**SEDUTA DEL COLLEGIO DEI DOCENTI DEL 37°-38°-39°-40° CICLO**

**24 Ottobre 2024**

Il Collegio dei Docenti del 37°-38°-39°-40° ciclo del Dottorato di Ricerca in Scienze Fisiche e Chimiche dell'Università di Palermo, regolarmente convocato in modalità telematica dal Coordinatore Prof. Marco Cannas, si riunisce sulla piattaforma Microsoft Teams alle ore 14,30 del giorno 24.10.2024 con il seguente ordine del giorno:

1) **Adempimenti per l'esame finale di conseguimento del titolo di dottore di ricerca del 37° ciclo (I° sessione)**
2) **Bando CORI 2024 – Azione D1 "Mobilità di studiosi stranieri verso l'Università di Palermo "**
3) **Attivazioni di percorsi di Dottorato in Cotutela**
4) **Provvedimenti allievi (approvazione di periodi di permanenza all'estero)**
5) **Nomina di Cotutor**
6) **Varie ed eventuali**

Presiede il Coordinatore Prof. Marco Cannas, svolge le funzioni di segretario il Prof. Simonpietro Agnello

Sono presenti

M. Cannas, F. Giannici, S. Micciché, F. Lo Celso, A. Pettignano, F. Messina, G. Micela , S. Benatti, T. Di Salvo, G. Lazzara, A. Sciortino, F. Ferrante, M. Miceli, U. De Giovannini, F. Ciccarello, G.M. Palma, D. Valenti, S. Agnello, F. Reale, G. Marsella, P. Pagano, M. Paternostro, M. Scopelliti, S. Lorenzo, A. D'Ai, F. Bagarello, L, Rizzuto, A. Carollo

Sono assenti giustificati

C. Fazio, S. Milioto, L. Burderi, G. Cusumano, G. Buscarino, R. Iaria, B. Militello, A. Napoli, R. Passante, G. Cavallaro, M. Del Santo

Sono presenti inoltre C. Pinto e F. Pintore in qualità di cotutor

Il Presidente, prof. M. Cannas, verificato il numero legale, dichiara aperta la seduta e passa a discutere il primo punto all'ordine del giorno:

**1) Adempimenti per l'esame finale di conseguimento del titolo di dottore di ricerca del 37° ciclo (I° sessione)**

Il presidente illustra gli adempimenti necessari per il conseguimento del titolo di dottore di ricerca per gli allievi del 37° ciclo che concludono il loro dottorato il 31 ottobre 2024 e intendono sostenere l'esame finale nella prima sessione (15 Novembre – 19 Dicembre 2024).

In accordo al cronoprogramma. il presente collegio dei docenti dovrà occuparsi dei seguenti punti:

- formulazione della relazione del dottorando sulle attività svolte
- formulazione del parere per il titolo di Doctor Europaeus
- proposta di formazione delle commissioni giudicatrici
- nomina dei valutatori esterni

**Cozzo Gabriele**

(Tutor: Prof. Fabio Reale; Cotutor: Prof. Paolo Pagano)

Il collegio prende visione della relazione dell'allievo (**allegato 1 al verbale**).

Il collegio propone che la commissione giudicatrice per l'esame finale sia composta da:

Membri effettivi

1) **Prof. Marco Miceli**, Università degli Studi di Palermo, marco.miceli@unipa.it

2) **Prof. Andrea Verdini**, Università di Firenze

3) **Dott. Stefano Vercellone,** INAF - Osservatorio Astronomico di Brera

Membro supplente

**Dott.ssa Costanza Argiroffi** Università degli Studi di Palermo

Il collegio nomina i valutatori esterni:

1) **James A. Klimchuk,** NASA Goddard Space Flight Center Greenbelt, MD 20771 USA

email: James.A.Klimchuk@nasa.gov

2) **Tom Van Doorsselaere,** Centre for mathematical Plasma Astrophysics, Mathematics Department, KU Leuven, Belgium

email: tom.vandoorsselaere@kuleuven.be

**Alberto Ulgiati**
(Tutor: Dott. Giancarlo Cusumano; Cotutor: Dott. Fabio Pintore)

Il collegio prende visione della relazione dell'allievo (**allegato 2 al verbale**).

Il collegio propone che la commissione giudicatrice sia composta da:
Membri effettivi
1) **Prof. Marco Miceli**, Università degli Studi di Palermo, marco.miceli@unipa.it
2) **Prof. Andrea Verdini**, Università di Firenze
3) **Dott. Stefano Vercellone,** INAF - Osservatorio Astronomico di Brera

Membro supplente
**Dott.ssa Costanza Argiroffi** Università degli Studi di Palermo

Il collegio nomina i valutatori esterni:

1) **Antonio Stamerra**, INAF, Osservatorio Astronomico di Roma, Roma (RM), Italy,
email: antonio.stamerra@inaf.it

2) **Marina Manganaro,** University of Rijeka, Faculty of Physics, Rijeka, Croatia
email: marina.manganaro@phy.uniri.hr

**Maria Rita Caruso**

(Tutor: Prof. Giuseppe Lazzara; Cotutor: Prof. Giuseppe Cavallaro)

Il collegio prende visione della relazione dell'allieva (**allegato 3 al verbale**).

Il collegio propone che la commissione giudicatrice sia composta da:

Membri effettivi

1) **Prof. Francesco Ferrante,** Università degli Studi di Palermo, francesco.ferrante@unipa.it

2) **Prof.ssa Silvia Prati,** Università di Bologna

3) **Prof. Matko Erceg,** University of Split, Faculty of Chemistry and Technology – Spalato (Croazia)

Membro supplente

**Prof.ssa Maria Luisa Saladino,** Università degli Studi di Palermo

Il collegio nomina i valutatori esterni:

1) **César Viseras Iborra,** University of Granada, Spain

email: cviseras@ugr.es

2) **Magdalena Broda**, Poznan University of Life Sciences, Polonia

email: magdalena.broda@up.poznan.pl

Inoltre, per l'allieva Maria Rita Caruso, il collegio attesta che sono soddisfatti i criteri per conseguire il titolo di **Doctor Europaeus**, ed **esprime un parere positivo.**

**Chiara Nania**

(Tutor: Prof. Francesco Ferrante; Cotutor: Prof. Dario Duca)

Il collegio prende visione della relazione dell'allieva (**allegato 4 al verbale**).

