Electron Multiplier (WEM) placed at 30 degree angle, varying the magnetic field. In this way, we can work with a small number of ions and with a high resolution. Thus, Figure 3 shown a good deflection for aluminium ions (up to 30° angle deflection), due their small mass. However, when the mass goes up, like in tantalum case, we need more intense magnetic field to reach 30° angle deflections.

To use this device as a spectrometer, it is necessary to design an electromagnet with appropriate characteristics. For this design, we have used the COMSOL Multiphysics simulation program. The electromagnet consists of an iron core, having a “C” shape. The iron core design is shown in Figure 4.

The core structure consists of three pieces. The central part is the one on which the coil made of copper is inserted.

Various simulations with COMSOL Multiphysics were performed to evaluate the value of the magnetic field in the iron core cavity. In Figure 5 is shown a simulation of this electromagnet.

---

Figure 3: COMSOL Multiphysics simulations about Al^{1+}-ions and Ta^{1+}-ions, in the system of interest, with a transversal magnetic field module of 0.18 Tesla.

Figure 4: Design of the iron core of the electromagnet.

Figure 5: Simulation of electromagnet with 1000 copper windings cross by 5 current’s Ampere, and magnetic field in the core cavity.
The electromagnet consists of 1000 copper windings. The diameter of the copper wire section is 1.6 mm, in which a current intensity of 5 Ampere is simulated. The simulation was carried out using the B-H curve for iron, so to obtain non-linear solutions when a current is flowed into the solenoid. The magnetic field obtained in the centre of iron core cavity is shown in Figure 5. It reaches the maximum value of 0.31 Tesla, that value is sufficient to deflect also heavy ions at 30° angle. In this way, we can obtain a device with a high resolution, and the correlation between the magnetic field and the TOF for ions, may be indicative of the velocity distribution of plasma ions, similar like in the Ion Energy Analyzer case (IEA) [11]. In Figure 6 a picture of the electromagnet is shown.

![Figure 6: Picture of the electromagnet.](image)

The Figure 6 shows an assembly with 1200 copper windings with a wire's diameter of 1.25 mm. The next step will consist in the calibration of this assembled magnet, before its use for the study of plasmas generated by laser.

**Conclusion**

In this paper, we have introduced a device to characterization of laser-generated plasma in vacuum. The use of fixed magnetic fields can be a valid analysis when we work with small detectors that cover large angles. However, when high resolution measures are required, other types of detectors, often bulky, must be used. This means that it is more convenient to vary the magnetic field rather than the detection angle of the detector. Accordingly, by designing an appropriately studied electromagnet, it is possible to vary the magnetic field by varying the current flowing into the coil of the electromagnet. Thus an accurate study of the properties of the charged particles of the non-equilibrium plasma becomes quick and easy.

**References**


Random bit generators based on skyrmions

I. Medlej1,2* and G. Finocchio1

1Department of Mathematical and Computer Sciences, Physical Sciences and Earth Sciences, University of Messina, Messina, Italy
2Lebanese University of Science and Technology, Beirut Campus, Lebanon
*Corresponding Author email: medlej.israa@gmail.com

Abstract

Magnetic skyrmions are topologically protected non-uniform configuration of the magnetization which can behave as particles. They can be easily manipulated (nucleated, shifted and detected) by spin-polarized current, and for this reason they offer a wide range of applicability fields. In this work, we study the skyrmion dynamics driven by the spin-Hall effect in a synthetic antiferromagnet within a micromagnetic framework. We show that, in presence of thermal fluctuations at room temperature, the skyrmion motion is not deterministic. This feature, combined with a properly designed device, could be exploited for using skyrmions as building blocks of random bit generators.

Keywords: Magnetic Skyrmion, Spin-Hall effect, Micromagnetic modeling, bit generator.

Introduction

The skyrmion, proposed in the context of particle physics, [1] has been stabilized in magnetic materials exhibiting properties such as topological protection[2], [3]. Magnetic skyrmions range in sizes from 10 nm to approximately 100 nm depending on material parameters. They can be created and annihilated by spin currents and magnetic fields, and they can be easily moved by an electrical current [2] - [7]. Skyrmions are also chiral, which means the skyrmion has a definite “sense of rotation”. In other words, the skyrmion and its mirror image cannot be brought to coincide with each other by translation and rotation. A fundamental interaction for stabilizing a magnetic skyrmion is the Dzyaloshinskii-Moriya interaction (DMI) [8], [9] arising from inversion symmetry breaking in material with high spin-orbit interaction (bulk DMI) or from the interface between a ferromagnet and material with high spin-orbit interaction (interfacial DMI) [3], [10], [11]. Most bulk DMI materials belong to the category of B20 compounds and they host Bloch skyrmions, while in multilayered heterostructures Néel skyrmions can be stabilized [3].

