Current Status and Future Perspectives of Electron Interactions with Molecules, Clusters, Surfaces, and Interfaces

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Preamble

The following report is based largely on presentations and discussions at two workshops and on contributions, suggestions, and recommendations from the workshop participants. The first workshop on which this report is based primarily addressed questions regarding theory, computation, and simulation, whereas the second workshop focused largely on experiments.

1. Workshop on "Fundamental Challenges in Electron-Driven Chemistry", Berkeley, October 9 & 10, 1998

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2. Workshop on "Electron-Driven Processes: Scientific Challenges and Technological Opportunities", Stevens Institute of Technology, March 16 & 17, 2000

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EXECUTIVE SUMMARY

Electron-molecule and electron-atom collisions initiate and drive almost all the relevant chemical processes associated with radiation chemistry, environmental chemistry, stability of waste repositories, plasma-enhanced chemical vapor deposition (CVD), plasma processing of materials for microelectronic devices and other applications, and novel light sources for research purposes (e.g. excimer lamps in the extreme ultraviolet) and in everyday lighting applications. The life sciences are a rapidly advancing field where the important role of electron-driven processes is only now beginning to be recognized. It has been shown very recently [ES1] that low-energy electrons with energies significantly below the ionization energies of DNA molecules can initiate single and double strand-breaking in DNA molecules. Sanche and co-workers [ES1] identified some of the key mechanisms involved as electron attachment processes. Electrons also drive many of the key processes in chemical synthesis, in planetary atmospheres, and in low-pressure and high-pressure plasmas used in environmental remediation applications. Nonetheless, relatively little is known about these electron-initiated processes at a microscopic level. Only fragments of the fundamental physics and chemistry are well understood, and only a few of the required cross sections and reaction rates for the multitude of important molecules and processes are known with confidence. For instance, it was only recently that the simplest electron-impact ionization process, the ionization of atomic hydrogen $e^- + H \rightarrow H^+ + 2\ e^-$, was solved rigorously [ES2].

Many of the applications of electron-initiated chemical processes listed above require results in the near term. In environmental remediation of mixed radioactive waste, strategies for action must be developed now, before further damage and degradation at storage sites occurs. In plasma processing of microelectronics components, new technologies must be developed in a time frame of a year or less in order to sustain the rapid pace of innovation in that field. In addition, there is significant interest in using plasmas for molecular synthesis in order to develop new "green" chemical processes with reduced waste streams and novel chemistries.

At a microscopic level, electron-molecule collisions are much more complicated than electron-atom collisions because of the additional degrees of freedom that are introduced in the target (vibration and rotation of the nuclei) and in the collision process (dissociation of the molecule into two or more fragments). In addition to the dissociation of a molecule into neutral ground-state fragments (neutral molecular dissociation), dissociation can also be combined with other inelastic process resulting in dissociative excitation, dissociative ionization, and dissociative electron attachment. Dissociation also leads to new species (dissociation fragments), which are often much more reactive than the parent molecule. This intriguing aspect of electron-molecule collisions gives dissociation processes unprecedented significance in many applications and environments where the key processes are often initiated by the formation of secondary species via a primary dissociative electron-molecule collision.

Advances in electronic structure theory over the last fifteen years, combined with the emergence of Terascale computing platforms, on which many of those structure codes run, have provided an entirely new context in which to attack the electron-polyatomic molecule scattering problem. The last ten years have also seen separate advances in electron scattering theory that have made it possible to carry out multichannel electronic excitation calculations on polyatomics. In addition, access to Terascale computing platforms will become more broadly available to researchers in the next five years, completing the arsenal for addressing these problems successfully. This combination of advances arising in different research communities

has set the stage for the first comprehensive theoretical attack on the problem of electron-driven chemistry. The opportunity now exists to build the next generation of electron scattering codes and theories within the current context of the rich infrastructure of bound state quantum chemistry. Although major advances have been made in the application of quantum chemical methods to bound states, progress has been much slower for the development of theoretical approaches for studying problems in which the continua must be considered explicitly.

The time-scale for experimental studies of electron-driven processes is generally long. Experiments are difficult because of the large number of states of neutral fragments that can be produced in electron collisions with polyatomics. In addition, the number of possible target molecules is large. Nonetheless, many noteworthy advances have been made in the past decade in the experimental study of electron interaction with molecules in the gas phase as well as on surfaces and in the liquid phase. Gas phase studies have benefited greatly from the advent of new sources of projectiles and targets and new experimental techniques and instrumentation such as trapped atoms, free radicals and transient species, intense sources of spin polarized electrons and targets, large solid-angle, highly efficient position-sensitive detectors, and angle-changing electron spectrometers which enable differential measurements that cover the full angular range. However, the past decade has also witnessed a significant decline in the number of experimental groups worldwide that are engaged in the study of electron-driven processes and phenomena

Experiments that can test theoretical calculations of cross sections and reaction rates and predictions of computer simulations of reaction processes in certain benchmark systems will become indispensable. The lack of high quality theoretical results to compare with and to aid in the analysis of the experimental data may have played a major role in the above mentioned decline in the number of experimental research groups in the field. Novel concepts and strategies for experiments on more complex molecules are also necessary. A wide variety of factors can influence the cross sections and branching ratios that govern the dissociation of a molecule and the availability of theoretical data will be especially important for interpreting and guiding those experiments. The value of theory for these systems stems from its unique capability of providing a means of "dissecting" interactions and determining the relative contributions of different factors (e.g. long-range through-bond interactions, spin-orbit effects, or vibronic coupling) that can influence the magnitudes of the cross sections and branching ratios. The absence of theoretical data and feedback from theorists represents a significant handicap to experimentalists, and the lack of experimental data is a continuing impediment to theory. The central question of what reactive molecular fragments are present can only be answered by an understanding of how they are generated. The transient nature of the products, and the detailed nature of the required information about the states of the neutral fragments, makes the relevant experimental determinations on polyatomic dissociation extremely difficult. An additional complication is that these processes happen both in gas and condensed phases. They are not yet understood even in the gas phase, and the alteration of the gas phase processes in condensed media remains an almost completely unanswered question. Dissociation studies pose several key challenges to the experimentalist such as the detection of neutral ground-state fragments, the preparation of targets of unusual species for collision studies, and the exploration of the routes and time scales of the dissociation of electron-molecule collision products with sufficient internal energy to dissociate further.

