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Introduction: Laser Ablation of Molecular Substrates

"Ablatio" in Latin means "removal", and thus "laser ablation", strictly speaking, refers to laser-induced material ejection. However, as is usual with terminology in sciences, the expression has been associated with specific connotations and implications, so its physical scope is much more limited, but also more difficult to define. Usually, the term is associated with a "macroscopic" material removal and pronounced morphological changes that are effected on condensed phases upon irradiation with intense laser pulses. A number of other processes, such as plasma ignition, shock wave formation, etc., may accompany the phenomenon. In view of this violent nature, the process would appear to be too crude to be of any chemical interest. However, contrary to conventional chemical wisdom, in the early 1980s Srinivasan's and Namba's groups demonstrated the potential of intense UV laser pulses for "clean" structuring of polymers, with minimal collateral thermal or chemical decomposition of the remaining material. Industry was quick in exploiting the material processing/fabrication potential afforded by this violent phenomenon. Laser ablation is also the first step in pulsed laser deposition for the generation of structured layers on substrates. Similarly, in medicine, laser ablation schemes gained increasing importance in clinical practice. Yet, chemistry and chemists have largely neglected the fundamentals of ablation, despite the evidently many chemical issues involved in these applications.

In its broader "material removal" sense, ablation relates to a number of other applications. The most relevant one concerns the various schemes that employ laser irradiation for ejecting molecules in the gas phase for their characterization and/or spectroscopic study. These techniques, many of them questionably denoted as "desorption", have evolved to such an extent that today they constitute a major analytical tool in chemistry and the life sciences. In fact, it was largely through the success of matrix-assisted laser desorption/ionization (MALDI) technique that the attention of chemists was drawn to the unique features of the interaction of intense laser pulses with molecular substrates. Today, these diverse techniques and applications are widespread and exploited in many fields of chemistry, biology, and medicine. Furthermore, they have been amply described in highly informative and excellent reviews in the literature.

So, why have an issue of *Chemical Reviews* dedicated to the mechanisms of laser ablation of molecular substrates? Two main factors, in order of increasing importance, have prompted and justified this attempt.

First, the attention in the field has focused almost exclusively on applications, whereas work on the fundamentals of the phenomenon has remained rather limited. Thus, in sharp contrast to the burgeoning scope of applications, the mechanistic aspects, physical as well as chemical, are still largely obscure. This is clearly illustrated by the large number of models and the proliferation of terms, at times confusing or even contradictory, for describing pulsed laser ablation. Even the underlying fundamental physical processes have not been clearly elucidated, which in turn raises considerable doubts about the cases that may be classified under the term. Aggravating the problem further, as a result of the diverse interests of the various applications, the relevant literature is scattered over a wide variety of largely different journals, ranging from polymer sciences through general analytical chemistry as well as biochemistry and biology, all the way into medicine. This further hinders the recognition of any common concepts. Yet, despite all the success at the level of applications, the need for a better mechanistic understanding becomes increasingly important. The ever-increasing demands that material processing and analytical applications have to address, as well as the introduction of new technologies, such as ultrafast laser systems and near-field optics, foster the need for more rational and sophisticated approaches than the empirical one or the qualitative reasoning that has been employed thus far. A thorough presentation of the relevant studies and a critical assessment of the various views and models advanced in the literature thus fills a real gap and can provide the necessary framework for more detailed and quantitative studies. This objective is further justified by obvious similarities of answers and conclusions that have evolved recently in the different research areas. Thus, it was timely to consider the comprehensive coverage of the work in the different directions in one and the same issue.

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Toward this end, contributions were solicited focusing predominantly on the mechanisms underlying the various processes rather than on analytical or instrumental aspects.

Thus, there is good reason for anybody interested in the field to consult this issue. But what about the general chemist reader? Why should she or he be interested in the mechanisms of laser ablation? After all, at a very basic level, laser ablation may be described as "a very fast boiling off of the material". Yet, behind this deceptively simple description, there lie hidden highly complex phenomena, entailing a number of unique features: a large number of molecules are excited, ultrafast heating rates are attained, high-amplitude stress waves are induced, and the "physical" state of the substrate may go through a rather unusual transition. All these occur in parallel on a very fast time scale. No model exists in conventional photophysics/chemistry for the appropriate description of the high degree of coupling between such diverse processes. Certainly, the evident complexity does not lend itself to the usual approach of studying separately processes at higher and higher resolution. Because of all this, the ablation of molecular/organic substrates constitutes a fascinating, highly interdisciplinary topic, spanning the fields of thermodynamics, photophysics/chemistry, hydrodynamics, etc. As a result, the study of laser ablation mechanisms is expected to result in new information about molecular physics/chemistry and in the introduction of new concepts that may be of far-reaching scientific impact. This high scientific potential is the second and most important reason that justifies this special issue of *Chemical Reviews*.

To meet the above objectives, the adopted thematic development of the issue follows naturally from simpler systems to more complex ones, with a balanced representation of the theoretical and the experimental work in the field. This line of development is chosen merely for the purposes of presentation and does not represent the actual historical or scientific development of the field. In the opening article, Zhigilei et al. describe the use of molecular dynamics techniques in simulating the interaction of intense laser pulses with molecular solids. Though the involved time and length scales are too disparate to be realistically modeled, the simulations have provided a detailed microscopic picture of material ejection dynamics and most valuable insights for the interpretation of the experimental work. Thus, this article encompasses many aspects of the experimental work discussed in the following contributions and serves as an introduction to them. In particular, ablation is shown to differ distinctly from (molecular) surface thermal desorption, entailing instead the unselective volume ejection of material largely in the form of clusters. The second article, by Georgiou and Koubenakis, overviews the experimental work on simple (van der Waals) molecular films and on liquids. These systems offer the advantage that the various parameters can be well controlled and specified, thereby facilitating interpretation of the observations. Experimental results are largely correlated with the previous computer simulations, but the importance of accounting for electronic and chemical processes is also stressed.