In order to manipulate skyrmions, spin-polarized current can be used. For instance, single skyrmion nucleation has been predicted by the use of a perpendicular spin-polarized current [12]. Skyrmion motion has been driven by spin-transfer torque, and, more efficiently, by pure spin currents generated by the spin-Hall effect (SHE) [11]. Skyrmion detection can be performed by optical techniques, such as neutron scattering, or, in the real space, by the Lorentz transmission electron microscopy [6], as well as electrically by a magnetic tunnel junction read-head [13]. Because of their small size, their stability, the demonstration of their individual creation and annihilation, and their facile movement with low current, they are being investigated for information storage (memory). In fact, the most promising technological applications of skyrmion is in racetrack memory [14], where the presence of a skyrmion code the bit “1”, while its absence code the bit “0” [11]. However, several further uses of skyrmion has been predicted, such as in microwave oscillator and detectors [15]–[17], or in logic gates [18]. In this report, we predict the use of skyrmions in random bit generators [19].

A random bit generator is a system whose output consists of fully unpredictable (i.e., statistically independent and unbiased) bits[19]. Here, we provide, by means of micromagnetic simulations, the proof of concept of a random bit generator based on magnetic skyrmions. We exploit the stochastic behavior of skyrmions in presence of thermal fluctuations to achieve the generation of random bits, here represented by the skyrmion. In particular, we drive the skyrmion motion by the SHE in a synthetic antiferromagnetic (SAF) device [20] composed of one input branch and two output branches. We show that, under the same current, skyrmions, which are continuously nucleated in the input branch, are divided randomly in the two output branches. Our results pay the way for the design of a novel application of skyrmions as well as of a new generation of random bit generators.
Device and Modeling

Micromagnetic simulations of a multilayered nanowire with two output branches have been performed (see Figure 1(a)). It is composed of a 3 nm thick Platinum heavy metal (HM) (lower HM) with on top two perpendicular CoNi ferromagnetic layer (FMs) separated by a thin Ruthenium (Ru), layer designed to provide an antiferromagnetic exchange coupling [21] (see Figure 1(a)), and a second HM on top of the whole stack (upper HM) [22].

The device is 1900 nm long and the width of the input and output branches is 320 nm. The thickness of both ferromagnets and Ru layer is 0.8 nm. The physical parameters of CoNi layers taken from [23], [24], and equal for both ferromagnets, are: saturation magnetization $M_s = 600 \, kA/m$, exchange constant $A = 20pJ/m$, uniaxial perpendicular anisotropy constant $k_u = 0.5 \, M_J/m^3$, and damping $\alpha = 0.1$. The interlayer exchange coupling (IEC) constant $A^{ex}$ is fixed to $-5.0 \times 10^4 \, J/m^2$ [23], [24]. We use a discretization cell of $4 \times 4 \times 0.8nm^3$, and introduce a Cartesian coordinate system with the x-, y- and z-axes lying along the length, the width and the thickness of the device, respectively (see inset Figure 1(a)).

The numerical study is carried out by means of a self-implemented micromagnetic solver (it includes the SHE, IDMI and IEC) and post-processing tools [25]–[27].

The total micromagnetic energy density of the system under investigation is (the superscripts L and U refer to lower and upper FMs):

$$
\epsilon_{tot}^{LU} = A(\nabla \cdot \mathbf{m})^2 + e^{ex} + D^{LU} [m^{LU}_z \nabla \cdot \mathbf{m}^{LU} - (\mathbf{m}^{LU} \cdot \nabla) m^{LU}_z] - k_u (m^{LU}_z \hat{z})^2 - \frac{1}{2} \mu_0 M_s m^{LU} \cdot H^{LU}_m
$$

(1)

where $m_x$, $m_y$ and $m_z$ are the x-, y-, and z-components of the normalized magnetization, respectively. The interlayer exchange energy is given by $e^{ex} = -(A^{ex}/l_{Ru}) \cdot (\mathbf{m}^{L} \cdot \mathbf{m}^{U})$ (same contribution for both FMs), where is the thickness of the Ru layer [28]. $D$ is the parameter taking into account the intensity of the IDMI. More specifically, $D^L(D^U)$ refers to the lower (upper) FM. According to our definition, $D^L$ and $D^U$ are materials properties (they are not related to the multilayer geometry), i.e. in the specific case where both lower and upper FMs are the same (see inset Figure 1(a)), one would have $D^L = D^U$. We fixed $D^L = D^U = 2.5 \, mJ/m^2$ [22].

The Pt/FM interface produces the lower IDMI, while the upper IDMI derives mainly from an upper HM. $\hat{z}$ is the unit vector along the z-direction, $\mu_0$ is the vacuum permeability. $H_m$ is the magnetostatic dipolar field, which is computed by considering both ferromagnetic layers. The boundary conditions related to the IDMI are [29], [11]:

$$
\frac{d\mathbf{m}^{LU}}{dt} = \frac{1}{\xi^{LU}} (\hat{z} \times \mathbf{n}^{LU}) \times \mathbf{m}^{LU}
$$

where $\mathbf{n}$ is the unit vector normal to the surface and $\xi^{LU} = 2A/D^{LU}$ is a characteristic length.