Il collegio propone che la commissione giudicatrice sia composta da:

Membri effettivi

1) **Prof. Giuseppe Lazzara**, Università degli Studi di Palermo, giuseppe.lazzara@unipa.it

2) **Prof. Francesco Arena,** Università degli Studi di Messina

3) **Prof. Orlando Crescenzi,** Università degli Studi di Napoli «Federico II»

Membro supplente

**Prof.ssa Delia Chillura Martino**, Università degli Studi di Palermo

Il collegio nomina i valutatori esterni:

1) **Dmitry Murzin,** Laboratory of Industrial Chemistry and Reaction Engineering - Åbo Akademi University, Turku (Finlandia)

email: Dmitry.Murzin@abo.fi

2) **Mauro Stener,** Dipartimento di Scienze Chimiche e Farmaceutiche - Università di Trieste

email: stener@units.it

**2) Bando CORI 2024 – Azione D1 "Mobilità di studiosi stranieri verso l'Università di Palermo "**

Il comunica che in data 06/08/2024 ha emesso il seguente decreto trasmesso alla commissione CoRI dell'Università degli Studi di Palermo

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**Oggetto:** Ciclo di lezioni nell'ambito del progetto CoRI 2024 (Azione D)

Proponente: Prof. Davide Valenti

Studioso straniero: Prof. Eugene Demler, ETH Zurigo (Svizzera),

Il Coordinatore,

- visto il Bando CoRI 2024 (pubblicato all'Albo Ufficiale al n. 2841 del 10/07/2024);
- vista la richiesta di partecipazione del Prof. Davide Valenti al Bando Cori 2024, Azione D, linea di finanziamento 3 (mobilità breve incoming);
- visto che le tematiche dei seminari proposti sono attinenti all'attività formativa del Dottorato di Ricerca in Scienze Fisiche e Chimiche;
- considerata l'urgenza e che in tempi brevi non è previsto un Collegio di Dottorato;

DECRETA

che, qualora finanziato nell'ambito del progetto CoRI 2024 (Azione D), il ciclo di lezioni del Prof. Eugene Demler, come da piano didattico allegato dal proponente, verrà incluso nell'offerta formativa del Dottorato.

Il presente decreto sarà portato a ratifica nella prima seduta utile del Consiglio.

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Il Prof. Davide Valenti illustra il programma del corso previsto nel 2025.

*Many-body physics with ultracold atoms*

che è rivolto agli allievi di Dottorato e consiste in un ciclo di lezioni frontali, 4 lezioni della durata di 2 ore, per complessive 8 ore.

**Il collegio approva all'unanimità la ratifica del decreto.**

Alle ore 15:00 lasciano la riunione del collegio i Proff. D. Valenti, T. Di Salvo, L. Rizzuto

**3) Attivazioni di percorsi di Dottorato in Cotutela**

Il Coordinatore comunica che è pervenuta la richiesta da parte del Prof. G Giampiero Buscarino e della Dott.ssa. Alice Sciortino di avviare una procedura di co-tutela di tesi di dottorato per il dottorando Giuseppe Ficarra, iscritto al primo anno del dottorato di ricerca in "Scienze Fisiche e Chimiche" (39° ciclo) dell'Università degli Studi di Palermo, interessato ad attivare una co-tutela con il Dottorato in "Sciences Ingénierie, Santé" dell'Università Jean Monnet di Saint-Étienne (France), al fine di conseguire il doppio titolo di dottore di ricerca.

La tesi di dottorato del predetto dottorando ha per tema "*Variazione delle proprietà ottiche di Metal Organic Framework sotto sollecitazioni radiative, termiche ed esposizione a gas*.

Il dottorando trascorrerà un periodo di circa 12 mesi presso l'Université Jean Monnet, Saint-Étienne

I Direttori della tesi presso l'Ateneo di Palermo sono il Prof. Giampiero Buscarino (tutor) e la Dott.ssa Alie Sciortino (cotutor).
I Direttori della tesi presso l'Ateneo di Saint-Étienne sono il Prof. Prof. Aziz Boukenter (tutor) e il Prof. Vincenzo De Michele (cotutor)

Il Collegio, esaminata la richiesta, riconosce la validità didattica per l'arricchimento del percorso formativo del dottorando in questione e la coerenza con quello del corso di dottorato dell'Università Jean Monnet di Saint-Étienne. Approva, pertanto, all'unanimità la richiesta di co-tutela di tesi avanzata dal dottorando Giuseppe Ficarra.

La relativa convenzione di co-tutela, nonché la documentazione di rito, dovrà essere presentata agli Uffici amministrativi del Rettorato (Settore Strategia per la Ricerca – UO Dottorati di Ricerca") nelle forme e nei modi opportuni.

**4) Provvedimenti allievi (approvazione di periodi di permanenza all'estero)**

Il coordinatore comunica di aver ricevuto da parte dell'allieva **Rashida Aslam** (XXXVIII ciclo) la richiesta di autorizzazione per recarsi in missione presso:

**Department of Physics at National Central University, Taiwan**

da Novembre 2024 ad Aprile 2025, per un periodo complessivo di mesi 6.

L'allieva Rashida Aslam svolgerà attività di ricerca e formazione inerente il proprio progetto di ricerca, sotto la supervisione del Prof. Yu-Jung Chen.

**Il collegio approva all'unanimità**

**5) Nomina di Cotutor**

Il coordinatore comunica di aver ricevuto da parte della Prof.ssa Tiziana Di Salvo la richiesta di l'attività di ricerca e formazione dell'allieva Claudia Maravetano (39° ciclo) sia supervisionata dai cotutor

Dott. Giancarlo Ghirlanda (INAF - Osservatorio Astronomico di Brera, Milano)

Dott.ssa Lara Nava (INAF - Osservatorio Astronomico di Brera, Milano)

**Il collegio approva all'unanimità**

**6) Varie ed eventuali**

Non ci sono varie ed eventuali

Il verbale è approvato seduta stante. La seduta si chiude alle ore 15:30.

Il Presidente
Prof. Marco Cannas

Il Segretario
Prof. Simonpietro Agnello

**Allegato 1**

**PHD IN PHYSICAL AND CHEMICAL SCIENCES, XXXVII COURSE**

**PhD Candidate:** GABRIELE COZZO

**Transcript of Records**

**Tutor:** FABIO REALE

**Cotutor:** PAOLO PAGANO

**Courses**

- **PROJECT MANAGEMENT IN THE SCIENTIFIC – SPATIAL CONTEXT.** Score: A;
- **CLOUD AND HIGH-PERFORMANCE COMPUTING.** Score: A;
- **QUANTUM FIELD THEORY IN CURVED SPACETIMES OR NON-INERTIAL FRAMES.** Score: A;
- NUMERICAL METHODS FOR OUT OF EQUILIBRIUM STATISTICAL PHYSICS;
- ASTROPHYSICS LABORATORY OF THERMAL X-RAY PLASMAS;
- FLUCTUATION INDUCED PHOENOMENA.

**Schools**

- VIRTUAL SCHOOL ON NUMERICAL METHODS FOR PARALLEL CFD (13/12/2021-17/12/2021);
- VIRTUAL PLUTO SIMPOSIUM (28/06/2021-29/06/2021);
- SCHOOL OF COMPUTATION FLUID DYNAMICS AND SUPER COMPUTING (L'Aquila, 16/07/2023-22/07/2023);
- 1st EUROPEAN SOLAR PHYSICS DIVISION SUMMER SCHOOL – "ENERGISATION AND HEATING IN THE SOLAR PLASMA" (Dubrovnik, 29/04/2023-03/05/2023);
- SCUOLA ITALIANA DI MODELLI 3D E REALTA' VIRTUALE E AUMENTATA PER L'ASTROFISICA E L'INCLUSIONE NELLA SCIENZA (Palermo, 18/09/2023-22/09/2023).