In view of the above stated facts, a large-scale, multidisciplinary and collaborative effort should be mounted to solve these problems in a timely way so that their solution will have the needed impact on the urgent questions of understanding the physico-chemical processes initiated

and driven by electron interactions. A theoretical and computational program which is well-coordinated with an experimental effort is all the more urgent in view of (i) the decades that would be necessary to address the issues by experiment alone or (ii) the persistent uncertainty of having results of calculations, computations, and simulations not benchmarked against reliable experiments. Each of the vast number of required experiments is intrinsically difficult, and can require extensive theory for interpretation. Moreover, it will take years to reverse the decline in the number of research groups engaged in measuring electron-molecule collision phenomena, notwithstanding some noteworthy recent experimental advances. The scale of computer resources required for calculations involving molecular dissociation rivals that of any quantum chemistry application to the bound electronic states of even very large molecules. The complications of simultaneously treating the continuum and bound electrons, even for targets with less than ten atoms, will stress the largest massively parallel computers currently available in the world. The extension of these calculations to the condensed phase is a daunting computational task. It is as great as any that has been contemplated for the future computational resources that are likely to exist as massively parallel computers extend to tens of thousands of processors.

References

[ES1] B. Boudaïffa et al., Science **287**, 1658 (2000)
[ES2] T.N.Rescigno et al., Science **286**, 2474 (1999)

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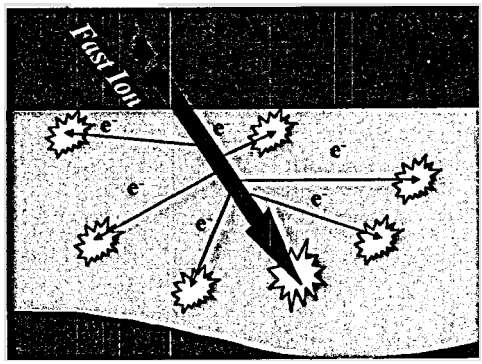
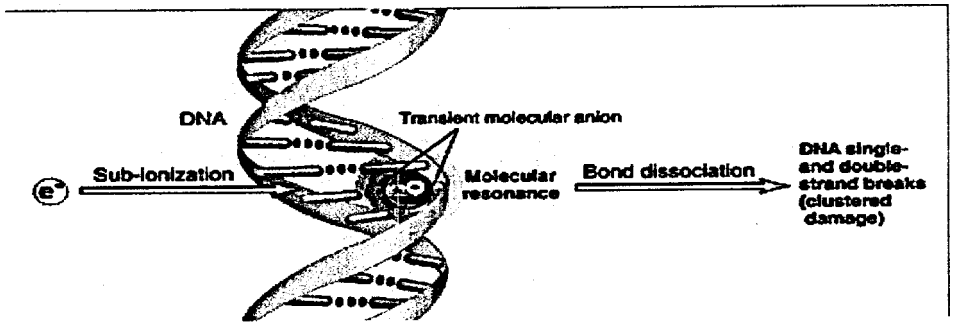
I. Introduction: The Importance of Electron-Driven Processes

Collisions of electrons with molecules and atoms create the energetic species that drive chemical and physical changes of matter in environments that range from plasmas to living tissue. The molecules used to etch semiconductor materials do not react with silicon surfaces unless they are subjected to electronic collisions in the low-temperature, high-density plasmas used in plasma etching and in plasma enhanced chemical vapor deposition. Breaks in the DNA of living systems caused by ionizing radiation have been shown to be due primarily to collisions with secondary electrons that attach to the components of DNA molecules or to the water around them and drive bond dissociation. Secondary electron cascades in mixed radioactive/chemical waste drive much of the chemistry that determines how those materials age, change, and interact with the natural environment. Electron collisions molecular fragments in the plasma



Secondary electrons are produced by fast ion tracks in radioactive waste

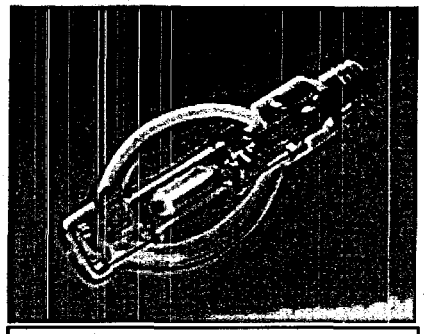


Most energy deposited in cells by ionizing radiation is channeled into free secondary electrons between 1 and 20 eV [I.1]

Plasma-etched gate 0.12 microns wide (Bell Labs - Lucent Technologies)

experimental and theoretical capabilities and demand the development of new techniques.

Electronic collisions are uniquely effective in transferring energy to and from the electronic degrees of freedom of the target atom or molecule. That is the fundamental reason that new developments in modern fluorescent lighting and plasma displays are distinguished by their energy efficiency. The fact that the incident electron not only has the same mass as those that bind the target molecule together, but is physically indistinguishable from them, means that at low energies the coupling to the molecule's internal degrees of freedom is especially strong. In Section II of this report the fundamental reason for this property of electronic collisions is explained further and the individual processes are explored in detail. This aspect of the electron collisions with matter appears as a consistent theme in every context in which they occur, whether in the liquid solution medium of living cells or in the extreme environment of a plasma discharge.