We wish to underline that, when considering the dynamical analysis, the presence of two HMs gives rise to a lower and upper SHE when an electric current is passed through them (the electrical current here denotes a flow of electrons). In order to model this behavior, it is necessary to introduce two spin-Hall angles, $\theta_{SH}^{L}$ and $\theta_{SH}^{U}$, for the lower and upper FMs, respectively (see inset Figure 1(a)). As for $D^L$ and $D^U$, according to our definition, the two spin-Hall angles are only linked to material properties. We fixed $\theta_{SH}^{L} = \theta_{SH}^{U} = 0.10$ [24].

![Figure 1](image.png)

**Figure 1**: (a) 2D view of the SAF multilayer under investigation, where the input branch and two output branches are indicated. Inset: 3D sketch of the input branch, where the ferromagnets (FM), separated by a Ru layer, are sandwiched between different heavy metals (HM). (b) Snapshot representing examples of the spatial distribution of the magnetization for SAF Néel skyrmion (Skx). A color scale, linked to the z-component of the magnetization, is also indicated.

The thermal effects are accounted into the micromagnetic solver as a stochastic term $h_{th}$ added to the deterministic effective magnetic field in each computational cell $h_{th} = (\chi/M_S)\sqrt{2/(\alpha K_B T/\mu_0 \Delta V M_S \Delta t)}$ with $K_B$ being the Boltzmann constant, $\Delta V$ the volume of the computational cubic cell, $\Delta t$ the simulation time step, $T$ temperature of the sample, and $\chi$ a three-dimensional white Gaussian noise with zero mean and unit variance [30].
Results

We carry out a micromagnetic study at room temperature $T = 300$ K and zero external. We apply an electrical current $jHM$ only through the lower HM. All the results are shown for $jHM = -2.0 \times 10^8$ A/cm$^2$, but similar results are obtained for current densities in the range $-2.25 \times 10^8$ A/cm$^2 \leq jHM \leq -0.25 \times 10^8$ A/cm$^2$.

We perform micromagnetic simulations within a simulation time of 60 ns, where we continuously nucleate a single Néel skyrmion in the input branch. In order to simulate such a periodic nucleation, we modified our micromagnetic code such that, every 5 ns, a skyrmion is nucleated in the input branch.

We observe that the skyrmions divide randomly in the two output branches (see example in Figure 2). This is because of the stochastic behavior of skyrmions in presence of thermal fluctuations [13].

![Figure 2: Example of spatial distribution of the magnetization for the lower ferromagnetic layer after 30 ns. Two skyrmions went to the upper output branch, three skyrmions went to the lower output branch, while another skyrmion is coming from the input branch.](image)

Conclusion

We have shown via a full micromagnetic simulations the possibility to move randomly skyrmions in presence of spin-Hall effect and thermal fluctuations in a synthetic antiferromagnets. We have observed that, under the steady action of the current, skyrmions stochastically divided in the two output branches of our device starting from a continuous nucleation in the input branches. Our results open the path for the designing of random bit generators based on skyrmions.

References


Temperature-Dependent FTIR-ATR Spectral Variations in pure 1-propyl Alcohol: a 2D Correlation Spectroscopy and Statistical Analysis

Giuseppe Paladini*

Department of Mathematics, Computer Sciences, Physics and Earth Sciences, University of Messina.

*Corresponding Author email: gpaladini@unime.it

Abstract

In this work, the temperature-dependent middle-infrared (MIR) spectral variations of pure 1-propyl alcohol have been studied by 2-dimensional (2D) correlation spectroscopy over a range between 253 K and 347 K. Experimental data were used as dataset for the computation of the synchronous and asynchronous correlation maps, which contain the modulated intensity profile induced by the perturbation variable (temperature). The original absorbance dataset, composed of 10 spectra, was recorded in the 400 - 4000 cm\(^{-1}\) region using the attenuated total reflectance geometry (ATR), although only the 2700 - 3700 cm\(^{-1}\) region was studied in detail (-CH and -OH stretching region). Furthermore, the position of isosbestic point was calculated with high accuracy by mathematical manipulation of the raw data.

Keywords: FTIR - ATR, 1- Propanol, 2D Correlation Spectroscopy Analysis, Isosbestic point.

Introduction

The study of H-bond (HB) dynamics in liquids (e.g. polymers, alcohols, etc.) represents a challenging task for most research groups. As is well known, it plays a fundamental role in driving some important biological phenomena and it is the main cause of water diffusion mechanism in polymers.

