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Editorial

Topical issue on dynamics and photodynamics: from isolated molecules to the condensed phase

Luis Bañares[2], Ramón Hernández-Lamoneda[3], Pascal Larregaray[4], Germán Rojas-Lorenzo[1], and Jesús Rubayo-Soneira[1,a]

[1] Instituto Superior de Tecnologías y Ciencias Aplicadas (InSTEC), Universidad de La Habana, Ave. Salvador Allende 1110, Plaza de la Revolución, 10400 Havana, Cuba
[2] Departamento de Química Física, Facultad de Ciencias Químicas, Unidad Asociada I+D+i CSIC, Universidad Complutense de Madrid, 28040 Madrid, Spain
[3] Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, 62210 Cuernavaca, Morelos, Mexico
[4] CNRS, Bordeaux INP, ISM, UMR5255, Univ. Bordeaux, 33400 Talence, France

Abstract. The well-established and rapidly expanding field of molecular processes in excited systems, facilitated by the use of light sources, garners significant research interest from numerous experimental and theoretical groups worldwide. This highly interdisciplinary field establishes extensive connections with atomic, molecular and optical physics, astrophysics, biophysics, physical chemistry, solid-state physics and even molecular biology. The present topic provides an advanced overview of research activities in cutting-edge areas such as ultrafast lasers, nanoscale systems, atomic and molecule collisions on surfaces and molecular photofragmentation processes. The contributions to this subject encompass experimental, theoretical and computational studies conducted both at the fundamental level, exploring elementary mechanisms, and at a more applied level, addressing the requirements of diverse applications in nanotechnology and materials science.

1 Introduction

In recent years, there has been remarkable progress in the development of experimental, theoretical and computational methods for analyzing the structure and dynamics of atomic, molecular and biomolecular systems across various levels of complexity [1–4]. This advancement has opened up new opportunities to study dynamic phenomena and investigate many-body effects that manifest in atomic clusters, nanoparticles, nanostructures, as well as molecular and biological systems, irrespective of whether they exist in the gas phase, are deposited on surfaces, or are embedded within molecular environments. These comprehensive investigations have primarily focused on addressing critical challenges such as structure formation, stability, calculations of potential energy surfaces and fragmentation phenomena [5,6]. Moreover, they have shed light on phase transitions, structural transformations and an array of other intriguing phenomena. Experimental and theoretical research has widely recognized that atomic clusters and complex molecular systems often exhibit unique and captivating properties, making them highly relevant and fascinating subjects for in-depth exploration.

Recent advancements in experimental techniques have revolutionized the study of atomic and molecular clusters, facilitating a deeper understanding of the transition from the gas phase to the condensed phase. In particular, researchers commonly explore the structural and dynamic properties of cluster systems by employing photon, electron and atomic collisions as investigative tools. Moreover, cutting-edge approaches have emerged in the investigation of complex molecular systems and clusters, leveraging the remarkable capabilities offered by femtosecond and attosecond lasers. These ultrafast laser sources enable researchers to temporally resolve and investigate intricate ultrafast processes, thus providing valuable insights into the behavior and dynamics of these systems.

The continuous advancement of experimental techniques, both in the frequency and time domains, has made significant contributions to the exploration of molecular system dynamics. Extensive research efforts in this field have been dedicated to investigating a diverse range of complexes, encompassing gas phase systems, clusters, surface collisions and condensed phase environments. In parallel, high-level ab initio quantum chemistry methods have emerged as indispensable tools for unraveling the intricate structural, spectroscopical and dynamical properties of small- to medium-sized molecules.

[a] e-mail: jrubayo@gmail.com (corresponding author)

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Nevertheless, as molecular systems increase in size, the computational demands escalate rapidly, posing a challenge for accurate simulations. To tackle this issue, the molecular fragmentation approach has emerged as a viable solution, offering a systematic hierarchy of approximations for calculating the molecular electronic energy. This strategy involves dividing large molecules into smaller, manageable fragments, enabling high-level ab initio calculations to be performed within a reasonable computational time frame.

By combining cutting-edge experimental techniques with sophisticated computational methodologies, scientists are pushing the boundaries of our understanding of molecular dynamics and paving the way for groundbreaking discoveries in various research fields.