High-intensity plasma arc lamp (OSRAM-Sylvania)

In this report we discuss most of the fundamental processes driven by electronic collisions and the challenges they present to both experiment and theory, so to define our elementary vocabulary it is useful to make a partial catalog of them:

$e^- + M \rightarrow e^- + M$	***elastic scattering***
$e^- + M \rightarrow e^- + M^*$	***electronic excitation***
$e^- + M(v) \rightarrow e^- + M(v')$	***vibrational excitation***
$e^- + M(j) \rightarrow e^- + M(j')$	***rotational excitation***
$e^- + M \rightarrow A + B + e^-$	***electron impact dissociation***
$e^- + M \rightarrow A^- + B$	***dissociative attachment***
$A^- + B \rightarrow e^- + AB$	***associative detachment***
$e^- + M \rightarrow M^+ + 2e^-$	***electron impact ionization***

All the inelastic processes can of course occur in any combination, and their analogs also occur in collisions with ionic molecular targets, in which case "attachment" is called "recombination" and can have quite large cross sections.

In many of these elementary processes it is the dissociation of polyatomic molecules that is the key step. Only the rudiments of those dissociative collisions are understood, and it is not an exaggeration to state that it is currently beyond the state of the art to predict the branching ratios of the fragments and their excited states. The central question of what reactive molecular fragments are present can only be answered by an understanding of how they are generated. The transient nature of the products, and the detailed nature of the required information about the states of the neutral fragments, makes the relevant experimental determinations on polyatomic dissociation extremely challenging. There is a paucity of even benchmark experimental data.

Plasma flat panel display (Fujitsu Corp.)

All of these processes happen both in gas and condensed phases. They are not yet understood even in the gas phase, and the alteration of the gas phase processes in condensed media remains an almost completely unanswered question. In the key application areas of environmental remediation and radiation damage to living tissue they happen almost exclusively the liquid or solid phases. Thus a key challenge for this field is identified in this report in sections III and IV, which address the connection between investigations in the gas phase and the still more difficult work that remains to be done in clusters, at interfaces and in condensed media.

References

[I.1] B. Boudaïffa et al., Science **287**, 1658 (2000)

II. Electron Collisions with Atoms and Molecules in the Gas Phase

Electronic collisions are uniquely effective in transferring energy to and from the electronic degrees of freedom of the target atom or molecule. For example, unlike "collisions" with photons, which obey a set of selection rules determined primarily by dipole interactions, collisions with electrons can produce singlet-to-triplet transitions with the same or larger probabilities than singlet-to-singlet or triplet-to-triplet transitions. Electronic collisions do not obey selection rules with regard to singlet-to-triplet excitation because the incident electron can exchange with those of the target and thereby change its spin state. Thus electron impact can excite any dissociative state of a molecule and reduce it to fragments, and this is a key mechanism by which radicals and molecular fragments are produced in many environments ranging from planetary atmospheres to molecular beam sources for experiments in molecular collisions. Another important process is electron-impact ionization, because this is the mechanism by which any ionic state of the target can created.

Electron interactions with atoms and molecules in the gas phase have been studied experimentally since the early part of the 20th century. It is safe to say that the current level of understanding of electron-atom collisions far exceeds our insights into the electron-molecule collision process. It is also safe to say that the vast majority of experiments to date have been linked to atomic or molecular targets in the electronic ground state and, in the case of excitation, have focused on the excitation of only a few low-lying excited target states.

II.1 Introduction and Background

The experimental study of electron interactions with ground state atoms has evolved from the Franck-Hertz experiment, arguably the first electron-atom collision study, to the realization of the "perfect electron scattering experiment" in which all relevant quantum numbers of the collision complex "electron + atom" are quantified before and after the collision. To date, the "perfect electron scattering" experiment has been carried out for elastic electron scattering from Ne atoms and the combined results of several inelastic electron collision studies in He and Na come close to constituting a "perfect inelastic electron scattering experiment". A wealth of data can be found in the literature on inelastic electron-atom scattering experiments where the process has been probed at the level of quantum mechanical scattering amplitudes and their interference with the objective of elucidating the finer details of the scattering process such as the role of exchange and explicit spin-dependent interactions. Other areas where significant progress has been made include the study of resonances and the effect of electron correlations in electron-atom collisions.

The most promising opportunities and challenges for future work in the area of electron-atom collisions are determined by the fact that

- our level of understanding of electron-atom collisions decreases rapidly as one goes beyond a rather limited group of atoms such as H, the rare gases, the alkalis, the earth alkalis, and some metal atoms; there are no electron-atom collision data available for more than half the atoms in the periodic table
- our level of insight into the electron-atom collision process even with the atoms in the small group listed above decreases dramatically when one is interested in the excitation of excited states other than a few lowest-lying excited states and even more dramatically, when one looks at electron collisions with atoms in excited states (e.g. laser-excited targets or metastable targets). The few experiments that have been carried out indicate

