



Rendiconti
Accademia Nazionale delle Scienze detta dei XL
*Memorie e Rendiconti di Chimica, Fisica,
Matematica e Scienze Naturali*
141° (2023), Vol. IV, fasc. 2, pp. 319-324
ISSN 0392-4130 • ISBN 978-88-98075-56-0

Non equilibrium processes and laser chemistry: from biosphere to cosmos A tribute to Anna Giardini (1934-2021)

VINCENZO AQUILANTI^{a*} – DANIELE CATONE^b – STEFANO ORLANDO^c
ALESSANDRA PALADINI^d – SUSANNA PICCIRILLO^{e***}
FLAMINIA RONDINO^f – MAURO SATTA^g

^a Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, 06123 Perugia, Italy; Istituto di Struttura della Materia – CNR (ISM-CNR), 00015 Monterotondo (Rome), Italy. E-mail: vincenzoaquilanti@yahoo.it

^b Istituto di Struttura della Materia – CNR (ISM-CNR), EFSL Laboratory, 00133 Rome, Italy. E-mail: daniele.catone@cnr.it ORCID: 0000-0002-7649-2756

^c Istituto di Struttura della Materia – CNR (ISM-CNR), Zona Industriale di Tito Scalo, 85050 Potenza, Italy. E-mail: stefano.orlando@cnr.it ORCID: 0000-0001-5116-3908

^d Istituto di Struttura della Materia (ISM) - CNR, EFSL Laboratory, 00015 Monterotondo (Rome), Italy. E-mail: alessandra.paladini@cnr.it ORCID: 0000-0002-2059-1552

^e Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma “Tor Vergata”, 00133 Rome, Italy. E-mail: piccirillo@fisica.uniroma2.it ORCID: 0000-0002-7938-6852

^f ENEA, C.R. Casaccia, Via Anguillarese 301, 00123 Roma, Italy.
E-mail: flaminia.rondino@enea.it ORCID: 0000-0001-7832-6535

^g Istituto per lo Studio dei Materiali Nanostrutturati - CNR (ISMN-CNR), Sapienza University of Rome, P. le Aldo Moro 5, Rome 00185, Italy. E-mail: mauro.satta@cnr.it

* Uno dei XL.

*** corresponding author.

Abstract – This collection of papers originated from presentations at the scientific conference that took place on 29 March 2023 at the Library of the Accademia Nazionale delle Scienze detta dei Quaranta. The conference, titled “Non-equilibrium processes and laser chemistry: from biospheres to cosmos”, was tributed to the memory of Anna Giardini, who had left us on 7 October 2021.

A brief history of the scientific and academic activities of Anna Giardini is here presented with particular emphasis on the last years of her career and the scientific legacy she left. Her intense, interdisciplinary, and stimulating approach to science is attested by the large number of topics and collaborations she was involved in and by the research advancements she contributed to promote. Further evidence of the comprehensive scientific interests of Anna Giardini is the amount and variety of research works that have been presented as a tribute to her memory. A selection of them will be described in this collection.

Keywords: Advanced molecular spectroscopies; physicochemical and biochemical processes; nanotechnologies; chirality; cultural heritage

1. Introduction

Anna Giardini's retirement from her position as the professor of Molecular Spectroscopy at Sapienza University of Rome in 2009 (Fig. 1), did not signify the conclusion of her outstanding research activity, given the attention she paid to supporting that of her collaborators, as demonstrated by the references to paper published since 2009 [1-10]. They complete the long list of her previous articles appeared in a special issue celebrating her career (see [11]) with a retirement event held at Sapienza.



Fig. 1. Anna Giardini visiting Berkeley, Lawrence Laboratory, (23.08.1978).

This collection of articles originated from contributions presented on the occasion of the conference “Non-equilibrium processes and laser chemistry: from biospheres to the cosmos”, held on March 29, 2023, at Villa Torlonia in Rome (see poster in Fig. 2). The venue was the Library of the Accademia Nazionale delle Scienze detta dei Quaranta (National Academy of Sciences, known as of the Forty). This conference was a tribute to the memory of Anna Giardini, who passed away in October 2021, and brought together contributions from numerous colleagues and students who had collaborated with Anna Giardini over the years.

The topics covered during the conference spanned various aspects of her activity in the last decade, with a primary focus on physicochemical methodologies utilizing lasers and advanced spectroscopic techniques. These methodologies were employed to investigate systems of biological, astrochemical, or applicative relevance in the fields of energy, cultural heritage, and nanotechnology.