Alcohols represent an example of amphiphilic hydrogen-bonded liquids containing both polar hydrophilic hydroxyl and nonpolar hydrophobic alkyl functional groups, which are the responsible for the bio-compatibility of these systems respect to a given chemical environment. For this reason, understanding the properties associated to the $\nu_s(OH)$ in alcohols and how these oscillators are correlated to different functional groups of the same sample can provide useful informations in terms of diffusion performances and chemical affinity. Here, we focused our attention on an important example of aliphatic alcohol named 1 - Propanol (or 1 - Propyl Alcohol (1PR)). 1PR is an isomer of propan-2-ol and it is usually used as solvent in the pharmaceutical industry and for resins and cellulose esters (fig. 1).

![Structure formula of 1 - Propyl Alcohol.](image)

Figure 1: Structure formula of 1 - Propyl Alcohol.

Only in recent years, due to its high "octane number" (118) has it been used also as engine fuel, despite its high production costs.

In order to characterize the temperature dependent variation of the OH stretching band (3000-3700 cm\(^{-1}\)) and the "in-phase" and "out-of-phase" intensity changes respect to the $-\text{CH}_2$ and $-\text{CH}_3$ modes (2700 - 3000 cm\(^{-1}\)) we analysed the FTIR-ATR spectra of 1PR by means of 2D correlation spectroscopy. This technique allowed us to compute correlation intensity among different functional groups as a function of $T$.

Recently, the physical structure of 1PR has been widely studied by means of different approaches based on infrared, Raman and microwave spectroscopy [1, 2]. The results reveal that 1PR can be found (in liquid state) in two different conformations: -trans and -gauche, which differ in the relative position of the hydroxyl group compared to the methyl group. For the 1PR molecules in gauche conformation, the hydroxyl and methyl groups are separated by an angle of about 180°, whereas, in the second configuration, the same groups are spatially closer. In 1963, P. J. Krauter [3] demonstrated that the fundamental OH stretching mode of 1PR in a CCl\(_4\) solution can be considered as the mathematical convolution of three sub-bands, each of which is associated to three different structural conformations (2 to trans-conformation and 1 to the gauche). Furthermore, we will see that 3 kinds of O-H oscillators coexist in the investigated liquid with different cooperativity.

Each absorption band has a unique temperature evolution due to structural modifications which oc-
cour by increasing/decreasing the temperature applied. The aim of this work was to study this evolution as a function of $T$, trying to obtain useful information about the structural and dynamical properties of IPR. Finally, the isosbestic point in the 3000 - 3700 cm$^{-1}$ wavenumber region was also calculated by means of a statistical approach recently proposed by Vardevanyan et. al.

**Material and Methods**

**Material**

1 - Propanol was purchased from Sigma - Aldrich (Steinheim, Germany) with a 99.5 % purity level and used without any further purification. FTIR - ATR measurements were performed between 253 and 347 K.

**Methods**

**FTIR - ATR measurements**

The FTIR-ATR spectra of IPR were collected over a wavenumber range between 400 - 4000 cm$^{-1}$ using a Bomen DA8 Fourier Transform Spectrometer. It is equipped with a Globar source (10 - 1000 cm$^{-1}$ emission range) and a DTGS detector. A horizontal ATR Ag-based crystal was positioned in the sample compartment of the BOMEM DA8 and fixed by means of a proper support. 100 scans were carried out to reduce the thermal noise with a spatial resolution of 0.5 cm$^{-1}$.

**2D Correlation Spectroscopy Analysis**

An accurate comparison of the spectral intensity variation profile due to a temperature-perturbation was evaluated by the 2D correlation spectroscopy technique (2DCorrS), first proposed by Noda in 1986. Basically, starting from a set of raw data (experimental spectra), affected by some external perturbations (e.g. temperature), we can estimate the so-called synchronous and asynchronous maps which contain all the information on the intensity correlation between the temperature-dependent input data. Generally speaking, the spectral intensity can be defined as $I(\nu, t)$, where $\nu$ is wavenumber and $t$ is the external variable (temperature in this case). Then, the correlation function between two different spectra $I(\nu_1, t)$ and $I(\nu_2, t)$ can be written as:

$$A(\nu_1, \nu_2) = \langle \tilde{I}(\nu_1, t) \cdot \tilde{I}(\nu_2, t) \rangle \quad (1)$$

where $\tilde{I}(\nu_1, t)$ and $\tilde{I}(\nu_2, t)$ represent the dynamical spectra defined as $\tilde{I}(\nu, t) = I(\nu, t) - \tilde{I}(\nu)$. $\tilde{I}(\nu)$ can be considered as the reference spectrum of the system which can be chosen arbitrarily. Eqn. (1) can be rewritten as a complex function and splitted into two different contributions called synchronous ($\phi(\nu_1, \nu_2)$) and asynchronous ($\varsigma(\nu_1, \nu_2)$) parts of the correlation function:

$$A(\nu_1, \nu_2) = \phi(\nu_1, \nu_2) + i \varsigma(\nu_1, \nu_2) \quad (2)$$

For a set of discrete intensity columns (10 in this case, one for each spectrum) and assuming that measurements are approximately equidistantly spaced in T, we can compute the synchronous and asynchronous maps using the following relations:

$$\phi(\nu_1, \nu_2) = \frac{1}{k-1} \sum_{m=1}^{k} \tilde{I}(\nu_1) \cdot \tilde{I}(\nu_2) \quad (3)$$

$$\varsigma(\nu_1, \nu_2) = \frac{1}{k-1} \sum_{m=1}^{k} \tilde{I}(\nu_1) \cdot N \cdot \tilde{I}(\nu_2) \quad (4)$$

Where $k$ is the number of measurements and $N$ is the Hilbert-Noda trasformation matrix. The first term of the correlation function (eqn. 3) describes the coincidental variation of the intensity associated to the original dataset; in other words, peaks on the synchronous map develop only if the band intensities of the measured spectra at $\nu_1$ and $\nu_2$ increase or decrease together. On the other hand, the second term (eqn. 4) shows the "out-of-phase" or non-sequential intensity changes of the measured data.

**Results and Discussion**

Fig. 2 shows the FTIR - ATR spectra of IPR in a wavenumber region between 2700 - 3700 cm$^{-1}$ over the whole range of temperature (253 - 347 K).

![Figure 2: FTIR - ATR spectra (2700 - 3700 cm$^{-1}$) of 1 - Propyl Alcohol collected over a temperature range between 253 and 347 K.](image)
raw data and subsequently connected by interpolation, giving as a result the subtracted spectra. Finally, all spectra were properly normalized. In fig. 2 we can distinguish three different peaks in the 2700 - 3000 cm$^{-1}$ range due to the methyl groups vibrations centred at 2872 ($\nuCH_2$) and 2963 ($\nuCH_3$) cm$^{-1}$, and one due to the methylene mode at 2935 cm$^{-1}$. Furthermore, the multi-component broad band centred at 3330 cm$^{-1}$, due to hydroxyl oscillators, was also detected.

At first glance, all the presented spectra show a specific temperature evolution characterized by a decrease/increase of the absorption peak intensities, and by a shift of the $\nu$(OH) towards higher energy. This wavenumber shift can be attributed to a modification of the relative percentage of the -OH modes ranging from "strongly arranged" to "free" OH oscillators (between 3000 and 3450 cm$^{-1}$), induced by the increasing temperature. In order to take into account this variation, we carried out a deconvolution of the OH stretching absorption band in three sub-bands, according to the three different structural conformations of the OH stretching mode in 1PR, centred at 3219, 3329 and 3443 cm$^{-1}$. For each sub-band, the percentage area (number of relative oscillators) was calculated in order to evaluate the population of each "arrangement" with increasing temperature. Here, we report these results over a T range between 297 and 347 K, as example.

The first sub-band (sub-band 1) can be attributed to the strongly arranged OH oscillators (or bonded O-H). Whereas, the second and third sub-band (sub-bands 2 and 3) can be attributed to partially formed and free hydrogen bonded O-H, respectively. From fig. 3 we observe a decrease of the percentage area associated to sub-band 1 with increasing temperature, at the expense of an increase of both sub-band 2 and 3, as expected. This is due to thermal effects, which lead to de-structuration processes promoting a monomeric dispersion instead of a supramolecular aggregate.

2D correlation IR spectroscopy was also used to evaluate the temperature-dependent intensity correlation in 1PR in a wavenumber range between 2700 and 3700 cm$^{-1}$. The synchronous and asynchronous map were calculated using MATLAB (2015) by considering $I(\nu_1,t)$ and $I(\nu_2,t)$ as n-dimensional vectors, where n is the number of rows (or, equivalently, the number of Y values). In fig. 4, the synchronous and asynchronous maps are displayed in the region of 2700 - 3700 cm$^{-1}$.

![Figure 3: Behaviour of the percentage area of the three sub-bands over a temperature range between 253 and 347 K.](image)

![Figure 4: synchronous and asynchronous map in the 2700 - 3700 cm$^{-1}$ obtained by the temperature-dependent FTIR-ATR absorption spectra of 1PR.](image)
bond network in 1PR, reveal the presence of an isosbestic point somewhere between these two frequency values. Finally, the last 3 peaks (blue circles) are due to strong cross-correlation between =CH and -CH₃ functional groups.