**Research and training periods abroad**

- RESEARCH PERIOD AT **ST. ANDREWS UNIVERISTY** (ST. ANDREWS, UK) FROM **21/03/2022** TO **30/07/2022** UNDER THE SUPERVISON OF **PROF. INEKE DE MOORTEL** AND **PROF. ALAN W. HOOD;**
- RESEARCH PERIOD AT **LOCKHEED-MARTINS SOLAR AND ASTROPHYSICS LABORATORY** (PALO ALTO, CALIFORNIA, USA) FROM **04/11/2023** TO **31/01/2024** UNDER THE SUPERVISON OF **DR. PAOLA TESTA.**

**Papers published:**

- Cozzo, G. et al., "Asymmetric Twisting of Coronal Loops." Symmetry 15.3 (2023): 627.
- Cozzo, G. et al., "Coronal energy release by MHD avalanches. Effects on a structured, active region, multi-threaded coronal loop." Astronomy & Astrophysics, Volume 678, id.A40, 14 pp (2023).

- Cozzo, G. et al., "Coronal energy release by MHD avalanches II. EUV line emission from a multi-threaded coronal loop." Astronomy & Astrophysics, 689 (2024) A184.

- Cozzo, G. et al., "Coronal energy release by MHD avalanches. III. Identification of a reconnection nanojet". Submitted on Astronomy & Astrophysics.
- Wojtczak, J. A., et al. ,"The GRAVITY Young Stellar Object survey--IX. Spatially resolved kinematics of hot hydrogen gas in the star/disk interaction region of T Tauri stars." Astronomy & Astrophysics, Volume 669, id.A59, 40 pp (2023).
- D'Anca et al., "Mechanical qualification of metal-coated carbon nanotubes optical blocking filters developed for the NASA MIDEX solar mission MUSE" in [Proceedings of the International Conference on Space Optics (ICSO 2024)], (October 2024). Accepted for publication.
- Barbera et al., "Metal coated carbon nanotube ultra-thin pellicles: a high-performance solution for the optical blocking filters of the NASA MIDEX solar mission MUSE" in [Proceedings of the International Conference on Space Optics (ICSO 2024)], (October 2024). Accepted for publication.
- Alaimo et al., Investigation on the Role of Optical Filters on the Point Spread Function of the NASA MIDEX Solar Mission MUSE in [Proceedings of the International Conference on Space Optics (ICSO 2024)], (October 2024). Accepted for publication.

**Conferences/workshop attended:**

Talks:

- *Study of the accretion phenomena of T Tauri stars with the GRAVITY instrument*, Solar And Magnetospheric Theory Group seminars, 23/03/2022, St Andrews University;
- *Asymmetric twisting of coronal loops, 10th coronal loop workshop*, Paris, 28/06 - 1/07/2022;
- *Coronal energy release by MHD avalanches: EUV diagnostics of a flaring multi-threaded coronal loop*, Science with current and future solar physics missions, Roma, 1 - 3/02/2023;
- *HPC MHD modelling of unstable reconnecting plasma in the solar corona and EUV diagnostics with the MUSE mission*, INAF USCVIII - Calcolo Critico, Catania, 15 - 16/06/2023;
- *MHD modelling of unstable reconnecting plasma in the solar corona and EUV diagnostics with the MUSE mission*, 12th Young Researcher Meeting, Roma, 2 - 4/10/2023;
- *MHD modelling of unstable reconnecting plasma in the solar corona and EUV diagnostics with the MUSE mission*, MUSE team meeting, Roma, 15 - 16/10/2023;
- *MUSE EUV spectroscopy of a coronal loop system undergoing MHD-avalanche*, SoHe 2023 - Fourth Meeting of the Italian Solar and Heliospheric Community, Florence, 25 - 27/10/2023;
- *MUSE EUV spectroscopy of a kink-unstable coronal loop system*, Solar and Astrophysics seminars, Lockheed Martin advanced technology center, Palo Alto, 29/11/2023;
- *MUSE EUV spectroscopy of a kink-unstable coronal loop system*, American Geophysical Union (AGU) Fall Meeting, San Francisco, 11 - 15/12/2023;
- *MUSE EUV spectroscopy of a kink-unstable coronal loop system*, Solar Group seminars at Stanford University, Palo Alto, 16/01/2024.
- "The MUSE NASA Space Mission: Technology, Science and the Italian Contribution", Astrophysics seminars, Dipertimento di Fisica e Chimica - Emilio Segré, UniPa, Palermo, 27/03/2024;
- *MUSE EUV spectroscopy of a kink-unstable coronal loops system,* 11th Coronal Loops Workshop, San Cristóbal de La Laguna, Spain, 25/06/2024-28/06/2024;
- *3D MHD coronal loops modelling with the Pluto Code,* ISWAT Meeting - Origins of the Solar Spectral Irradiance and its Intermediate Timescale Variability, Maryland, Washington, USA*;*
- *Where is Atropos hiding?* 13th Young Researcher Meeting, Palermo, 24/09/2024-27/09/2024.

Posters:

- *MHD avalanches and DC heating in solar coronal loops: MHD and forward modelling of nanojets*, 11th Coronal Loops Workshop, San Cristóbal de La Laguna, Spain, 25/06/2024-28/06/2024;
- *Forward and MHD modelling of nanojets driven by magnetic reconnection during MHD avalanches*, The 17th European Solar Physics Meeting (ESPM-24).