In the following, we briefly present a summary of Anna Giardini's scientific history [11-13] and then we pro-

vide a presentation of the four contributions featured in this issue, which are closely tied to Anna Giardini's main interests during her more recent and post-retirement activities.

2. Anna Giardini and her journey from atoms to biomolecules

In more than fifty five years of scientific activity, (1959-2017) Anna Giardini has developed and pioneered numerous advanced methodologies to study relevant chemical-physical and biochemical processes. Trained as a physicist on atomic interactions, she was led by a deep insight into experimental techniques with an endless curiosity to investigate systems of increasing complexity. She was internationally recognized as a brilliant scientist with a significant involvement in studying processes of relevance both to theoreticians and applied scientists.

She graduated in physics in 1958 and then continued in the Giangualberto Volpi's Mass Spectrometry Laboratory in the Institute of General and Inorganic Chemistry at the University of Rome [12]. In 1960 she started intense research activity in the field of ion-molecule reactions in the gas phase in order to obtain information on kinetics and interaction mechanisms in such systems. Ion-molecule reaction rate constants and binding energy values of even simple molecular ions were not well determined experimentally at that time. The development of an *ad hoc apparatus* (a tandem mass spectrometer in the University of Rome in 1968) allowed to obtain information on elementary processes through collision-induced dissociation [13].

In 1971, at ENEA Laboratories in Frascati, she set up electron scattering and ionization experiments in the gas phase both for valence and inner valence shells of atoms and molecules, obtaining direct information on their momentum wavefunctions. The spectroscopic process in which a fast projectile electron is used to eject a bound electron from an atomic or molecular target with the simultaneous detection of the two out-going electrons is called “(e,2e) spectroscopy”. Under specific conditions for the electron energy (when the impulse approximation can be used), the spectroscopic process provides a detailed map of the wavefunctions of the single atomic or molecular orbitals. During this period, she published numerous articles on the momentum wavefunctions (the counterpart of spatial wavefunctions).

In the mid-seventies, Anna Giardini became the director of a small research group in the ENEA research cen-

PROCESSI DI NON-EQUILIBRIO E LASER-CHIMICA: DALLE BIOSFERE AL COSMO

Conferenza in ricordo della Prof.ssa Anna Giardini

29 Marzo 2023

Diretta streaming <https://www.accademiasl.it/live>

10.00 Accoglienza e saluti istituzionali

10.20-10.40 Susanna Piccirillo
Introduzione

10.40-11.00 Debora Scuderi
Applicazioni della spettroscopia IRMPD per sondare la struttura e la reattività di biomolecole in fase gassosa

11.00-11.20 Lorenzo Avaldi
Applicazione di esperimenti PEPICO a molecole di interesse biologico

11.20-11.40 Caterina Fraschetti
Dagli ioni isolati alle architetture supramolecolari. Il caso della galattosammina protonata

11.40-12.00 Valter H. Carvalho-Silva
Nonequilibrium kinetics in chemistry, biology and biotechnology

12.00-12.20 Matthew J. Guberman-Pfeffer
Seeing Beyond Our Senses: How I Bonded with Chemistry

12.30-14.00 Lunch

14.10-14.30 Roberta Fantoni
Caratterizzazione remota ed in situ di superfici dipinte mediante diagnostiche laser

14.30-14.50 Antonio Morone
Nanoparticelle prodotte via Ablazione Laser Pulsata per applicazioni in microbiologia

14.50-15.10 Daniela Ascenzi
Ruolo della chimica ionica nei processi astrochimici

15.10-15.30 Savino Longo
La cinetica di non equilibrio delle reazioni prebiotiche in un'atmosfera primordiale

15.30-15.50 Marcel Snels
Assorbimento indotto da collisioni nell'atmosfera planetaria

15.50-16.20 Coffee Break

16.20-16.40 Walther Caminati
Chiralità e Spettroscopia nelle Microonde

16.40-17.00 Stefano Stranges
Prospettive per il riconoscimento chirale mediante spettroscopia fotoelettronica angolarmente risolta

17.00-17.20 Antonio Santagata
Dall'equazione di Schrödinger ai laser di Potenza

17.20-17.40 Vincenzo Aquilanti
Conclusioni

L'evento sarà trasmesso in diretta dalla Sede della Biblioteca dell'Accademia Nazionale delle Scienze detta dei XL



CNR
Istituto di Struttura
della Materia



LA
RICERCA
VENUTA
DAL
FUTURO

Il Centenario del CNR è realizzato con il contributo della
Presidenza del Consiglio dei Ministri e con il Patrocinio di Rai