Subsequent papers are devoted to more complex systems, in which questions are much more difficult to formulate and answers become much more convoluted. In the MALDI section, Dreisewerd examines the correlation of the ejection process of the (neutral) biopolymers with the laser and matrix parameters in order to address the relative merits and limitations of the various models. Biopolymer ejection is indicated to be akin to the suggested volume ejection of material, though still several features remain to be accounted for in a consistent way. The subsequent two articles deal with the most crucial but also the most difficult problem of all, ion formation in MALDI. The two articles take two complementary views. Relying on the postulation that cluster ejection is a fundamental feature of the process, Karas and Krüger present the case for MALDI ion formation via an explosive-like separation of the ejected ionized clusters. To establish their point, a detailed analysis of the plausible processes responsible for the primary ionization of matrix and analytes in the condensed phase is presented. In contrast, Knochenmuss and Zenobi argue for the importance of secondary charge-transfer processes in the plume, in which case final ion patterns should be governed by thermodynamic factors. To substantiate their hypothesis, the authors go through an exhaustive correlation of the observed ion patterns with thermochemical data. Certainly, the problem of ion formation remains far from resolved, but the clear and balanced argumentation of the two articles sets the stage for guided experimentation in addressing it.

In the section concerning laser ablation of polymers, Lippert and Dickinson address the issue of the induced chemical processes and effects, accentuating in particular the use of specifically designed polymers as mechanistic probes. What this article underscores is the inefficiency of conventional thermal and photochemical degradation models in describing laser ablation and the need for concepts that take into account the synergy and/or competition between the corresponding processes. On the other hand, Paltauf and Dyer in their contribution highlight the role of photomechanical processes and the possibility of effecting "cold ablation", i.e., material removal at low temperatures. Given the importance of the subject and its possible unfamiliarity for chemists, the principles of laser-induced stress wave formation are succinctly outlined, followed by a critical evaluation of the relative importance of stress-induced spallation mechanisms for a wide range of molecular substrates and laser irradiation conditions. Complementing the previous experimental presentations, the article by Bityurin et al. is dedicated to the challenges posed by the theoretical description of the intertwined thermal, chemical, and mechanical processes. To this end, the justifications, relative merits, and limitations of the various simplifications and boundary conditions assumed in analytical formulations are delineated in depth. Despite the difficulties, progress has been sufficient for attaining analytical solutions with good predictive power. Chrisey et al. focus on

the specific issue of mechanisms and procedures in the laser deposition of organic substrates. To this end, they sort through the various laser irradiation and material combinations that have been investigated in order to delineate the main factors of the laser-induced ejection process that affect the properties of the deposited films. They show, on one hand, how knowledge of the laser/matter interaction can be used in judiciously tuning (optimizing) the properties of the deposited films and, on the other hand, how the development of new deposition methods leverages mechanistic understanding.

Medical applications have been one of the driving forces of the field. In a most impressive overview, Vogel and Venugopalan go far beyond the scope of detailing the specifics of ablation of soft tissues. They "synthesize" between the manifold aspects and models of laser ablation in order to attain a consistent—at least as far as possible at present—understanding of laser processing of tissues. They demonstrate how even fundamental concepts can be employed to bear on the ablation of the highly complex tissues and bridge the gap between basic science and applications.

So, what is this issue then all about? Certainly, as compared to other issues of *Chemical Reviews*, the present one succeeds more in defining questions than in providing answers. Nonetheless, reading through the issue, enough common ground is indicated between the different subfields to justify the effort. In fact, the issue clearly shows that a lot has been unraveled about laser ablation of molecular substrates. Novel experiments employing a wide variety of spectroscopic tools have been performed to monitor the evolution of the various processes, as well as to establish correlations between them. From a theoretical standpoint, the initially qualitative and overly simplistic models have grown into highly sophisticated analytical and computer simulation approaches, the predictions of which are, to a satisfactory degree, validated by the experiments. Through this synergy of experimental and theoretical work, some general concepts, at least as far as the basic mechanisms of material ejection are concerned, have gradually been established. What seems to be still lacking is "putting together" all the different pieces, encompassing the immense complexity of the processes.

Rather than being exotic and relevant only for a few special applications, the questions related to laser ablation of molecular substrates are compellingly shown to be of a fundamental and general nature. Important issues concerning nonequilibrium phase transformations, electronic excitation and deactivation processes, fluid flow, material dynamics, etc. have already been raised and studied in the field. Concepts from diverse areas of physics, chemistry, and biology are being adopted and appropriately modified or fused to describe the many different facets of the phenomenon. In doing so, new ideas for investigating problems in established fields are being applied, and even tenets of fundamental theories have been put to stringent test.

Thus far, ablation has been largely viewed as a tool, as the means to achieve the seemingly simple goals of material removal or material ejection. Although applications will certainly remain the driving force of the field, the present issue demonstrates laser ablation to be a subject of high scientific interest in its own right, defining essentially a new frontier of molecular photochemistry. It is hoped that the issue will succeed in raising further interest among chemists in studying the fundamental aspects, thereby complementing the highly successful and innovative applications.

Finally, we would like to thank the authors for their efforts in producing this issue. In many cases, this comprised a heroic attempt not only to summarize the state of the art in the field but also to point the way to future research and development. Furthermore, this issue would not have ever been completed without the immense editorial efforts of Prof. John Gladysz and the capable assistance of Birgit Haltrich.

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