**Thesis title:**

MHD modeling of energy release in coronal closed magnetic flux tubes

**Abstract:**

This thesis addresses coronal heating as a result of slow photospheric motions, modelled by twisting of magnetic field lines at the footpoints of isolated or multiple and interacting magnetic flux tubes. This work aims at studying the phenomenon of magnetic energy release in coronal loops and their atmospheric response to impulsive heating, to explain the dramatic rise in temperature from the Sun's relatively cool surface to its multi-million Kelvin degrees corona. Coronal heating is attributed to magnetic activity, with several mechanisms proposed: magnetohydrodynamic (MHD) instabilities, such as the kink instability, are known to trigger energy dissipation in the form of bursty, intermittent events, termed 'nanoflares', evolving from turbulent current sheets. A prominent hypothesis involves 'MHD avalanches'.
Energy is transferred from the Sun's interior through photospheric convective motions, into the corona. The magnetic field within coronal loop strands becomes highly twisted, leading to an ideal kink-mode instability. This instability propagates outward, destabilizing neighboring magnetic threads and triggering a cascade of magnetic reconnections, releasing energy impulsively and contributing to coronal heating.
Understanding the conditions under which these processes occur, as well as their observational signatures, is critical for interpreting solar phenomena and improving our models of the solar corona. To tackle this question, we performed time-dependent 2.5D and 3D MHD simulations to model the evolution of coronal loops subjected to footpoint motions and eventually MHD instabilities. Our model includes a stratified, magnetised atmosphere extending from the chromosphere to the corona, and accounts for key physical processes such as thermal conduction, optically thin radiation, and the transition from high- to low-beta regions, including magnetic field expansion from the footpoints. Additionally, we synthesized spectral data in extreme-ultraviolet (EUV) lines for comparison with the anticipated observational capabilities of the forthcoming MUltislit Solar Explorer (MUSE).
Our results show that the high Alfvén velocities in the solar corona enable coronal loops to maintain a high degree of symmetry, even under prolonged asymmetric footpoint motions. Furthermore, we confirmed that kink instabilities can lead to MHD avalanches, also in a realistic solar atmosphere, driving significant heating up to microflare temperatures (~10 MK) and inducing chromospheric evaporation. Footpoints EUV emission in the Fe IX MUSE channel will mark early plasma responses to heating, while Fe XV will track denser plasma at intermediate heights, and Fe XIX will reveal flaring plasma within current sheets. Finally, we identified a nanojet — a small, high-velocity reconnection outflow — as key observable signature of impulsive energy release, with temperature reaching 8 MK, outflow velocity of several hundred km/s, and duration of less than one minute. Our simulations suggest that MUSE will be able to detect these features, providing crucial insights into the heating mechanisms of the solar corona.

The PhD Board Dean

Prof. Marco Cannas

**Allegato 2**

**PHD IN PHYSICAL AND CHEMICAL SCIENCES, XXXVII COURSE**

**PhD Candidate: Alberto Ulgiati**

**Transcript of Records**

**Tutor:** Giancarlo Cusumano

**Cotutors:** Fabio Pintore e Simona Paiano

**Courses/school/exam scores:**

- ASTROTWINCOLO 2021 (online school, 22/11/2021 - 03/12/2021)
- Hands On the Extreme Universe - Sexten school (Sexten, 18/07/2022 – 22/07/2022)
- Project management in the scientific - spatial context (Palermo University, exam score A)
- Experimental techniques in Astroparticle physics (Palermo University, exam score A)
- ISAPP School 2022 (school in presence, 28/03/2022 – 08/04/2022, exam score A)

**Research and training periods abroad:** Research period at the European Southern Observatory (ESO) 15/10/2023 - 15/04/2024

**Papers published:**

- Ulgiati et al. 2024: "Spectroscopy of a Sample of Unidentified Gamma-ray Fermi Sources", MNRAS, 530, 4626, https://doi-org/10.1093/mnras/stae587
- Ulgiati et al. 2024: "Fast X-ray/IR observations of black hole transient Swift J1753.5–0127: From an IR lead to a very long jet lag", Astronomy & Astrophysics, 690, A239, https://doi.org/10.1051/0004-6361/202450545

**Conferences/workshop attended:**

- Gammapy workshop (INAF-IASF Palermo, 14/06/2022 – 17/06/2022)
- Congresso Nazionale Oggetti Compatti (CNOC) XII [Sala delle Capriate del Palazzo Municipale di Cefalù (Palermo), 27/09/2022 - 30/09/2022)
- AVENGe - Advances in Very-High Energy Astrophysics with Next-Generations Cherenkov Telescopes (Sala conferenze dei cappuccini, Roma, 29/05/2023 - 31/05/2023)
- CTA symposium 2024 (Teatro Duse, Bologna, 15/04/2024 - 18/04/2024)

- Talks:
  - CNOC XII, "Timing analysis of Black Hole Transient Swift J1753.5-0127".
  - ISAPP School 2022, "Unveiling the nature of the Unassociated Gamma-ray Sources in the fourth Fermi catalogue: a multi-wavelength approach".
  - AVENGe, "Search for new TeV sources from our MWL and spectroscopic survey".

- Posters:

**Thesis title:** Unveiling the nature of the Unassociated Gamma-ray Sources in the fourth Fermi catalog: a multi-wavelength approach

**Abstract:** Fifteen years have passed since the launch of the Fermi Gamma-ray Space Telescope, a space observatory designed to study celestial objects emitting in the γ-ray energy range. Equipped with two main instruments, the Large Area Telescope (LAT) and the Gamma-ray Burst Monitor (GBM), Fermi has transformed our understanding of the high-energy universe.
Fermi's all-sky monitoring capabilities have provided an unprecedented view of the universe in γ-rays, detecting a wide variety of sources such as active galactic nuclei (AGN), pulsars, supernova remnants, and γ-ray bursts with exceptional precision. Its observations have unveiled the dynamic and energetic processes driving these objects, offering new insights into extreme astrophysical phenomena and shedding light on some of the most energetic events in the cosmos.
By significantly improving sensitivity and spatial resolution compared to its predecessors, Fermi has uncovered thousands of previously unknown γ-ray sources, enriching our understanding of high-energy astrophysics.
One of the key achievements of the Fermi mission has been the development of comprehensive γ-ray source catalogs, essential resources for the high-energy astrophysics community. These catalogs list and characterize the γ-ray sources detected by the LAT, providing critical data on their locations, energy spectra, and variability. Over the years, several iterations of these catalogs have been released, each incorporating new data and refined analysis methods.
The most recent and extensive catalog is the Fourth Fermi-LAT Gamma-ray Source Catalog (4FGL), first released in 2019. In 2023, the Fermi collaboration published an incremental update to this catalog, referred to as 4FGL-DR4. This version reports sources detected over 14 years of LAT observations, cataloging a total of 7195 objects. Of these, 4765 have been associated or identified at other wavelengths through positional overlap, correlated variability, or multi-wavelength spectral properties. Among the associated and identified sources, the majority are blazars—a subclass of active galactic nuclei (AGNs) with relativistic jets pointing at an angle of $\theta \leq 10°$ with respect to the observer's line of sight.
However, a significant portion of the Fermi catalog remains unclassified. Approximately 30% of the sources have no known association with lower-energy counterparts and are collectively referred to as unassociated gamma-ray sources (UGSs). UGSs play a key role in the high-energy sky, potentially concealing new blazars or other types of AGN. Identifying and classifying these sources can enhance our understanding of the most extreme environments in the universe, such as those involving supermassive black holes, and may reveal missing components in our current models of the high-energy universe.
Moreover, UGSs are typically faint, with lower γ-ray fluxes (on average, UGSs have fluxes around $\sim 5.3 \times 10^{-12}$ erg cm$^{-2}$ s$^{-1}$, compared to $\sim 1.6 \times 10^{-11}$ erg cm$^{-2}$ s$^{-1}$ for associated AGN in the 100 MeV to 100 GeV range). As a result, they may represent a higher redshift AGN population and/or lower luminosity sources. Identifying UGSs is crucial for population studies, developing physical models, and understanding the cosmic evolution of γ-ray sources. Moreover, identifying these sources is essential for estimating the very high-energy (VHE) cosmic background.
The goal of this thesis is to associate and classify extra-galactic UGSs from the fourth Fermi catalog, with the aim of unveiling new blazars and, more broadly, new AGN. To achieve this, the analysis focuses on the 1284 UGSs located outside the Galactic plane ($|b| \geq 10°$), searching

for X-ray, optical, and radio counterparts that coincide with the γ-ray positions. Given the large uncertainty regions in γ-rays, the search begins in the X-ray band, where the potential counterpart confusion is limited compared to lower energy bands such as optical and radio, and where positional uncertainties are more constrained relative to γ-rays. This strategy allows for a more focused search region.