PRESIDENZA DEL CONSIGLIO
DEI MINISTRI



illumina.info.contact@gmail.com

Fig. 2. Poster of the conference “Non-equilibrium processes and laser chemistry: from biospheres to the cosmos”, held on March 29, 2023, at Villa Torlonia in Rome.

ter in Frascati, which was involved in innovative activities concerning laser applications in chemistry, accompanied by the development of new laser sources. One important achievement was related to the realization of a Raman laser for IR frequency conversion, to be applied to multiphoton spectroscopy studies. She obtained outstanding results from gas phase studies on the selective absorption of one or more coherent laser photons by atoms, molecules, and clusters. The research on multiphoton excitation and dissociation of polyatomic molecules led to isotopic separation of sulfur, carbon, and uranium isotopes with a high yield (see related contribution [14]). Her activity in this field was widely recognized and for these studies she was awarded the ‘SASP Erwin Schrödinger Gold Medal’ in 2004 (see Fig. 3). The experiments on uranium isotopic enrichment ended in 1984 since this technology was considered proliferating and was definitively abandoned with the conclusion of the Italian nuclear fission program after the post-Chernobyl referendum in 1986. Nevertheless, the experimental and theoretical study on multiphoton excitation and dissociation processes continued, giving rise to a new line of research: the growth of nanostructures by Laser Chemical Vapor deposition.

The year 1987 marked her return to university: she was appointed full professor at the University of Basilicata in Potenza and, in 1989, director of the CNR Institute of Advanced Materials in Potenza. In both institutions she initiated setting up further experimental laboratories. She carried out experiments on laser photodeposition techniques starting from gaseous compounds (silane, hydrocarbons, and fluorocarbons) and developed apparatus for the pulsed laser ablation and deposition. The experimental apparatus was conceived to allow full spectroscopic, dynamic, and mass spectrometric characterization of the processes (see related contributions [15-16]). She studied the laser-matter interaction process both experimentally and theoretically.

Returning to Rome University in 1991, yet continuing to follow what was going on at the Basilicata laboratories, she developed spectroscopic methodologies for the study of gas phase supramolecular complexes formed in supersonic expansion also in combination with laser ablation. In particular, she applied resonant enhanced multiphoton ionization (REMPI) spectroscopy coupled with time of flight (TOF) mass spectrometry. From 1997, this was extended to the study of chiral molecules and non-covalently bound diastereomers (see related



Fig. 3. In February 2004, Anna Giardini was granted the “SASP Award for Outstanding Scientific Achievements”, consisting of the Erwin Schrödinger Gold Medal.

contribution [17]). These studies focused on discerning the factors influencing chiral recognition processes and enantioselectivity within non-covalently bound aggregates. This was achieved through the analysis of absorption spectra, the measurement of binding energies and reaction activation energies within aggregates containing chiral organic molecules of biological significance. It's worth noting that the first experimental determination of chirodiastaltic energy in gas phase molecular aggregates was carried out in the laboratory directed by her. Anna Giardini devoted a considerable part of her fruitful scientific career to studies concerning molecular chirality, a topic transversal across many disciplines that has relevance also for evolutionary sciences. Besides REMPI, she employed other methodologies for chirality investigations, such as Photoelectron Circular Dichroism (PECD), Electrospray Ionization coupled with Collision Induced Dissociation (ESI-CID) Mass spectrometry, and Infrared Multiphoton Dissociation (IRMPD).

In the years preceding her retirement, she started to study ultrafast photophysical and photochemical processes employing femtosecond lasers. She conducted pump-probe spectroscopy experiments on molecules of biological interest dissolved in liquid solutions.

As we have already noted, after retirement in 2009, she continued to be active as demonstrated by several articles in which she is co-author, among those listed as [1-10]. Indeed, in 2012, she was active assisting IRMPD experiments performed at the Centre Laser Infrarouge Orsay (CLIO) using a Free Electron Laser.

3. Contributions to this issue

The paper of Cicconi et al. [14], describes the possible reactions and strategies to enrich different isotopes via laser methods, such as AVLIS (Atomic Vapour Laser Isotope Separation) and MLIS (Molecular Laser Isotope Separation). At ENEA, under the direction of Anna Giardini a research line on MLIS was set up between the end of the 70's and the beginning of the 80's, reaching the preindustrial demonstrator stage for sulfur, carbon, and uranium isotopic enrichment.