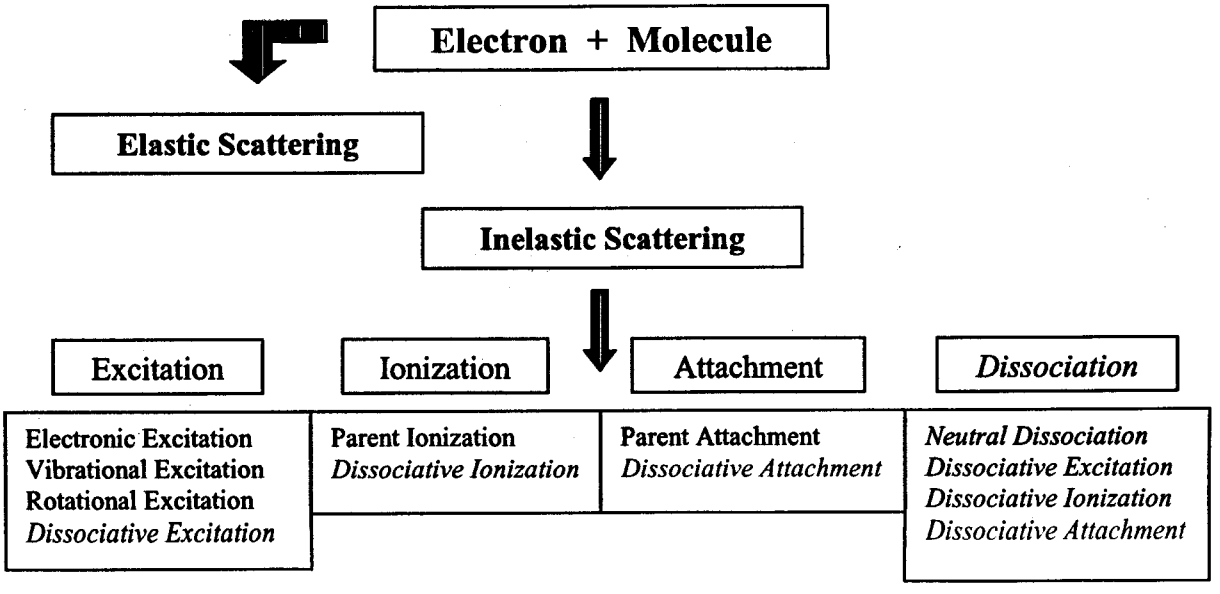
that there may be interesting features and science issues associated with the interaction of an electron and an excited atom that deviate significantly from what we know to be true in electron collisions with ground-state atoms

Future challenges also include (but are not limited to) experiments in areas such as

- collisions in the presence of intense fields
- the decay of high-lying excited states (above the ionization limit) via autoionization and other competing processes

The simple fact that a molecule consist of least two atoms causes electron-molecule collisions to be much more complicated than electron-atom collisions. Additional degrees of freedom are introduced in both the target (vibration and rotation of the nuclei) and in the collision process (dissociation of the molecule into two or more fragments). This is illustrated schematically in figure 1. There are additional inelastic channels in electron-molecule collisions that one does not find in electron-atom collisions molecule such as vibrational and rotational excitation and, perhaps most importantly, dissociation. Dissociative electron collision processes are of particular relevance. In addition to the dissociation of a molecule into neutral ground-state fragments (neutral molecular dissociation), dissociation can be combined with any other inelastic process. This results in dissociative excitation, dissociative ionization, and dissociative electron attachment which greatly increases the number of possible final states of an electron-molecule collisions process.

Fig. 1: Schematic flow chart elucidating the complexity of inelastic electron-molecule collisions (elastic collisions have been omitted for clarity of presentation). Processes that are the result of the ability of the molecule to dissociate are shown in *italics*. Processes such as dissociative excitation, dissociative ionization, and dissociative attachment are color-coded and have been listed twice, first under "Dissociation" and secondly also under "Excitation", Ionization", and "Attachment", respectively.



From a basic science viewpoint, there are several important distinguishing features between atomic and molecular targets in electron collision experiments:

- with the exception of diatomic molecules, which have potential energy curves, molecules have multi-dimensional potential energy surfaces whose dimensionality and complexity increase quickly as the number of constituent atoms of the molecule increases
- many polyatomic molecules have no bound electronically excited states, so that electronic excitation inevitably leads to dissociation
- molecules may form parent ions with amounts of internal energy that exceed the dissociation limit of the ion, so that stabilization of the ion via dissociation (dissociative stabilization) becomes a competing stabilization route to radiative stabilization
- dissociative stabilization of a molecular ion with sufficient internal energy may occur on a time scale from 10^{-12} s to seconds (prompt to extremely metastable)

The ability of a molecule to dissociate as a consequence of an electron collision adds the possibility that the collision process generates new species, which are often much more reactive than the parent molecule and chemically and physically very different from the parent molecule, e.g., CF_3 produced from CF_4 is very different from the parent molecule and O is certainly very different from O_2. This intriguing aspect of electron-molecule collisions gives dissociation processes unprecedented significance in many applications and environments where the key processes are initiated by the formation of secondary species via a primary dissociative electron-molecule collision; this may be a neutral molecular dissociation process or a dissociative excitation, dissociative ionization, or dissociative attachment reaction.

Another interesting aspect of electron-molecule collisions as mentioned above is the possibility to form collision products with sufficient internal energy to undergo dissociative decay. Dissociative decay of the molecular ion becomes a stabilization route that now competes with other possible stabilization mechanisms such as radiative stabilization. Moreover, dissociative decay can occur on a time scale ranging from prompt to extreme metastability with many interesting and important dissociative metastable decay processes occurring on a time scale of microseconds.