In the past decade, the Swift X-ray satellite has been conducting a dedicated observational campaign targeting Fermi's unassociated sources, providing real-time access to its data. This thesis begins by analyzing all the available Swift X-ray images, which cover the γ-ray positions of the UGSs.

The number of UGSs with Swift observations is 714. From this analysis, I found that 274 of these γ-ray emitters have at least one X-ray source detected with a significance of $\sigma \geq 3$ within their Fermi error box. Among these, 193 UGSs have a single potential X-ray counterpart (referred to as UGS1), while 81 have multiple potential X-ray counterparts within the Fermi error box (referred to as UGS2). Of the UGS2, 54 have two X-ray counterparts, 11 have three, and the remaining 16 have more than three.

Starting from the X-ray positions and error boxes, optical and radio counterparts are searched within several catalogs or by dedicated observations. I found that each UGS1 has a potential optical counterpart, and 113 also could be associated to a radio counterpart. Regarding the UGS2 sub-sample, a large degeneracy of possible counterparts is found, making the association process more difficult. With the aim of assessing the reliability of potential associations, the absolute and relative fluxes of the potential counterparts are compared with those of blazars from the fourth Fermi catalog. From this comparison, I found that, in general, X-ray sources that also emit in the optical and radio bands have emission profiles similar to those of blazars, making them strong candidates for counterparts. On the other hand, radio-quiet sources tend to deviate from the typical behavior of blazars, suggesting they may be false counterparts. However, a more in-depth analysis is necessary to confirm this.

I found that 33 UGS1 have optical spectra already published in the literature. The analysis of optical spectra is a fundamental step for the classification of extragalactic UGSs, as it allows for the differentiation of AGN, particularly by dividing them into various subclasses, and estimating their distances. From the analysis of these 33 UGSs, I found that the X-ray emitter located within their Fermi error box is a BL Lac (a subclass of blazars with an optical spectrum described by a featureless power law or weak emission lines) for 21 of them, a Flat Spectrum Radio Quasar (FSRQ, a subclass of blazars distinguished from BL Lacs by its strong and broad optical emission lines) for one source, a radio galaxy (a subclass of AGN characterized by extended radio emission) for one, and a Seyfert or Quasi Stellar Object (subclasses of AGN with strong emission lines in the optical but weak or absent radio emission) for 10 of them. The presence of radio-quiet AGNs in the Fermi catalog is unexpected and potentially interesting, as all AGNs discovered by Fermi so far are radio-loud.

The 33 UGSs associated and classified in this thesis, along with a sample of 44 UGSs from the second and third Fermi catalogs, which were associated and classified by Paiano et al. (2017a,2019), are characterized through their multi-wavelength emission. Specifically, I analised the spectral energy distributions (SEDs) of these 77 γ-ray emitters to confirm or reject the previous associations. In addition, the emission intensities of the BL Lacs in the sample are studied in order to identify new masquerading BL Lacs (FSRQs with featureless optical spectra typical of BL Lacs, due to their strong continuum masking the spectral lines). The relative and absolute emissions are compared to empirical values designed for identifying masquerading BL Lacs.

The SED analysis leads to the conclusion that radio-loud AGNs in the sample are well-associated, as they exhibit continuity between the emission of the counterpart and the γ-ray emitter. These objects are then classified into the blazar subclasses low synchrotron peak (LSP), intermediate synchrotron peak (ISP), and high synchrotron peak (HSP), based on the position of the synchrotron emission peak in their SEDs.
For the 13 radio-quiet objects in the sample, there is an discrepancy between the emission of the counterpart and that of the γ-ray emitter. No emission mechanism can explain both components, which appear uncorrelated. As a result, alternative counterparts are sought for this sample. For 7 out of 13 sources, these alternative counterparts are found among the radio sources coincident with the γ-ray position but previously unidentified due to a lack of X-ray emission. The remaining 6 sources lacked plausible counterparts within the 3 σ γ-ray error boxes.
In the search for masquerading BL Lacs, 9 bona fide candidates are identified based on their absolute and relative emission intensities, representing approximately 20% of the sample, with a possible upper limit of 33%. This proportion is lower than in previous studies, likely due to the lower spectral quality of the dataset.

The PhD Board Dean

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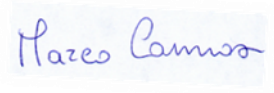

**Allegato 3**

**PHD IN PHYSICAL AND CHEMICAL SCIENCES, XXXVII COURSE**

**PhD Candidate: Maria Rita Caruso**

**Transcript of Records**

**Tutor: Giuseppe Lazzara**

**Cotutor: Giuseppe Cavallaro**

**Courses/school/exam scores:**

- Webinar on Light in Optics and Optometry - Diagnostiche ottiche in arte, Scuola di scienze Matematiche, Fisiche e Chimiche, Massimo Gurioli and Raffaella Fontana (INO-CNR), April 30th,2022, Università degli studi di Firenze (2h).
- "Thermodynamic techniques for the characterization of nanostructured materials", May 30th – June 6th, 2022, G. Cavallaro, University of Palermo (10h).
- "Organic/Inorganic nanocomposites: properties and applications", June 7th – 13th, 2022, G. Cavallaro, University of Palermo (10h).
- Lessons on "Neutrons Scattering Analysis", October 12th – 27th, 2022, I. Hoffman, University of Palermo (8h).
- Chimica Fisica delle Interfasi, Chemistry, September 27rd – December 19th, 2022, G. Cavallaro, University of Palermo (48h).
- Webinar on "La Reologia delle Dispersioni: come studiare la stabilità a riposo e la viscosità", Netzsch February 28th 2023 (2h).
- Training on "Potenzialità e utilizzo della microscopia elettronica a scansione (SEM): microscopio Fei-Thermofisher versa 3D ", Professor Vincenzo La Carrubba and Giorgio Nasillo, Laboratory of Electronics Microscopy of ATeN Center, May 10th, 2023, University of Palermo (8h).
- Porto School on Calorimetry and Thermal Analysis, 18th July 2023 (8h).
- ILL Soft Matter Summer School at Institut Laue Langevin, Grenoble, France, 4-6 July 2023 (24h).
- Workshop online on "Preserving Our Past: Advancements in Cultural Heritage Conservation through Chemistry and Sustainable Matateriales", Associate Professor Maite Maguregui, Seinor Scientist Scott G.Mitchell, Facultad de Ciencia y Tecnologia de la Universidad del Pais Vasco, Leioa, September 20th 2023 (2h).
- VIII National School of Division of Environmental Chemistry and Cultural Heritage, SCI - Italian Chemical Society, Rome, (Italy). January 31st - February 2nd , 2024 (18h).
- Soft Matter Course 2024, Manuele Marino and Thomas Kodger, University of Palermo, February-March 2024 (18h).