Information about the unsynchronized (or sequential) cross-correlation profile were obtained by the analysis of the asynchronous spectrum displayed in the triangle below the diagonal line of fig. 4. In particular, the two negative cross-peaks (band "D") at (3246,3377) and (3211,3377) (light blue circles) suggest that, with increasing temperature, the intensity at 3246 and 3211 decrease predominantly (or faster) respect to the increase of the 3377 cm⁻¹ absorption peak. This means that there is an initial breaking of the highly cooperative O-H oscillators followed by the formation of "free" O-H, as expected. In addition to this, we can distinguish 6 different positive cross-peaks related to the out-of-phase intensity changes between the O-H and the =CH₂ and -CH₃ oscillation modes. Accordingly, peaks associated to high cooperative O-H groups (3211 and 3246 cm⁻¹) decrease before the increase of both methyl and methylene groups of 1PR implying that, with increasing temperature, =CH₂ and -CH₃ stretching vibrations are effected by temperature less than OH stretching modes.

A statistical approach, firstly proposed by P. O. Vardevanyan et. al, was used to calculate the isosbestic point (IP) in the O-H stretching mode region (3000 - 3700 cm⁻¹) with high accuracy.

Let $I_i(\nu)$, with $1 < i < 10$, be the $i$-th spectrum of the original dataset. They demonstrated that the mean square deviation $\sigma(\lambda)$ (MSD) of all spectra can provide the position of the isosbestic point by calculating its minimum value. In order to do this we computed $\sigma(\lambda)$ with ORIGIN software by using the following algorithm:

$$\sigma(\lambda) = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (I_i(\lambda) - \bar{I}(\lambda))^2}$$

where $\bar{I}(\nu)$ represents the average spectrum of the origin set of measured data. In fig. 5 we report the MSD profile and its first derivative in the wavenumber region between 3000 and 3700 cm⁻¹. As we can see, a clearly visible minimum of the MSD function was detected. In order to evaluate the frequency associated with that value with high precision, we calculated the first derivative (bottom figure) trying to figure out where this function crosses the zero line. As a results, we found the presence of an isosbestic point at 3332 cm⁻¹ in the region between 3150 - 3400 cm⁻¹, which is in accordance with the 2D correlation results in the same region. At this point in 1PR no intensity variation was observed with increasing temperature.

Figure 5: MSD function (top) and its first derivative (bottom) calculated from the set of 10 original measured spectra

**Conclusions**

In this work, the FTIR-ATR technique was used to evaluate the temperature dependent intensity variation of hydroxyl and methyl groups in 1-propanol alcohol. In order to do this, 2D correlation spectroscopy was also used revealing features otherwise un-recognizable. In particular, the intensity correlation profile was calculated as a function of T revealing how the OH and =CH₂ and -CH₃ modes are strongly affected by temperature. Peaks at 3284, 2986, 2931 and 2877 were found to change intensity in the opposite direction to that of peak at 3337 cm⁻¹ with increasing temperature. Finally, the isosbestic point in the O-H stretching region was also evaluated by means of a statistical approach proposed Vardevanyan in 2015 showing an IP centred at 3332 cm⁻¹ implying the presence of at least two different OH arrangements.

**References**


V. Romano* and G. D’Angelo

Dipartimento di Scienze Matematiche ed Informatiche, Scienze Fisiche e Scienze della Terra, viale F. Stagno d’Alcontres 31, Messina, Italy

*Corresponding Author email: vromano@unime.it

Abstract

Graphene shows astonishing properties that can be exploited in many applications, for example high performance microcircuits. Many physicochemical procedures are being used for the production of such devices, one is the local reduction of graphene oxide to graphene by means of laser ablation. Of course, it is necessary to investigate the structure of the irradiated samples to get detailed insights into the as-produced material. For this reason, micro-Raman spectroscopy is used as a characterisation technique either for its non destructive nature and for its ability to distinguish between the plethora of existing carbon materials. We report the results we got by irradiating GO with a Nd:YAG laser (1064 nm) using different laser fluences: 15 J/cm², 7.5 J/cm² and 5 J/cm². We studied the laser-induced changes in the main Raman contributions of graphitic materials: the D, G and 2D bands. We used as figure of merit (FOM) parameters the intensity ratios \( I_D/I_G \) and \( I_{2D}/I_G \) computed for the different laser treated samples, finding out that higher fluences do not lead to a better reduction process.

Keywords: graphene, laser ablation, Raman spectra.