The growing demand for radionuclides for medical purposes, in the electronics industry for semiconductors, in fusion reactors, and as tracers in industry has renewed interest in the Laser Isotope Separation methodology, also thanks to the nowadays availability of high power, pulsed, tuneable and narrow band lasers. The new challenges to which ENEA is preparing to contribute at a national and international level are also outlined in the article.

The contribution from Morone et al. [15] concerns magnetic SmCo nanoparticles (SmCo-NPs) synthesis by Pulsed Laser Ablation in Liquid (PLAL) and their chemico-physical and biological characterization. Laser Ablation strategy began in mid-1980's at the CNR Institute of Advanced Materials in Potenza, under the direction of Anna Giardini, with the deposition of thin films of High Temperature Transition Superconductors, such as YBCO and BISCO. Nowadays, numerous materials advantageous for biosensing and for medical applications are synthesized by PLAL. This is due to the low environmental impact of this technique, as it does not require precursors or reducing chemicals and is able to produce high-purity colloids without generating harmful waste.

The paper of Fantoni et al. [16] reports on the fruitful use of remote applications of Laser Induced Fluorescence (LIF), Raman and Laser Induced Breakdown Spectroscopy (LIBS) on Cultural Heritage samples. As director of the Molecular Spectroscopy and Laser Application Laboratory at ENEA Frascati in the 80ies, Anna Giardini promoted the use of laser sources both for material processing (laser isotope separation and photochemistry) and spectroscopic diagnostics (laser induced fluorescence, multiphoton ionization, photofragments spectroscopy). As the authors of the article cite in the acknowledgement, the successive development of the laser Diagnostic and Metrology Laboratory at ENEA Frascati towards different laser applications in the fields of environment, security, forensics, and cultural heritage was to a certain extent a natural consequence of her vision.

In the contribution of Piccirillo et al. [17] some relevant results obtained by Resonant Two-Photon Ionization (R2PI) spectroscopy on the investigations of chiral discrimination effects in gas-phase molecular complexes are reported. Some salient achievements concern the experimental measurement of the chirodiastaltic energy, the possibility to discriminate enantiomers and to potentially enrich a racemic mixture. Structural characterization with the aid of theory allowed to ascertain the role of specific electrostatic and dispersive interactions in chiral recognition.

4. Concluding dedication

This collection of papers aims to celebrate not only a brilliant scientist but also a compassionate mentor, a visionary leader, and a trailblazer who left an indelible mark on the landscape of scientific discovery. The legacy of Anna Giardini endures not only in the pages of research journals but in the hearts and minds of those she

inspired, encouraging many female students to continue in scientific research. Her life's work serves as an everlasting source of inspiration for the continued pursuit of knowledge and the boundless possibilities that lie at the intersection of science and imagination. The evidence of her success is measured by the acknowledgment and appreciation from all her collaborators. Their names can be retrieved from the bibliography (below), which demonstrates also how numerous they were.