**Research and training periods abroad:**

I did research activity at the Analytics Chemistry department of Universidad del País Vasco/EHU in Bilbao with professor Maite Maguregui, October 2023 - April 2024. I focused the research on the analysis of archaeological wood samples coated with Chitosan/HNTs and on the preparation of oil in water Pickering

Emulsion stabilised by cellulose nanocrystals as a removal treatment for cultural heritage conservation protocols.

**Internship at a local enterprise:**

Scancarello s.r.l, Via Ugo Betti, 3, 90147 Palermo PA, Italia, 2022 (PON 2014-202- D.M. 1061/201).

**Papers published:**

- Caruso M.R., Cavallaro, G., Gomez-Laserna, O., Maguregui, M., Lazzara, G.," Ecofriendly Conservation: Chit/HNTs as sustainable treatment for the preservation of waterlogged archaeological wood", In preparation.

- Caruso M.R., Cavallaro, G., Gomez-Laserna, O., Caruso, F., Lazzara, G., Maguregui, M., "Oil-in-water Pickering emulsion stabilised by cellulose nanocrystals: new advanced formulation for cultural heritage application", In preparation.

- Caruso M.R., Calvino, M.M.*, Šiler, P., Cába, V., Milioto, S., Lisuzzo, L., Lazzara, G., Cavallaro, G., "Self-Standing Biohybrid Xerogels Incorporating Nanotubular Clays for Sustainable Removal of Pollutants", Small, Submitted, (2024).

- G. D'Agostino, Caruso M.R., G. Cavallaro, G. Lazzara, and S. Milioto, "Pickering Emulsion Gel Based on Funori Biopolymer and Halloysite Nanotubes: A New Sustainable Material for the Cleaning of Artwork Surfaces, ACS Applied Polymer Materials 2024 6 (13), 7679-7690, DOI: 10.1021/acsapm.4c01152.

- Caruso M.R., Wasserbauer, J., Šiler, P., Cavallaro, G., Milioto, S., & Lazzara, G., "Filling of Chitosan Film with Wax/Halloysite Microparticles for Absorption of Hydrocarbon Vapors", Advanced Sustainable Systems, 8(7), 2400026, (2024). https://doi.org/10.1002/adsu.202400026.

- Caruso M.R., D'Agostino G., Milioto S., Cavallaro G., Lazzara G., "A review on biopolymer-based treatments for consolidation and surface protection of cultural heritage materials", Journal of Materials Science, 58 (32), pp. 12954 – 12975, (2023). https://doi.org/10.1007/s10853-023-08833-5.

- Caruso, M.R., Cavallaro, G. Milioto, S. Lazzara G., "Halloysite nanotubes/Keratin composites for wool treatment", Applied Clay Science, Volume 238, 2023, 106930, ISSN 0169-1317. https://doi.org/10.1016/j.clay.2023.106930.

- Caruso, M.R., G. Cavallaro, G. Lazzara, S. Milioto, "Pectin/microwax composites for surface coating and protection", Materials Letters, Volume 333, 2023, 133567, ISSN 0167-577X. https://doi.org/10.1016/j.matlet.2022.133567.

- G. Cavallaro, Caruso, M.R., S. Milioto, R. Fakhrullin, G. Lazzara, "Keratin/alginate hybrid hydrogels filled with halloysite clay nanotubes for protective treatment of human hair", International Journal of Biological Macromolecules,228-238, Volume 222, Part A, 2022, ISSN 0141-8130, https://doi.org/10.1016/j.ijbiomac.2022.09.170.

- Caruso, M.R.; Lisuzzo, L.; Cavallaro, G.; Mirto, G.; Milioto, S.; Lazzara, G. "Thermal and Mechanical Characterization of Yarn Samples from Flemish Tapestry of the Sixteenth Century" Molecules 2022, 27, 8450 https://doi.org/10.3390/molecules27238450.

- Giordano, A., Caruso, M.R. & Lazzara, G. "New tool for sustainable treatments: agar spray-research and practice", Herit Sci 10, (2022), DOI: 10.1186/s40494-022-00756-9.

- Caruso, M.R., Megna, B., Lisuzzo, L. et al. "Halloysite nanotubes-based nanocomposites for the hydrophobization of hydraulic mortar", J Coat Technol Res 18, 1625–1634 (2021). https://doi.org/10.1007/s11998-021-00522-9.

- L. Lisuzzo, Caruso, M.R., G. Cavallaro, S. Milioto, and G. Lazzara, "Hydroxypropyl Cellulose Films Filled with Halloysite Nanotubes/Wax Hybrid Microspheres", Industrial & Engineering Chemistry Research, 2021 60 (4), 1656-1665, DOI: 10.1021 / acs.iecr.0c05148.

**Conferences/workshop attended:**

**Talks:**

- Congresso Nazionale Italiano sui Geopolimeri –New frontiers in innovative and green materials for cultural heritage conservation and building industry, CATANIA, Italy, February 24th - 25th, 2022.
  **Caruso, M.R.,** Cavallaro, G., Lisuzzo, L., Lazzara, G., Milioto, S., Oral Communication *"Wax/HNT Pickering Emulsion as a Coating for Cultural Heritage"*
- CONGRESSO ABC-XIX Congresso Nazionale della Divisione di Chimica dell'Ambiente e dei Beni Culturali, TORINO, Italy, June 20th – 23th, 2022.
  **M.R. Caruso**, G. Cavallaro, G. Lazzara, and S. Milioto, Oral Communication *"Green and Innovative material based on biopolymer and Wax/HNT microspheres for coating artwork surface".*
- CHEMCH - 6th International Congress Chemistry for Cultural Heritage, RAVENNA, Italy, July 4th-8th, 2022.
  **Maria Rita Caruso**, Giuseppe Cavallaro, Giuseppe Lazzara, Stefana Milioto, Oral Communication *"Composite biofilms based on biopolymer and wax/HNT microspheres for coating artwork surface".*
- MEDICTA2023-Mediterranean Conference on Calorimetry and Thermal Analysis, PORTO, Portugal, July 19th – 21st, 2023.
  **Maria Rita Caruso,** Giulia D'Agostino, Lorenzo Lisuzzo, Giuseppe Cavallaro, Stefana Milioto, Giuseppe Lazzara, Oral Communication *"Characterization of yarns from a Flemish tapestry of the XVIth century and a new Keratin/HNT protocol for the conservation of artwork".*
- CONGRESSO ABC2023- XX Congresso Nazionale della Divisione di Chimica dell'Ambiente e dei Beni Culturali, ISCHIA (NA), Italy, September 28th- October 1st, 2023.
  **Maria Rita Caruso**, Giulia D'Agostino, Lorenzo Lisuzzo, Giuseppe Cavallaro, Stefana Milioto, Giuseppe Lazzara, Oral Communication *"New treatment for the consolidation and the protection of wool yarns from a flemish tapestry of the XVIthcentury".*

