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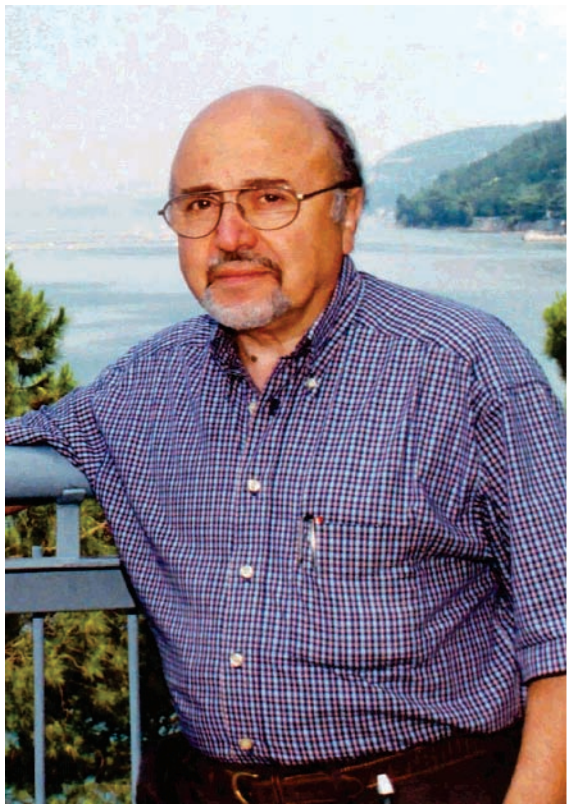

It's All a Matter of Intermolecular Forces—A Tribute to Giacinto Scoles

It is a great pleasure to introduce this special issue of the *Journal of Physical Chemistry A* in celebration of Giacinto Scoles' scientific accomplishment at this transitional moment of his career, from Donner Professor of Science (in phased retirement) at Princeton to his new Structure-of-Matter professorship at the International School for Advanced Studies, in conjunction with the Elettra Synchrotron Laboratories in Trieste, Italy. Giacinto's independent scientific career spams over four decades and three countries, Italy, Canada, and the USA. This short tribute, from one of his peers, a close collaborator, and a former student, aims at highlighting his landmark scientific contributions in physical chemistry especially in the fields of intermolecular forces, molecule−surface interactions in the context of gas phase clusters, surface monolayers and thin films, as well as biological systems. It is a nice coincidence that the research of the three guest editors focuses on intermolecular interactions, spectroscopy, and surface science, respectively, three fields in which Giacinto has made a major impact. He is a leading physical chemist who has a deep understanding of the forces present in nature, great insight into chemical dynamics, as well as a broad knowledge of molecular beam technology, laser spectroscopy, surface science, and theory.

The Scoles name has been closely linked to an innovative molecular beam detector, the cryogenic bolometer, an idea conceived in a discussion of Giacinto with a junior colleague, Gaetano Gallinaro, at the University of Genova, Italy, in the late 1960s. The bolometer, proposed and originally developed mainly by the astrophysics community as an infrared radiation detector, was used by Giacinto to detect the kinetic energy of molecular beams. The test apparatus, set up together with M. Cavallini and G. Gallinaro (*Z. Naturforsch., A* **1969,** *24*, 1850.), offered great advantages with respect to then conventional

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techniques and allowed Giacinto to build "cheap" molecular beam experiments that nevertheless to obtain the state-of-the-art results. This invention enabled a series of key findings that included the determination of quantum effects in the energy dependence of the integral collision cross-section of He scattered by He, the first observation of "Rainbow Scattering" between two crossed beams of argon, and the first measurement of orbiting resonances in the scattering between two atoms (Hg and H).