Introduction

In 1935 Peierls [1] stated that 2D crystal could not exist since they are thermodynamically unstable. The discovery of graphene in 2004 by Novoselov et al [2] gave a huge thrust through the search of 2D materials, since they show astonishing physicochemical properties [3], the electrical ones being of great potential for use in micro-electronics [4][5]. However, high resolution transfer printing methods are needed to produce high quality microcircuits [6], so many procedures have been used. One chance is to adopt a top – down approach, using as a starting material graphite oxide (GO). The oxidation of graphite is obtained with strong oxidizing compounds (like \( KMnO_4 \)) [7]. However this procedure induces modifications of graphite structure since epoxy and hydroxyl groups occur in the basal plane, while carboxylic groups arise at the edges [8][9]. These defects are responsible for the insulating or semiconducting properties of GO. The reduction of graphite oxide can be accomplished with dehydration, thermal reduction, UV-assisted photocatalysis [10] and finally laser ablation [11]. However high intensity laser beams (\( 1 \sim 1010W/cm^2 \)) induce changes in the composition, foil thickness, mechanical properties and morphology [12], i.e. light treatment induces many defects on the material. This means that a thorough and reliable structural analysis is needed to understand the quality of the graphene produced by laser ablation. In this perspective, micro-Raman spectroscopy is fundamental owing to its sensitivity to geometric structure, allowing its use for the study of carbon allotropes (i.e. diamond, carbon nanotubes [13], buckminster fullerenes [14], graphene nanoribbons [15], etc.). In this work we report on the results of a micro-Raman investigation on laser irradiated GO samples, using different laser fluences.

The Raman spectra of pristine and defected graphene

Pristine graphene is characterised by a Raman spectrum where two main contributions occur: the \( G \) band (1582 \( cm^{-1} \)) and the \( 2D \) band (around 2700 \( cm^{-1} \)) [16]. (Fig. 1, top, shows an example of this spectrum, taken from [17]).
The G band arise from an $E_{2g}$ symmetry phonon mode which is due to an in plane vibration of $sp^2$ carbon networks, while the 2D peak is the overtone of the D peak (a defect induced contribution that is not present in pristine graphene). The latter peak originates from a process where no defects are required for its activation, so the 2D peak is always present [16]. In high quality graphene a single G peak and a sharp 2D peak, roughly four times more intense than the G peak, occur. As concerns few layers and/or defected graphene, both the G and 2D regions are affected by many defect-induced contributions [17]: 1350 cm$^{-1}$ ($D$ band), 1620 cm$^{-1}$ ($D'$ band), 2445 cm$^{-1}$ ($D+D''$ band), 2923 cm$^{-1}$ ($D+D'$ band) and 3160 cm$^{-1}$ ($2D'$ band) [16]. This means that the intensity ratio for the $D$, $G$ and 2D Raman bands can be used to verify the graphene quality: minimum of $I_D/I_G$ and maximum of $I_{2D}/I_G$ characterise the highest quality of graphene and, in the perspective of the present work, provide information on the best conditions for the GO-to-graphene reduction. In fact, the first ratio relates to the in-plane crystallite sizes [16], while $I_{2D}/I_G$ is used to distinguish a single layer, from bilayer from few (less than 5) layers [17].

**Experimental**

**Material Synthesis**

The graphite oxide (GO) foils were prepared using the Hummer method as described in detail in [18].

**Laser treatment**

We used a Nd:YAG laser with the following characteristics: fundamental wavelength of 1064 nm, 3 ns pulse duration, 300 mJ maximum pulse energy, 1 mm$^2$ spot size focus, about $10^{10}$ W/cm$^2$ intensity. It can be used in single pulse or up to 10 Hz repetition rate. The ablation of GO occurred in a sample chamber using a transparent window and an external lens with 50 cm focal length. Different laser pulse energies have been employed: 150 mJ, 75 mJ and 50 mJ, with a fluence of 15 J/cm$^2$, 7.5 J/cm$^2$ and 5 J/cm$^2$, respectively. A scheme of the experimental set up is reported in Fig. 2.

![Experimental set-up for graphene irradiation.](image)

**Characterisation**

Raman microscopy was used to investigate the structural transformations in GO samples. Raman measurements were performed with 532 nm excitation light by using the LabRam HR800 (Horiba Jobin Yvon) spectrometer with the 1800 gr/mm grating and a CCD camera cooled with liquid nitrogen. The laser power used was 1 mW and the spectra were taken with the 50x objective lens. The overall integration time was 100 s.

**Results and Discussion**

Different laser fluences (5 J/cm$^2$, 7.5 J/cm$^2$ and 15 J/cm$^2$) have been used to irradiate the GO samples in air atmosphere. We measured the Raman spectra of all the ablated samples and compared them to the reference one. The results are shown in Fig. 3.
Two different regions can be recognised: the medium-Raman-shift region (below 2000 cm$^{-1}$) and the high-Raman-shift region (above 2000 cm$^{-1}$). The $D$ and $G$ bands dominate the first area, while a broad bump occurs in the high Raman shift region. The reference spectrum is characterised by a similar intensity of both the $D$ and $G$ peaks while the high frequency bump has a low intensity. The latter observation underlies that the sample is made up by several layers and that defects (e. g. structural, chemical, etc) are present (otherwise a sharp 2D peak would be visible). As concerns the irradiated samples, the $D$ peak has a higher intensity the $G$ peak, emphasising that a higher quantity of defects is present with respect to the reference sample, although the 2D peak is more intense.