The exploration of properties exhibited by molecular clusters as they interact with surfaces or become embedded in condensed media represents a highly relevant and dynamic area of scientific and technological research. Over the past years, cluster-based materials, including supported clusters, ligand-protected clusters, and cluster composites, have garnered substantial attention from both the realm of fundamental science and practical applications. Gaining a comprehensive understanding of the elemental composition, structure and electronic properties of these systems is paramount for advancing the fabrication of novel materials and nanostructures, enabling the production of thin films and surface coatings, facilitating the design of pharmaceuticals and radiosensitizing agents and delving into the fundamental intricacies of nanoscale phenomena. Moreover, such knowledge serves as a crucial foundation for unraveling the mechanisms governing the formation and self-assembly of complex many-atom systems.

The field of dynamics and photodynamics: from isolated molecules to the condensed phase, is highly interdisciplinary and has numerous connections with traditional branches of physics and chemistry. The original conference in this field, the Photodynamics meeting, took place in Havana in February 2000. Since then, eleven editions have been held, enabling countries in Latin America, especially young researchers, to interact with the latest findings in this branch of science. The first six editions were held in Havana. Starting in 2012, the conference took place in Maresias, Brazil (2012), Oaxaca, Mexico (2014), Mendoza, Argentina (2016), Cartagena de Indias, Colombia (2018), and once again in Havana, Cuba (2022). In this latest edition, we celebrated the 20th anniversary, which could not be commemorated in 2020 due to the COVID-19 pandemic.

Initially, the Photodynamics Conference focused primarily on the structure and dynamics of molecular systems in the gas and condensed phases. Since then, its scope has significantly expanded to include the dynamics of nanosystems, biomolecules and macromolecules, with an emphasis on the similarity of aggregation phenomena that arise in different areas of physics, chemistry and biology.

This topical issue provides a snapshot of current research in different areas of molecular systems science. It consists of 12 contributions [7–11,13–19] representing both experimental and theoretical studies, ranging from fundamental mechanisms to more applied levels, which are essential in numerous applications of nanotechnology and material science.

The contributions featured in this issue encompass a wide range of areas, including spectroscopy, photodissociation, dynamics of reactions involving neutral and charged cluster systems, carbon nanotubes and various other subjects. A number of esteemed participants from the Photodynamics Conference have made valuable contributions by presenting their groundbreaking and innovative findings.

2 Spectroscopy and experimental works

Several articles in this thematic issue describe recent advances in experimental techniques as infrared and Raman 2D spectroscopy, as well as photoisomerization processes.

The paper by Mohamed Abdessamia Chakchouk et al. [7] reports the bond force constants of CO_2 molecule in gas phase state and trapped in a nanocage by applying group theory to the normal vibrational modes of the symmetric ($^{16}O^{12}C^{16}O$, 626) and the asymmetric ($^{16}O^{12}C^{18}O$, 628) CO_2 isotopic species. Wilson's force, F and inverse-mass and G matrices were calculated for the CO_2 (626 and 628) species. The effect of Fermi resonances was included in the analysis. Results are given in terms of bond force constants for stretching and bending modes of CO_2 molecule trapped in nanocages of rare gas matrices and of clathrate hydrates.

In the contribution by Daniel Codorniu-Pujals et al. [8], Raman spectroscopy is used to study the modifications caused by Compton electrons, originated by gamma quanta of Co on the crystalline structure of graphite. The samples were irradiated in a dose range between 40 and 160 kGy. The analysis of the Raman spectra allowed to corroborate the electrons that occur at these radiation doses are able of causing appreciable modifications in the graphite structure. These modifications have a complex dependence of radiation dose due to the concurrence of the "radiational damage" and "radiational annealing" processes. The analysis of the fine structure of the Raman 2D band shows that the effect of the Compton electrons goes beyond the production of vacancy–interstitial pairs, since it leads to the modification of the disposition and stacking order of the planes in the structure of graphite.

In the reference [9], the authors performed gas phase excited-state lifetime studies on indigo to study these processes in a solvent-free environment, combined with excited-state calculations. They found two decay pathways, a fast sub-nanosecond decay and a slow decay on the order of 10 ns. Calculations of the excited-state potential energy surface found that both hydrogen and proton transfers are nearly isoenergetic with an estimated barrier of 0.1 eV. To further elucidate these dynamics, they also report a study with deuterated indigo, using resonance-enhanced multi-photon ioniza-

tion and pump-probe spectroscopy with mass spectrometric isotopomer selection.