A critical review of available data on electron-molecule collision processes reveals the following noteworthy facts:

- comprehensive collisional data bases for electron interactions exist only for a few simple diatomic molecules such as N_2, O_2, and H_2; even in these cases, the data bases are far less complete that for the well-studied atoms H, He, and Na
- there exists virtually no quantitative information on the neutral dissociation of most molecules (with a few notable exceptions)
- experiments aimed at revealing finer details of the collision process such as spin-dependent interactions, resonance phenomena, electron correlation effects, etc. are limited to but a few diatomic and simple polyatomic molecules
- collision studies with molecular targets in quantum mechanically well-characterized states (i.e. in states that are fully characterized in terms of all relevant quantum numbers) are non-existent

From a practical viewpoint, experiments with molecular targets are inherently more complicated than electron-atom collisions for the following reasons:

- molecular targets at room temperature are in a statistical mixture of various rotational (and sometimes also vibrational) states; the exact rotational (or vibrational) population distribution depends on the spacing of the rotational energy levels compared to the thermal energy of the gas target under study at room temperature (approximately 0.025 eV); even supersonically cooled molecular target beams rarely consist of molecules in a single rotational state, albeit usually in a well-defined vibrational state
- many interesting neutral molecular targets are open-shell free radicals whose generation in suitable abundance for collision experiments requires considerable efforts (e.g. in a discharge source in conjunction with a charge transfer cell or by laser-induced bond-breaking of a stable molecule)

II.2 Status, Advances and, Challenges of Gas-Phase Electron-Driven Processes

As molecular dissociation is the single most distinguishing feature between electron-atom and electron-molecule interactions, future studies of electron-collision-induced molecular dissociation processes including collisions with secondary products such as free radicals represent perhaps the most promising field of experimental research in electron-molecule collisions with gaseous molecular targets. Therefore, dissociation processes will be discussed in some detail in this report and are placed before the discussion of elastic scattering and all other inelastic electron scattering processes. Molecular dissociation induced by electron collisions gives rise to a wide array of challenges and opportunities for future experiments in the area of electron-molecule collisions from both a basic science viewpoint as well as from an application-motivated viewpoint. These include the investigation of neutral molecular dissociation processes with and without specificity in terms of the final dissociation products. Since neutral molecular dissociation leads in many cases to the formation of secondary species, which cannot easily be generated by conventional methods, electron collisions with these secondary species (e.g. free neutral and ionic radicals) is an important facet of future electron-molecule collision studies.

II.2.1 Dissociative Processes

Dissociation studies pose several key challenges to the experimentalist such as the detection of neutral ground-state fragments either final-state specific or without regard for the final state of the dissociation product, the preparation of targets of unusual species for collision studies, and exploration of the routes and time scales of the dissociation of electron-molecule collision products with sufficient internal energy to dissociate (metastable dissociative decay). To the theorist, the multitude of dissociation pathways and branching ratios are difficult if not impossible to calculate and no calculations performed to date have attempted to provide this kind of detailed information. Excited-state dynamics is a field of its own and the difficulty in computing excited state surfaces, much less computing the relevant spin-orbit and non-adiabatic coupling matrix elements, has limited the number of workers in this field. It is possible to put a correlated wave function on a dissociative surface and follow the gradient to the dissociation products. It is also possible to obtain the coupling matrix elements along this trajectory. If only this piece of the excited state surface is adequate, then considerable progress can be expected in this area as well. Several codes are currently available to compute these quantities, but they need to be updated and are definitely not user friendly.

II.2.1a Neutral Molecular Dissociation

The first serious experimental attempt to study electron-induced neutral molecular dissociation processes (i.e. processes in which the neutral dissociation fragments are formed in the ground-state) in a single-collision gas-phase environment were the experiments by Corrigan [II.1] and later by Winters and co-workers [II.2] who used a chemical getter technique to trap the neutral fragments. This method allowed the determination of total dissociation cross sections (i.e. no selectivity as to the nature of the specific dissociation product) for a few molecules for which a suitable chemical getter could be found. More recently, Moore and co-workers [II.3] revisited this method by using a more efficient and more selective tellurium getter. Other recent experiments utilized the fast-neutral beam technique in conjunction with the correlated detection of two dissociation fragments by two position-sensitive detectors which is applicable primarily to diatomic and simple triatomic molecules [II.4]. Threshold ionization mass spectrometry is another technique to detect certain neutral dissociation fragments by selectively ionizing them with a low-energy electron beam of suitable energy [II.5]. Each of these techniques has limited applicability to only a small group of target molecules and requires extremely careful absolute calibration which, in some cases, is further dependent on other previously measured or calculated data. McConkey and co-workers [II.6] were the first to utilize laser-induced fluorescence (LIF) techniques in the quantitative determination of neutral ground-state dissociation products following electron impact dissociation of a molecule under single collision conditions. More recently, Becker and co-workers have used a variant of this technique to determine absolute cross sections for the formation of state-selected ions or neutral ground-state fragments following single electron impact on molecules [II.7].

Several detection schemes for neutrals have been used by chemists in reaction dynamics studies. A majority of these techniques are used in a pulsed rather than in a continuous mode. This must be considered in the design of future electron-molecule collisions experiments in beam environments that aim to exploit these techniques in the analysis of collision processes carried out in single-collisions environments. A summary of these techniques is given in section II.4.4.

Electron impact dissociation resulting in the formation of neutral fragments remains a process where the available data is sparse and further progress will be slow. The development of new computational and experimental techniques is therefore needed. An exciting possibility is a new type of experiment utilizing ion storage rings that may provide a major advance in the study of molecular dissociation (see below). Initial experiments may not include those molecular systems directly involved in plasma processing but should provide valuable information on the dynamics of electron impact dissociation. The characterization of how a molecule fragments following electron impact excitation is perhaps the single most important process to understand in modeling low temperature plasma processing and electron-driven environmental chemistries. Many of the low-lying electronic states of polyatomic molecules are dissociative (indeed for technologically important systems like CH_4 or CF_4, *all* electronically excited states are believed to be dissociative). It will be important to extend current methods to be able to handle large numbers of excited states and to incorporate the most recent advances in quantum chemistry in describing these states. Coupling the study of the post-electron-collision dissociation dynamics to the electron-molecule scattering problem will require excited-state energy surfaces, coupling elements and chemical dynamics in a truly interdisciplinary effort.