- CHEMCH – 7th International Congress Chemistry for Cultural Heritage, BRATISLAVA, Slovakia, July 1st-4th, 2024.
  **Maria Rita Caruso**, Olivia Gómez-Laserna, Giuseppe Cavallaro, Francesco Caruso, Giuseppe Lazzara, Maite Maguregui Oral Communication *"Nanocellulose-stabilized oil-in-water pickering emulsions for removing natural resin varnishes from canvas paintings".*

**Posters:**

- ILL Soft Matter Summer School at Institut Laue Langevin, Grenoble, France, 4-6 July 2023
  **Maria Rita Caruso**, Giulia D'Agostino, Lorenzo Lisuzzo, Giuseppe Cavallaro, Stefana Milioto, Giuseppe Lazzara, Poster Presentation *"HNT/Biopolymers composite materials as a new green alternative for cultural heritage"*, ILL, Grenoble, France, 4-6 July 2023 (12h).
- M.R. Caruso, M. Romani, G. Cavallaro, O. Gómez, Laserna, M. Maguregui, G. Lazzara, Poster Presentation, "New sustainable treatment based on chitosan and halloysite nanotubes for the conservation of waterlogged archaeological wood".
  InArt 2024- Conference on Innovation in Art Research and Technology, OSLO, Norway, June 4th-7th 2024.

**Thesis title:** Hybrid materials based on biopolymers and natural nanofillers as new treatments for Cultural Heritage

**Abstract:**

In recent decades, the widespread use of petroleum-based polymers has significantly improved human living standards, yet it has also introduced serious environmental and health challenges. In response, researchers have turned to biopolymers, materials derived from renewable sources like plants, animals, and microorganisms, as a promising alternative. Unlike synthetic polymers, biopolymers are biodegradable, non-toxic, and produce lower carbon emissions, making them a more sustainable solution.

This research explores biopolymers, combined with nanomaterials, that offers sustainable solutions in the field of cultural heritage conservation. Biopolymers such as chitosan, pectin, and cellulose derivatives provide environmentally friendly options for cleaning, reinforcing, and protecting artifacts. Their gentle and effective properties make them ideal for preserving artwork. Nanomaterials, known for their exceptional mechanical, thermal, and optical properties, also play a critical role in enhancing conservation techniques. Materials like nanoclays and cellulose nanocrystals (CNCs) are particularly effective in improving the performance of protective coatings and cleaning agents. The fusion of biopolymers and nanomaterials not only enhances the sustainability of cultural heritage conservation but also covers the way for more effective and eco-friendly treatments for a wide range of materials, from archaeological wood to human hair.

The research highlights the potential of biopolymer-nanofiller hybrids systems as treatment for artwork. CNC-based emulsions are emerging as effective tools for cleaning aged varnish from paintings, while HNTs/keratin protocols are preserving tapestries. Hybrid hydrogels protect organic materials such as human hair, demonstrating the versatility and adaptability of these materials. A Chit/HNTs dispersion was also developed for preserving waterlogged archaeological wood, providing an eco-friendly solution.

By addressing environmental control, such as air quality in museums, sustainable technologies were analysed with two different system based on chitosan and HNTs as adsorber of pollutants such as hydrocarbons vapours, dyes, metals, from air and water.
This research emphasizes the importance of sustainable materials in reducing the environmental footprint of industrial practices, with biopolymers and nanomaterials leading the way toward a greener future.

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The PhD Board Dean

Prof. Marco Cannas

Marco Cannas

**Allegato 4**

**PHD IN PHYSICAL AND CHEMICAL SCIENCES, XXXVI COURSE**

**PhD Candidate: Chiara Nania**

**Transcript of Records**

**Tutor: Prof. Francesco Ferrante**

**Cotutor: Prof. Dario Duca**

**Courses/school/exam scores:**

**Courses**

- "Advanced microscopy and spectroscopy techniques applied to nanomaterials" by prof. Simonpietro Agnello and prof. Giampiero Buscarino, from April 26 to June 9, total hours: 20.
- "Organic/Inorganic Nanocomposites: thermodynamics, structure, and applications" by dott. Giuseppe Cavallaro, total hours: 20. Exam taken.
- "Experimental Techniques in Astroparticle Physics" by prof. Giovanni Marsella, Feb. 18 to March 22, 2022. Exam sustained on April 26, 2022. Exam taken.
- "Python and Quantum Mechanics" by prof. Salvatore Lorenzo, March 15 to April 5, 2022. Exam taken.

**Seminars**

- Seminar: "Training SEM – ATeN Center" by dott. Giorgio Nasillo and by Vincenzo La Carrubba, AtenCenter, Feb. 17, 2023.
- Seminar: "Charge Carriers Trapping in Phosphors", speaker: prof. Eugeniusz Zych (Faculty of Chemistry, University of Wroclaw, Poland), November 12, 2021 (11:00 am – 1:00 p.m).
- Lecture series: "Modern platforms for quantum nonlinear optics" by Dr. Giuseppe Calajò, ICFO (Spain), Jan. 24-27, 2022 (11:00 am – 1:00 pm, total: 8 hours).
- Webinar ACS: "Addressing Sustainability Challenges with Earth Abundant Metal Catalysis" by Paul Chirik, Edward S. Sanford (professor at Princeton University), Oct 27, 2022 (8:00 pm - 9:00 pm).
- Seminar: "Microraman Training: Microscopia Raman" by dott. Luigi Tranchina and prof. Simonpietro Agnello, AtenCenter, Feb. 22, 2022.