Giacinto set up a very successful crossed molecular beam laboratory in Canada after moving to the University of Waterloo, where he became professor of Chemistry and Physics in 1971. His work mainly involved crossed beam differential scattering cross-section studies of atom−atom, atom−molecule, and molecule−molecule interactions, using his trademark liquid helium cooled bolometer detector technique. Two new branches began, however, to emerge in the direction of his research: (a) Giacinto was seduced by the "light side" and began a remarkable and productive collaboration with his gifted colleague, Terry Gough, and an extraordinary graduate student, Roger Miller, that introduced bolometer-detected infrared spectroscopy of molecular beams, leading to studies of vibrational predissociation of van der Waals complexes. (b) He also started to cross the "phase boundaries" and applied molecular beam scattering techniques to surface science to reveal the structure and molecule−surface potentials for surfaces and overlayers on surfaces (*J. Phys. Chem.* **1990**, *94*, 8511). We highlight his most cited work on the realistic modeling of the interaction potential between atoms (*Chem. Phys.* **1977**, *19*, 119). This paper is also quite characteristic for his working style to make solutions as simple as possible without compromising the correct physical description. ("Everything should be made as simple as possible, but not simpler", as Albert Einstein once said.) All of the model potential forms for the weak molecular interaction of closed shell systems at that time were limited by the fact that the simple addition of the repulsive and the attractive part of the potential contained an important error, the unmodified use of the attractive part at small distances. Most quantum chemists who were then dealing with that problem were more interested in performing rigorous calculations and did not believe in simple and transferable models with an empirical touch. Giacinto managed to convince Reinhard Ahlrichs of the utility of a semiempirical approach, and they came up with a realistic damping function for the so-called Hartree−Fock Dispersion model potential in which reliable Hartree−Fock calculations for the repulsive and dispersion coefficients for the attractive parts were used as input data.

After accepting the Donner Chair of Science at Princeton University in 1986, Giacinto pioneered the use of superfluid helium nanodroplets as the least-perturbing spectroscopic matrix (*Phys. Rev. Lett.* **1992**, *69*, 933; *J. Phys. Chem.* **1993**, *97*, 2236). This work arose from the "pickup technique" developed by Giacinto already at the University of Waterloo and widely used in the molecular beam community to study IR spectroscopy of molecules attached to inert gas clusters, particularly Ar and Xe clusters. In the case of He nanodroplets, the technique was applied to alkali metals, which provided a rich vein to explore chemical dynamics in this fascinating state of matter, as well as to set the stage for time-resolved investigations.

Combining molecular beam technology with spectroscopy, Giacinto and Kevin Lehmann began their long-term collaboration on intramolecular vibrational energy redistribution in the late 1980s. They first studied the carbon−hydrogen stretching fundamental and first overtone spectral regions and observed Lorentzian line shapes due to irreversible relaxation for large molecules with very high densities of states, a result that Giacinto particularly liked (*J. Phys. Chem.* **1995**, *95*, 8282). They developed IR−microwave and later IR−IR double resonance methods to provide unambiguous quantum assignments of even highly congested spectra and to reach higher in energy in the overtone region with very high resolution, again a first. Also, the pure rotational spectra of HCCCN and HCN in He nanodroplets were observed, which Giacinto referred to as the microwave cooking of the droplets. This established that a single droplet could absorb several thousand photons without "optically pumping" out of resonance.

Giacinto is among the first group of scientists using helium diffraction in conjunction with grazing incidence X-ray diffraction (in collaboration with Peter Eisenberger) to investigate a popular and promising new material known as self-assembled monolayers (SAMs) of organic thiols on gold surfaces, introduced by Nuzzo and Allara in 1982. These investigations established the basic structures of these layers including the basic periodicity, domain size, and existence of a superlattice (*J. Chem. Phys.* **1993**, *98*, 3503). To arrive, however, at the real structure of the SAMs took at least another 10 years of obstinate work by many people. Indeed, recently in Trieste using a combination of molecular dynamics and grazing incidence X-ray scattering, Giacinto and co-workers have unravelled the puzzle of the sulphur−gold interface (*Phys. Rev. Lett.* **2007**, *98*, 016102). By applying Fourier transformation to his research, Giacinto has recently moved from reciprocal space to real space, and after developing expertise in atomic force microscopy very quickly, he has imaged and performed nanofabrication of SAMs and biomolecules. He has revealed protein conformations upon immobilization on surfaces using this technique as well as the mechanical properties of various functionalized alkylthiol SAMs on gold. At present, Giacinto and his team are working on DNA hybridization on surfaces and the development of sensors for proteomics studies.