The paper by Alejandro Quintanilla et al. [10] revisit the existing work on the photoisomerization process in some of the fluorinated analogues of acetylacetone, i.e., trifluoroacetylacetone (F3-acac) and hexafluoroacetylacetone (F6-acac). They performed selective UV laser excitation of these molecules trapped in soft cryogenic matrices, namely neon and para-hydrogen, and probed by vibrational spectroscopy. Clear spectroscopy of three isomers of F6-acac and six isomers of F3-acac is well resolved, including the first characterization of a second open enol isomer of hexafluoroacetylacetone. In addition, they present the electronic absorption spectra of both molecules in cryogenic matrices before and after specific UV irradiations, giving new data on the electronic transitions of photoproducts.

In recent years, the development of battery technology has greatly improved the efficiency of solar energy utilization. Due to the limited band gap width of silicon, the energy provided by the photon with wavelength over 1107 nm is not enough to make the valence band electron transition, which greatly limits the conversion and utilization of solar radiation energy in silicon-based solar cells. Based on the local surface plasmon resonance effect, the optical band gap of semiconductor materials can be widened. In the paper by Daohan Ge et al. [16], porous silicon/gold (Au) nanocomposite structures were prepared by electrochemical anodic corrosion and added chloroauric acid solution in the corrosive liquids. The growth of gold nanostructures can be controlled by adjusting the concentration of chloroauric acid in the corrosive liquids. The spectral scanning in the wavelength range of 200–1400 nm shows that when the concentration of chloroauric acid is 0.01 mol/L, the best anti-reflection performance is obtained, and the average reflectance of porous silicon/gold nanocluster composite structure is reduced to 2.14%. This process provides a simple and economical method for the preparation of anti-reflection coating and has important research significance in the anti-reflection layer of solar cell devices.

3 Molecular dynamics simulations

Molecular dynamics simulation has been one of the subjects of interest in the history of the Photodynamics meeting. In this special issue, there are several contributions where the authors use different methods in order to study the structure and dynamics of molecular systems.

The effect of the ionizing radiation on the structure and properties of carbon nanotubes (CNTs) is of great theoretical and practical interest, due to their potential applications in electronics and other fields, including nuclear energy. Although several investigations have been devoted to this issue in the last years, many aspects of that interaction are still not well understood. With the objective of achieving a better understanding of these processes, in the work presented in this issue [11] the density functional-based tight-binding method is used to study CNTs of single and multiple layers, in which the kind of defects that typically appear under the action of the radiation (vacancies, divacancies, Stone–Wales defects and other) were introduced. The results related with the energy of formation of those defects and the geometric and energy modifications that take place in the CNTs with different chirality and number of layers are presented.

Since the experimental works published in 1993 [12], nested almost perfect graphitic spheres have been generated in the condensed phase by irradiation with high-energy electrons of graphitic particles. The quasi-spherical shapes of these molecular systems were more marked than those obtained by other authors by applying the arc-discharge method to amorphous carbon films. Although the work developed in [12] was able to describe the influence of parameters such as temperature and dose of electronic radiation on the transformation of these structures, theoretically it has not been possible to explain the causes of the triggering of the above-mentioned process because of the complexity of these systems. Using a computational method based on density functional theory with tight-binding approximation (DFTB), the geometries of fullerenes of order (2160 atoms) and carbon nano-onions (CNOs) of up to five layers were optimized, and the different energetic and geometric parameters of fullerenes and polyhedral CNOs were calculated [13]. By introducing in the structure of these nanomaterials the point defects that are commonly produced during their irradiation (monovacancies, divacancies and Stone–Wales), the possible structural deformations caused in these arrangements, as well as the formation energies were analyzed. The results obtained allow us to verify that divacancies can modify the outermost nano-onion layers with an effect similar to that described experimentally.

The study presented in the paper [14] reports atomistic structural characterization of 3.7-nm-diameter gold nanoparticles (NP) coated with polymer polyethylene glycol-based ligands of different lengths (containing 2–14 monomers) and solvated in water. The system size and composition are selected in connection to several experimental studies of radiosensitization mechanisms of gold NPs. The coating structure and water distribution near the NP surface are characterized on the atomistic level by means of molecular dynamics simulations. The connections between the coating structure and distribution of water are established for different NP sizes as well as lengths and surface densities of coating molecules. The quantitative analysis of water distribution in the vicinity of coated metal NPs can be used to evaluate the radiosensitizing effectiveness of a particular NP system based on the proximity of water to the NP metal core, which should impact the production of hydroxyl radicals and reactive oxygen species in the vicinity of metal NPs exposed to ionizing radiation.