**Schools**

**Research and training periods abroad**

**Papers published:**

**Related to the PhD project**

1) C. Nania, L. Gueci, M. Bertini, F. Ferrante, D. Duca, "Computational Investigation of Isoeugenol Decomposition Mechanism on Platinum Cluster" (in preparation).
2) C. Nania, M. Bertini, L. Gueci, F. Ferrante, D. Duca, "Decomposition of Guaiacol on a Subnanometric Platinum Cluster: a DFT Investigation Followed by Microkinetic Analysis" (in preparation).
3) C. Nania, M. Bertini, L. Gueci, F. Ferrante, D. Duca,"Computational Investigation of Isoeugenol Transformations on a Platinum Cluster – II: Hydrogenation through Deoxygenation to Propylcyclohexane", Molecular Catalysis, 64 (2024) 114298, https://doi.org/10.1016/j.mcat.2024.114298
4) C. Nania, "HDO dell'Isoeugenolo su Cluster di Platino", La Chimica & L'Industria, ISSN 2283-544X, n. 1/2023, http://dx.medra.org/10.17374/CI.2023.105.1.71
5) C. Nania, M. Bertini, L. Gueci, F. Ferrante, D. Duca, "DFT Insights into Competing Mechanisms of Guaiacol Hydrodeoxygenation on a Platinum Cluster", Phys. Chem. Chem. Phys., (2023) 25, 10460-10471, https://doi.org/10.1039/D2CP06077A
6) F. Ferrante, C. Nania, D. Duca, "Computational Investigation of Isoeugenol Transformations on a Platinum Cluster – I: Direct Deoxygenation to Propylcyclohexane", Molecular Catalysis, 529 (2022) 112541, https://doi.org/10.1016/j.mcat.2022.112541

**Other ISI papers:**

7) L. Gueci, M. Bertini, C. Nania, F. Ferrante, D. Duca, "DFT Study of Pt Particle Growth inside Zeolite Cages", J. Phys. Chem. C, 127 (2023) 14765–14775, https://doi.org/10.1021/acs.jpcc.3c02957.
8) L. Gueci, F. Ferrante, M. Bertini, C. Nania, D. Duca, "DFT Study on Zeolites' Intrinsic Brønsted Acidity: The Case of BEA", Computational Materials Science, 232 (2024) 112687, https://doi.org/10.1016/j.commatsci.2023.112687.
9) L. Gueci, F. Arena, S. Todaro, G. Bonura, A. Cajumi, M. Bertini, F. Ferrante, C. Nania, D. Duca, "CO-PROX on $MnO_2$ Catalysts: DFT-based Microkinetic and Experimental Macrokinetic Approaches", Catalysis Today, 434 (2024) 114698, https://doi.org/10.1016/j.cattod.2024.114698.

**Conferences/workshop attended:**

**- Poster sessions:**

- Workshop of the Theoretical and Computational Chemistry Division 2022 of SCI, "Hydrodeoxygenation of isoeugenol over Platinum cluster: DFT study and mechanistic analysis" (Poster Section), C. Nania, F. Ferrante, L. Gueci, M. Bertini, D. Duca, Florence, April 2022.
- YOURHETCAT–2022–1st Forum of Young Researchers on Heterogeneous Catalysis, "DFT insights into the DDO mechanism of Isoeugenol Catalytic Hydrodeoxygenation on Platinum Cluster" (Poster Section), C. Nania, F. Ferrante, L. Gueci, M. Bertini, D. Duca, Szeged (Hungary), July 11-13, 2022.
- Seventh Congress of the Theoretical and Computational Chemistry Division of SCI,"Hydrodeoxygenation of Isoeugenol on Platinum Cluster: DFT insights into HYD and DDO mechanism" (Poster Section), C. Nania, F. Ferrante, L. Gueci, M. Bertini, D. Duca, Modena, September 21-23, 2022. Awarding Nordio Prize 2022 for the best master's thesis on a computational theoretical topic.

UNIVERSITÀ DEGLI STUDI DI PALERMO
DOTTORATO DI RICERCA IN SCIENZE FISICHE E CHIMICHE

**Thesis title:** Computational Investigation of Model Biomass Compounds Conversion on isolated and supported metal clusters

**Abstract:**
Hydrodeoxygenation and bio-oil decomposition processes, produced by pyrolysis of biomass, represent one of the most effective strategies to obtain biofuels. The scope of the investigations performed in this PhD project, framed in a context of constant demand for renewable and eco-sustainable alternatives energy technologies, was a mapping as complete as possible of the reactions of two biomass model compounds, namely guaiacol and isoeugenol, as they occur when catalyzed by metal clusters.
The density functional theory studies of the energetics associated to the investigated processes enabled to conduct an innovative Christiansen-like microkinetic analysis that returns the kinetic constants at selected temperatures, providing as input the calculated direct and inverse energy barriers for all the elementary steps included in the various reaction mechanisms.
Microkinetic analysis allowed an unbiased interpretation of DFT results in order to find the most likely decomposition channels. Indeed, the possible reaction pathways of small molecules with so many functional groups, such as guaiacol, are affected by the structure and the shape of the metal catalyst, and the influence could be remarkably strong when ultra-small, subnanometric, metal clusters are considered, where different coordination numbers are present for the same atoms. Useful information was achieved by exploring a large number of different mechanisms (some of which are new if compared to those documented in the existing literature) both in absence and in presence of molecular hydrogen fragmented on the metal catalyst model. This allowed to distinguish the most important elementary steps and to creating a computational reference for cluster catalysis in the subnanometer size regime, necessary to undertake cumbersome investigations of the same reactions on supported clusters. In particuar, The kinetic and thermodynamic analysis of the hydrodeoxygenation reaction of guaiacol and isoeugenol revealed a clear preference for the direct deoxygenation mechanism pathway at all considered temperatures, opposing to the deoxygenation-through-hydrogenation mechanism. The results suggest that oxygen removal occurs sequentially: the -OCH3 group is removed as methanol, followed by removal of the -OH group as a water molecule.
From the point of view of the supported cluster, an original growing algorithm was devised to determine the most stable geometries of $Pt_n$ and $Ni_n$ clusters (n = 1-10) on a defective graphene support; their structures were interpreted in terms on inter-cluster and cluster-defect interactions. The atom-by-atom accretion of clusters on graphene surface with single vacancy was examined, showing that defective graphene improves the dispersion of metal clusters, preventing sintering and agglomeration phenomena, which limit the effectiveness of catalysts over time. In addition, graphene increases the stability of the clusters, enhancing their catalytic activity and reducing deactivation caused by coke formation or sintering in HDO reactions, a factor of high relevance for industrial applications where long-term stability is essential to ensure process efficiency. The use of graphene as a support also allows for a reduction in the amount of noble metals needed, lowering costs and improving the sustainability of catalytic processes, in line with the principles of green chemistry. The DFT results highlighted differences in the interactions of Pt and Ni with oxygen: nickel, in particular, shows a stronger interaction with the oxygen atom than platinum, a behaviour that doesn't appear to be affected by π interactions in the system, suggesting a significant impact on catalytic reactivity.

DIPARTIMENTO DI FISICA E CHIMICA Via Archirafi 36, 90123 Palermo, Italy

The $Pt_{10}$/C and $Ni_{10}$/C were later employed to detail the energetics of two important elementary processes for guaiacol valorization: the loss of the oxigenated hydroxy and methoxy groups.
The results obtained in this PhD project provide new perspectives for the use of advanced materials such as graphene in the design of more efficient and stable catalysts, improving the understanding of hydrodeoxygenation mechanisms of biomass-derived compounds and opening new possibilities for sustainable industrial applications.

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The PhD Board Dean

Prof. Marco Cannas

Marco Cannas