REFERENCES

- Refs [1-10] complement Anna Giardini list of papers presented in [11].
- [1] Ciavardini A., Dalla Cort A., Fornarini S., Scuderi D., Giardini A., Forte G., Bodo E., Piccirillo S. Adenosine monophosphate recognition by zinc-salophen complexes: IRMPD spectroscopy and quantum modeling study. 2017 *Journal of Molecular Spectroscopy*, 335, 108-116. DOI: 10.1016/j.jms.2017.02.014
- [2] Rondino F., Satta M., Piccirillo S., Ciavardini A., Giardini A., Speranza M., Avaldi L., Paladini A. Chlorine Para-Substitution of 1-Phenylethanol: Resonant Photoionization Spectroscopy and Quantum Chemical Calculations of Hydrated and Diastereomeric Complexes. 2016 *Journal of Physical Chemistry A*, 120 (27), 5023-5031. DOI: 10.1021/acs.jpca.5b12746
- [3] Rondino F., Ciavardini A., Satta M., Paladini A., Frascetti C., Filippi A., Botta B., Calcaterra A., Speranza M., Giardini A., Piccirillo S. Ultraviolet and infrared spectroscopy of neutral and ionic non-covalent diastereomeric complexes in the gas phase. 2013 *Rendiconti Lincei*, 24 (3), 259-267. DOI: 10.1007/s12210-013-0241-5
- [4] Bodo E., Ciavardini A., Giardini A., Paladini A., Piccirillo S., Rondino F., Scuderi D. Infrared multiple photon dissociation spectroscopy of ciprofloxacin: Investigation of the protonation site. 2012 *Chemical Physics*, 398, 124-128. DOI: 10.1016/j.chemphys.2011.05.018
- [5] Giardini A., Rondino F., Paladini A., Speranza M., Satta M., Piccirillo S. Enantioselective HF loss promoted by resonant two-photon ionization of supersonically expanded (R)-1-Phenyl-2,2,2-trifluoroethanol clusters. 2011 *Journal of Physical Chemistry A* 113 (52), 15127-15135. DOI: 10.1021/jp905322n
- [6] Rondino F., Paladini A., Ciavardini A., Casavola A., Catone D., Satta M., Barth H.D., Giardini A., Speranza M., Piccirillo S. Chiral recognition between 1-(4-fluorophenyl)ethanol and 2-butanol: Higher binding energy of homochiral complexes in the gas phase. 2011 *Physical Chemistry Chemical Physics*, 13 (3), 818-824. DOI: 10.1039/c0cp01401j
- [7] Speranza M., Rondino F., Giardini A., Paladini A., Hortal A.R., Piccirillo S., Satta M. Conformational landscape of supersonically expanded 1-(fluorophenyl) ethanols and their monohydrated clusters. 2009 *ChemPhysChem*, 10 (11), 1859-1867. DOI: 10.1002/cphc.200900011
- [8] Giardini A., Rondino F., Paladini A., Hortal A.R., Satta M., Speranza M., Piccirillo S. Monosolvation effects in chiral fluoroorganic compounds: An R2PI study. 2008 *Physica Scripta*, 78 (5), 058121. DOI: 10.1088/0031-8949/78/05/058121
- [9] Allocca L., Bonavolont C., Giardini A., Lopizzo T., Morone A., Valentino M., Verrastro M.F., Viggiano V. Laser deposition of SmCo thin film and coating on different substrates. 2008 *Physica Scripta*, 78 (5), 058114. DOI: 10.1088/0031-8949/78/05/058114
- [10] Speranza M., Rondino F., Satta M., Paladini A., Giardini A., Catone D., Piccirillo S. Molecular and supramolecular chirality: R2PI spectroscopy as a tool for the gas-phase recognition of chiral systems of biological interest. 2009 *Chirality*, 21 (1), 119 - 144. DOI: 10.1002/chir.20627
- [11] Aquilanti V., Piccirillo S. and Speranza M. Anna Giardini's journey from atoms to biomolecules. 2008 *Physica Scripta*, 78, 050401. DOI: 10.1088/0031-8949/78/05/050401
- [12] Boato G., Volpi G.G. Experiments on the Dynamics of Molecular Processes: a chronicle of Fifty Years. 1999 *Annual review of Physical Chemistry*, 50, 23-50.
- [13] Turco F. 2003 L'introduzione della spettrometria di massa in Italia. *Atti del X Convegno Nazionale di Storia e Fondamenti della Chimica*, Pavia, 22-25 October 2003, *Accademia Nazionale delle Scienze detta dei XL*, Rome p. 395.
- [14] Palucci A., Agostini P., Favuzza P., Raspa A., Cicconi F. Laser Isotope Selective Excitation techniques for efficient Atomic and Molecular Separation of isotopes in fusion and medical applications. *Rendiconti della Accademia Nazionale delle Scienze detta dei XL*, *Memorie e Rendiconti di Chimica, Fisica, Matematica e Scienze Naturali*, serie VI, vol. IV, fasc. 2, 2023.
- [15] Fantoni R., Palucci A., Caneve L., Colao F., Lazic V., Spizzichino V. Remote characterization of multilayered surfaces by means of laser spectroscopic diagnostics. *Rendiconti della Accademia Nazionale delle Scienze detta dei XL*, *Memorie e Rendiconti di Chimica, Fisica, Matematica e Scienze Naturali*, serie VI, vol. IV, fasc. 2, 2023.
- [16] Morone M.V., Chianese A., Zannella C., De Filippis A., Galdiero M., Morone A. Pulsed Laser Ablation in liquid: top-down approach against *Staphylococcus aureus* infection in vitro. *Rendiconti della Accademia Nazionale delle Scienze detta dei XL*, *Memorie e Rendiconti di Chimica, Fisica, Matematica e Scienze Naturali*, serie VI, vol. IV, fasc. 2, 2023.
- [17] Rondino F., Paladini A., Ciavardini A., Catone D., Satta M., Speranza M., Piccirillo S. Clusters of chiral molecules in the isolated state. *Rendiconti della Accademia Nazionale delle Scienze detta dei XL*, *Memorie e Rendiconti di Chimica, Fisica, Matematica e Scienze Naturali*, serie VI, vol. IV, fasc. 2, 2023.