In the contribution [15], the structures and energetics of Li-doped He clusters have been determined by means of evolutionary programming optimizations and

classical molecular dynamics simulations. The underlying interactions in the HeLi complexes are described by sum-of-potentials ab initio-based models. The classical picture of the He atoms surrounding the cationic dimer shows a selective growth of the clusters. By analyzing spatial distribution probabilities and single-atom evaporative energies from molecular dynamics calculations, they found pronounced drops in the computed energy for $N = 2$, 4 and 6, and smaller ones for $N = 10$, 13, 15, 18, 20, 22, 24, 27 and 29. The most energetically favored structure (compared to its neighbors) is found when six He atoms are attached in the Li_2^+-cation, forming He_3-motifs at each side and leading to the formation of the first solvation shell. In turn, as extra He atoms are added, a new shell is started to form at $N = 10$, with the He_3 triangles being the building blocks in all classical solid-like structural arrangements in $He_N Li_2^+$ clusters. By combining the outcome of the present work on the existence of such local solvation microstructures in Li_2^+-doped He clusters together with those from previous studies on alkali ions, the authors suggest that such microsolvation effects could influence the short-time solute-solvent dynamics and thus contribute to the observed slow ions' mobility in He droplets.

The SiCSi molecule has been detected in the interstellar medium (ISM) and is expected to play a key role in astrochemistry. To correctly determine the physicochemical conditions in typical molecular clouds, the use of non-local thermodynamic equilibrium models is essential. These models require the rate coefficients of the molecule analyzed with the most common ISM colliders. However, for SiCSi, these data are not available. The main objective of paper [17] has been to determine the first set of rotational rate coefficients for SiCSi collision with para-$H_2(j = 0)$. For this purpose, a recently reported reduced potential energy surface is employed. Quantum dynamics is studied from close-coupling calculations. Furthermore, a set of cross sections is computed using the coupled-states methods and compared with the close-coupling results. The rate coefficients are compared with the values of an approximation used recently in the literature, showing the need to determine these data from accurate calculations. Finally, the de-excitation rate coefficients are reported for the first 31 rotational states of SiCSi at low temperatures.

4 Related aspects

For systems modeled by the generalized Chafee–Infante equation with arbitrary nonlinear power index in $(1 + 1)$-dimensional and $(2 + 1)$-dimensional scenarios, in paper [18] soliton dynamics were investigated utilizing the modified F-expansion method and novel ansatz of F-base function. They derived the bright soliton solution and kink soliton solution supported by the generalized Chafee–Infante equation system in both $(1 + 1)$- and $(2+1)$-dimensional cases. The authors gave graphical illustrations of the derived soliton solutions in one and two dimensions and analyzed the stability of the bright soliton and kink soliton solutions in two-dimensional format. The theoretical results presented in this work can be used to guide the experimental observation of solitons in systems modeled by the generalized Chafee–Infante equation.

Finally, reference [19] has presented the results of a new quadrifocal diffractive lens designed using the silver mean sequence. The focusing properties of these aperiodic diffractive lenses coined silver mean zone plates are analytically examined. It is demonstrated that, under monochromatic illumination, these lenses present four foci located at certain reduced axial positions given by the Pell numbers that can be correlated with the silver mean sequence. This distinctive optical characteristic is experimentally confirmed.

5 Concluding remarks

Dynamics and Photodynamics science has continued its significant progress in recent years, but a large number of questions in the field still remain open. Different types of clusters, various cluster geometries and size ranges, composite and ligand-protected clusters, complex molecules (including biomolecules) and clusters on a surface and embedded into nanodroplets or matrices, all provide additional topics which make this field of science very rich and diverse. Laser techniques provide state-of-the-art tools for experimental studies of the cluster structures, dynamics and properties. Also, new computational facilities provide new possibilities to study the potential energy surfaces and dynamics of more complex systems.

All these questions remain among the key topics of the Photodynamics Conference. This Conference series continues and the next, 12th Photodynamics Conference will take place in Santiago de Chile from November 11 to 14, 2024. Similar to previous conferences, it will focus on the structure and dynamics of molecular systems; collision on surfaces; cluster–molecule interactions, reactivity and nanocatalysis; clustering in systems of various degrees of complexity; and other related aspects.

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Author contributions

All the authors were involved in the preparation of the manuscript and contributed equally to this work. All the authors have read and approved the final manuscript.

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