These qualitative observations are supported by the values of intensity ratios $I_D/I_G$ and $I_{2D}/I_G$, that we used as figure of merit (FOM) of our study. Minimum of $I_D/I_G$ and maximum of $I_{2D}/I_G$ indicate that the ablation procedure lead to a better quality graphene. The intensity ratios for the spectra of Fig. 3 are reported in Tab. 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_D/I_G$</th>
<th>$I_{2D}/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>0.96</td>
<td>0.68</td>
</tr>
<tr>
<td>5 J/cm$^2$</td>
<td>1.14</td>
<td>0.78</td>
</tr>
<tr>
<td>7.5 J/cm$^2$</td>
<td>1.17</td>
<td>0.69</td>
</tr>
<tr>
<td>15 J/cm$^2$</td>
<td>1.17</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Table 2: Computed values of the intensity ratios $I_D/I_G$ and $I_{2D}/I_G$ for the Raman spectra shown in Fig. 3.

These results confirm that irradiated GO samples are thinner but have more defect with respect to the reference sample. We believe that there are two possible reasons for this observation. First of all, the laser treatment was carried out in air atmosphere, so oxide species can be created ($CO$, $CO_2$) inducing more structural and chemical defects [19]. Finally, the irradiation causes the removal of layers (so the $I_{2D}/I_G$ ratio increases) but more edge defects occur.

**Conclusions**

Nanosecond laser pulses were used to reduce locally graphite oxide to graphene. Our results show that the as produced graphene is not of high quality for two main reasons. On the one hand, it is made up by too many layers (low intensity of the 2D peak), on the other hand the $I_D$ peak is higher in the irradiated samples than in the reference one. The latter can be ascribed to the presence of either edge – defects and oxidized chemical species, since the irradiation was performed in ambient atmosphere. We believe that better results should be get if the whole procedure is carried out in inert atmosphere or in vacuum. If this will be the case, nanosecond laser irradiation could compete with pico and femtosecond laser pulses treatments.

**Acknowledgements**

The authors want to thank Mariapompea Cutroneo and Vladimir Havranek, from the Nuclear Physics Institute (Rez, Czech Republic) for proving the graphene oxide samples and Professor Lorenzo Torrisi, from the MIFT Department of the University of Messina, for performing the laser irradiations. This research was supported by University of Messina Research e Mobility 2016 Project (project code RES AND MOB 2016 TORRISI). The research has been also carried out at CANAM infrastructure LM2015056 and Czech Science Foundation (GACR No. 16-05167S).
References


SEMINARI
DEL DOTTORATO DI RICERCA
IN FISICA
(Svolti nel 2017)
Chemical reactions driven by an electric field

Dr. Giuseppe Cassone

Institute of Biophysics - Czech Academy of Sciences, Brno

Abstract

Methanol is employed as a primary reactant in order to produce a multifaceted set of important chemical compounds, from hydrocarbons to di-hydrogen or dimethyl ether, just to cite some of the accessible derivates. In this respect, the importance of the simplest alcohol is remarked by the envisaged possibility to base on it the world economy by the Nobel laureate G. A. Olah [1]. Among the chemical pathways that stem from methanol, formaldehyde synthesis covers a privileged role due to its manifest economic importance, but it requires the presence of specific catalysts and it is industrially achieved only in the gas phase. 

*Ab initio* molecular dynamics studies have succeeded in predicting complex chemical reactions of organic molecules under extreme conditions of confinement and pressure. Moreover, the remarkable catalytic capabilities of static electric fields has been demonstrated by a series of similar quantum-based molecular dynamics investigations. However, the detailed action of the field is not understood and only very recently the first experimental evidence that electric fields are able to control chemical reactions has been provided [2].

In this talk I will present, *inter alia*, a recently published *ab initio* molecular dynamics study of liquid methanol under the effect of static electric field [3]. It turns out that an extremely simple, but so far unreported, chemical reaction occurs at ambient temperature: $2\text{CH}_3\text{OH} \rightarrow \text{H}_2\text{CO} + \text{CH}_4 + \text{H}_2\text{O}$. This reaction has been characterized by exploiting not only the standard Density Functional Theory tools but also a newly developed scheme for definition of efficient reaction coordinates [4] capable to reveal unexpected microscopic mechanisms and, at the same time, providing an accurate free-energy landscape, fully including the effect of the chemical environment and of the thermodynamics.

References


An interferometric technique for the study of gas-liquid and liquid-liquid interfaces

Prof. Mario Corti

CNR-Istituto per i Processi Chimico-Fisici

Abstract

A new interferometric technique to study gas-liquid and liquid-liquid interfaces is described. Bubbles and drops, either standing by buoyancy or attached to an electrode by surface forces, are subjected to a varying-frequency external excitation, either electric or acoustic, inducing a discrete spectrum of stationary oscillation modes of the interface. Amplitudes, frequencies and widths of such frequency modes are measured by a simple interferometric