Like many great researchers, Giacinto's contribution to science is multifaceted. In parallel to his research activities, Giacinto has, throughout his career, widely shared his knowledge of molecular beams and his vision and enthusiasm for the advances in molecular physics and chemistry that they allow. In the years from 1975 to 1979, Scoles contributed with Davide Bassi and others to the foundation of the experimental physics laboratory at the newly established University of Trento, Italy. He was a cofounder of the Guelph−Waterloo Center for Graduate Work in Chemistry and of the Chemical Physics series of Conferences at the University of Waterloo. Giacinto played a leading role in the establishment and early stages of the Princeton Materials Science Institute. He also promoted the International Symposium on Molecular Beams from an insider meeting of technical aspects in Cannes to the broad and top-level scientific basis that it continues to represent. The organization of the Enrico Fermi Summer Schools in Varenna on Molecular Beams in 1968, on Surface Physics in 1973, and on Clusters in 1988 proved to be timely milestones in these fields and represent a small fraction of the many meetings that he has organized or co-organized. Last, but not least, he edited the famous two-volume multiauthor book *Atomic and Molecular Beam Methods*, which still contains the key information needed by anyone designing and building a molecular beam machine and is considered a milestone in this important field of research.

In his characteristic way, Giacinto has improved the organization and the work environment for those around him whether he was in Italy, Canada, or the USA. At the end of his time in Genoa, he laid the foundation for a flourishing surface scattering group. During his time in Canada and together with R. J. Le Roy, he started the Waterloo Chemical Physics seminar group and with Gough and other colleagues the Centre of Molecular Beams and Laser Chemistry as well as the Centre for Surface Science and Technology. In Princeton, he worked with Peter Eisenberger and others to set up the Princeton Materials Institute and was instrumental in writing the school's first successful National Science Foundation Materials Research Science and Engineering Center application to establish the Princeton Center for Complex Materials.

Giacinto is an inspiring teacher, mentor, and group leader: He continuously stimulates new ideas and experiments and promotes international collaborations. We mention one important innovation that highlights his teaching style. When teaching a relatively small class (e.g., less than 20 students), he always asks the students to evaluate themselves before the final examination, what grade they have earned. Then he compares their results with his own. If the results are consistent within half of a letter grade, e.g., A^+ versus A, then the students could simply earn the lesser grade without taking a long, difficult, and, for some, intimidating final examination. If the difference is more than half a letter grade or if the students are unhappy with the outcome, then they must take the final exam to earn their final grade. It is always fun and exciting during the face-to-face interview where proposed grades are compared. In the spirit of scientific objectivity, fairness, and friendship, Giacinto, please let us know what score you give yourself in science, and we will let you know if you will be facing the "final exam" that we have prepared for you!

This special issue is for a celebration of Giacinto's scientific career as well as for him as a person. Everyone who has the pleasure to personally know him appreciates his extreme enthusiasm, energy, and charisma when dealing with science and scientific discussions (sometimes arguments). Giacinto's dedication to the pursuit of truth, his generosity in allocating credit to others, and his evident sincere concern and willingness to help colleagues, especially junior ones, continues to provide an excellent role model for what any scientist should try to become. May this issue bring more stimulating scientific discussions with Giacinto and among his fellow physical chemists and scientists. On behalf of Giacinto's legions of scientific colleagues, admirers, and close personal friends (which are highly overlapping sets), we wish to congratulate him and wish him many more productive years, which we will eagerly follow for the many pearls of insight and wisdom that they will provide.

Udo Buck, Kevin K. Lehmann, and Gang-yu Liu
Guest Editors