The scale of calculations involving *both* the steps of electron impact excitation of dissociative states of polyatomics *and* the subsequent heavy-particle dynamics is hard to exaggerate. Either of these steps alone is at the current limits of ambition of the theoretical

communities engaged in solving them separately. The challenges associated with predicting dissociation dynamics following electron-impact excitation are not, of course, new or unfamiliar; in particular, they have been encountered over the years in studies of photochemistry. What is perhaps new is the need to undertake such studies for rather large molecules, in which both the density of excited states and the dimensionality of the potential energy surface are increased. Moreover, excitations that are not relevant in photochemistry will figure prominently in electron-initiated chemistry, which does not respect optical selection rules. The number of dissociative states, their surface crossings and nonadiabatic nuclear motion which feature in this problem will require calculations of a scale that will tax the largest massively parallel computers envisioned for ten years from now.

II.2.1b Dissociative Electron Attachment in the Gas Phase

There are processes initiated by electron interactions in the energy range below the threshold for ionization which may induce "chemistry" in molecules: electronic excitation and electron capture thereby forming a transitory negative ion (TNI). Both processes can lead to bond cleavage producing either neutral radicals (electron impact dissociation) or a negative fragment ion and one or more neutral radicals (dissociative electron attachment, DEA). While the energy dependence of the cross section for electronic excitation is usually smooth with only little structure, electron attachment by its nature is a resonant process, i.e. significant only in a particular energy range. In addition, the general behavior of the attachment cross section is reciprocal with the primary electron energy which means that the DEA cross sections for different molecules (with the resonant attachment energies characteristic for the particular target molecule) are embedded in the overall reciprocal energy dependence. This renders DEA an extremely effective process in the gas phase as electrons with virtually zero energy can induce bond cleavage with cross sections exceeding 100×10^{-16} [II.8,II.9].

The DEA reaction, $e + ABC \rightarrow ABC^{-*} \rightarrow AB + C^{-}$ does not only break molecular bonds with very large cross sections, it also produces free radicals as well as stable negative ion fragments to induce further "chemistry". In some compounds, e.g., CCl_4, the electron is able to carry out this process efficiently with virtually zero kinetic energy. The DEA reaction is enormously sensitive to the energy and lifetime of ABC^{-*}, the temporary negative ion intermediate state, and the cross sections and rate constants for the process may vary over many orders of magnitude even within a family of related molecules. Because ABC^{-*} is a quasi-bound state, or "resonance", lying in the e + ABC continuum, calculation of its properties is a significant challenge to theory. To date, only diatomic molecules, or more complex compounds modeled by diatomics, have received attention and much of it is semi-empirical in nature. Although the rapid decrease of peak DEA cross sections with increasing temporary negative ion energies has been known for years in a broad range of compounds and resonance classes, the existing experimental data have not led to a ***quantitatively*** predictive picture. Consequently, there are fundamental as well as applied motivations for studying this key process.

The pervasiveness of the DEA reaction throughout other research areas is not fully appreciated, particularly by those working primarily in the gas phase. Studies of electron beam-induced chemistry on surfaces and in thin films on substrates are carried out by a number of groups in the U.S. and in Canada. Similar reactions can be produced by photon irradiation as well, promoting electrons from the metal substrate into a film. Studies of bond-breaking on surfaces using scanning tunneling microscopy (STM) are growing rapidly, and the process may be tied in part to the injection of electrons into the empty molecular orbitals of adsorbed species,

thereby forming temporary negative ion states. Many important chemical reactions in solution are induced by electron reduction, that is, transfer of an electron from a substrate or another compound, to a target molecule. Remediation of chlorine-bearing pollutants on the surface of iron filings, for example, is believed to take place by this mechanism. It is important to realize that the attachment energies of molecules in the gas phase provide a fundamental measure of the ease with which a compound can be reduced in the absence of any surrounding medium. This provides a valuable reference point from which to measure the effects of solvation. Finally, we note that there is accelerating interest in the role of DEA in the biological arena, most recently in the discovery of double-strand breaking of DNA by low energy electrons [II.10] and earlier by its connection to carcinogenicity and more broadly to radiation chemistry and radiation damage.

Progress in all these areas will be enhanced by an improved understanding of the fundamental nature of DEA in the gas phase in conjunction with the role played by surrounding or neighboring media in altering the parameters of the temporary negative ion state. Some of the barriers to progress are (a) the absence of researchers trained in more than one area or, at minimum, able to speak the language of other fields, (b) the parochial nature of most conferences, and (c) the difficulty of obtaining funding for interdisciplinary projects.

Regarding the current status of gas phase studies of DEA, our major ***interpretative*** framework arises almost entirely from theoretical studies and experiments that do not provide a means for understanding the central problem, which is to connect molecular structure with the cross sections or rate constants. This is an area where the inclusion of theoretical electron scattering methods in the quantum-chemical programs now widely used to study molecular electronic structure is imperative. Although recent studies have established a close, even predictive correlation between peak DEA cross sections and temporary negative ion properties such as vertical attachment energy and lifetime, the relationship is restricted to one class of simple compounds and only to the contribution from the lowest temporary anion state. It is not at all obvious that such correlations can be found for other simple "leaving groups", i.e., fragments with large electron affinities. However, such studies cannot readily be extended to more complex molecules which contain several temporary negative ion states of different types and local symmetries coupled together, such as unsaturated hydrocarbons substituted with halogens. It is even more remote to envision the prospect of predicting the DEA cross sections for the many possible fragment ions, i.e., different decay channels, arising from a given resonance. These challenges are exacerbated by the fact that only a small group of research groups are active in this area. The experimental challenges and difficulties are substantial, e.g. absolute cross sections for mass analyzed ion fragments are difficult to determine accurately and only a few groups have made efforts in this area.

Extension of DEA and temporary negative ion studies to more complex molecules of biochemical interest in the gas phase is only in its infancy. Although low-lying resonances and DEA in the DNA bases have been cursorily explored (no absolute cross sections, though !), at this time, there are no published studies in the amino acids, for example, the fundamental constituents of proteins. In general, measurements are presently restricted to those compounds that can be introduced into the gas phase without thermal decomposition, a severely limiting constraint. Other techniques for achieving reasonable densities of non-degraded ***neutral*** bio-molecules are urgently needed.

Dissociative electron attachment is perhaps the best characterized electron interaction with many of the molecular systems pertinent to plasma processing and is the subject of considerable theoretical effort. However, theory has used a simplified one-dimensional model for

the nuclear dynamics, which is only correct for diatomics. The importance of multidimensional effects in DA to polyatomic targets remains largely unexplored. Moreover, the role of internal excitation within the target remains to be quantified. In contrast, dissociative recombination (DR) remains a difficult process to study either theoretically or experimentally. The construction of storage ring facilities led to major advances in our understanding of the dissociative recombination process, but some key cross sections remain controversial. *Ab initio* theory has proven to be very useful in the interpretation of experimental DR data but may produce absolute cross sections that are in error by one or more orders of magnitude.

The chloroalkanes are an example of a class of molecules for which some of the experimental results on these processes are not well understood. Most noteworthy, the large differences in the vertical electron attachment energies (VAE) and dissociative attachment (DA) cross sections between C_2H_5Cl and CH_3Cl have yet to be accounted for on the basis of first principles calculations. Knowledge of the branching ratios is particularly important when different reaction pathways yield products of widely differing reactivity, as, for example, in the dissociation of oxygen containing compounds to yield $O(^3P)$, $O(^1D)$, and $O(^1S)$.

II.2.1c Dissociative Excitation by Electron Impact

Stable electronically excited states of molecules become increasingly scarce for larger molecules, so that electronic excitation inevitably leads to dissociation. Dissociative excitation refers to processes in which the dissociation fragments are formed in electronically excited states. These electronically excited states may relax subsequently in a variety of ways. Excited states that are coupled to one or more lower states (which may include the ground state) via optically allowed electric dipole transitions decay radiatively with typical lifetimes in the nanosecond range. These processes are comparatively easy to study experimentally by analyzing the emitted fluorescence. Absolute emission cross sections can be obtained, appearance energies can be measured which allow information about the possible dissociation pathways to be extracted, and branching ratios and ratios of direct excitation and cascade contributions can be determined. Such experiments are fairly routine and a broad and comprehensive data base for a large number of molecules already exists. Further studies do not pose much of a challenge for experimentalists. It should be noted that dissociative excitation processes have cross sections that are typically one (often two or more) order(s) of magnitude smaller than the cross sections for neutral molecular dissociation.

Excited states which cannot decay radiatively via electric dipole transitions may still decay radiatively via transitions corresponding to higher electric moments (electric quadupole, etc.) or via magnetic transitions (magnetic dipole, quadrupole, etc.). The radiative lifetimes of such states can range from microseconds to seconds and the emissions are generally much weaker than electric dipole emissions. Fluorescence analysis is in most instances not a suitable quantitative tool to probe these "metastable" dissociation fragments. Laser-induced fluorescence or other suitable optical techniques may be used, but such experiments are often difficult to quantify. If the "metastable" state lies sufficiently high above the ground state (about 7 eV or more), has a sufficiently long radiative lifetime to survive the transport from the place where it is formed to the detector (which means more than about 10 microseconds for the typical experimental set-up), and if experimental detection conditions are such that collisional quenching and other decay routes are negligible (which usually means low pressure), channel electron multipliers and other electron multipliers can be used to detect these metastable fragments, albeit without specificity as to the exact nature of the "metastable" state. Surface detectors such as the

one developed by McConkey and co-workers [II.11] for the detection of metastable O atoms/dissociation fragments are useful for the detection of specific species and the concept has the potential to be extended to other species of interest by using a variety of surface materials.

II.2.1d Dissociative Ionization by Electron Impact

Dissociative ionization of molecules, i.e. the formation of fragment ions, has been studied along with the formation of molecular parent ions since the early days of electron collision physics. However, the formation of fragment ions is complicated by the fact that these ions may be formed with excess kinetic energies ranging from a few tenths of an electronvolt (near-thermal) to more than ten electronvolts in some cases. In almost all cases, the distribution of excess kinetic energies is rather broad. This poses the challenges for the experiment to ensure 100% extraction of these energetic fragment ions from the ion source and a 100% efficiency in the transport of these ions from the ion source to the detector. The serious systematic errors that can be caused by ignoring these considerations plagued many absolute dissociative ionization cross section measurements before about 1990 [II.12] and render the reliability of many of the earlier data published in the literature highly questionable. Only those dissociative ionization cross sections measured after 1990 are deemed reliable, when ion trajectory simulations in conjunction with in-situ experimental studies were used to ensure 100% extraction and transport of energetic fragment ions or to quantify discrimination against energetic fragment ion extraction and transport, so that measured data can be appropriately corrected.

Another aspect of fragment ion formation is the fact that metastable decay processes may play a very important role in the fate of many fragment ions produced by dissociative ionization. It will be a challenge to future experiments to quantify metastable ion decay routes both in terms of their absolute cross sections and in terms of the time scale(s) of the decay process and the final products of the decay processes.

II.2.1e Electron Impact Dissociative Excitation and Ionization of Molecular Ions

Collisions of electrons with molecular ions are characterized by essentially the same features and complexities as electron collisions with neutral molecules; they also enjoy additional features as a consequence of the Coulomb interaction between the projectile electron and the ionic target. The study of collisions of electrons with molecular ions has for decades been dominated by the examination of dissociative recombination reactions. By contrast, dissociative excitation, dissociative ionization, and resonant ion-pair formation have received much less attention. However, incentives associated with controlled thermonuclear fusion stimulated efforts to study dissociative excitation and ionization of molecular ions on several occasions. Most recently, concerns about the important role of atomic and molecular processes in the edge plasmas of experimental reactors involving molecular ions led to an upturn of activities in the field in the past decade. A major reason for the increased level of activity can also be traced to the fact that ion storage rings present the exciting tool for studying electronically and vibrationally "cold" ions.

Essentially all experimental techniques to study electron-impact dissociation of molecular ions involve colliding beams of electrons and ions in various experimental arrangements. Several variants of crossed-beams set-ups have been introduced. Experiments with very specific goals e.g. the detection of light fragment ions from dissociative collisions, require special experimental set-ups. Alternatively, the kinematic benefits of merged-beams of electrons and ions have been utilized in studies where low collision energies are required. In addition to the

conventional merged-beam set-ups, ion storage rings provide unprecedented opportunities to expand the experimental capabilities for the study of electron collisions with molecular ions. Ion storage rings provide beams of high luminosity, long storage times (so that internal states can either decay or can be manipulated in a controlled fashion), excellent energy resolution, and high detector sensitivity. Four such storage rings have been built and are being used for low-energy electron-ion collisions: ASTRID in Aarhus (Denmark), CRYRING in Stockholm (Sweden), TSR in Heidelberg (GERMANY) and TARN in Tokyo (Japan). Most notably, there are no ion storage rings in the United States.

One may expect to see a significant increase in the experimental activities in the area of electron collisions with molecular ions and wealth of high quality data will be generated. What is seriously lacking is a meaningful level of theoretical activity. One would hope that the amount of theoretical activity will also increase as new data become available with which to compare.

II.2.2 Non-Dissociative Processes

The non-dissociative electron collision processes include elastic scattering as well as excitation (electronic, vibrational, rotational), ionization, and non-dissociative attachment. From an application point of view, in particular in the context of gas discharges and plasmas, elastic scattering, rotational, and vibrational excitation are often collectively referred to as electron transport phenomena.

II.2.2a Excitation

Experimental studies of electronic excitation of polyatomics have largely been neglected. Targets that have been studied are essentially limited to the diatomics H_2, N_2, and O_2 and a few simple polyatomics such as CO_2, H_2O, NO_2. The experimental capabilities to carry out measurements of electronic excitation of polyatomics do exist in principle and more measurements can be carried out with little additional investment. However, as the molecules become more and more complicated, the number of stable electronically excited states appears to decline and electronic excitation tends to lead to dissociation which renders standard experimental techniques for the measurement of excitation cross sections useless. Theory will have to assume a leading role in this field. The existing data base on vibrational excitation is somewhat broader than for electronic excitation, although again it has been the diatomic molecules and a few simple polyatomic that have been the preferred targets of experiments.

Electron impact electronic excitation plays a crucial role in molecular plasmas for a number of reasons: it is the main route to electron impact dissociation, electronically excited states are chemically very active, and the process leads to electron cooling. In many cases part of the energy transmitted into excited states will be lost to the plasma by emission of photons. The ability to compute accurate electronic excitation cross sections for polyatomic molecules, in coupled-state calculations that employ accurate wave functions for a large number of target states, is an undertaking that will require a major future investment. The need to carry out such an undertaking is especially important since electronic excitation of polyatomics has been largely neglected by experimental groups (see above) and therefore most of the recent theoretical calculations have little or no data with which to compare. Most likely, theory will be the major source for critically needed cross section data on electronic excitation of polyatomics for some time to come, so it is essential that the methods under development be reliable, accurate and benchmarked against the few existing experimental data.

Lastly, the experimental study of the rotational excitation of molecules is a field where up until recently the required energy resolution to separate the various rotational energy levels has been unattainable, so that rotational excitation and elastic scattering have often been combined in experiments. It has only been very recently that experiments are beginning to achieve the required energy resolution (< 1 meV) to enable measurements of rotational excitation cross sections, at least for some selected targets. At the same time, theoretical calculations are relaxing the fixed nuclei approximation in efforts to begin to probe rotational effects.

Reliable electron impact excitation calculations are based upon the simultaneous accurate representation of many electronic states of the target, and of the complicated interactions between these states and the impacting electron. So far only relatively crude target state representations have been used in collision calculations. This problem can be resolved by harnessing the latest advances in quantum chemistry. More difficult is the finding that the standard close-coupling expansions, used to represent polarization interactions, do not converge well. This problem is exacerbated by both the presence of low-lying diffuse (Rydberg) states in most molecules and the many such states at intermediate energies. New methods to address this problem will need to be developed. Possible approaches include the use of very large (pseudostate) expansions, now being widely used in electron-atom collision calculations, or the development of suitable optical potential methods to model these effects.

The simple observation that the mass of the projectile in an electron-molecule collision is at least three orders of magnitude less than that of the reduced mass associated with any vibrational degree of freedom would suggest that electronic collisions are not as effective in vibrational energy transfer as they are in electronic energy transfer, and that is generally the case. However there is an important exception to that rule, called resonant vibrational excitation, because an electron can attach temporarily to a molecule and change the forces between its atoms for a time comparable to a vibrational period. The cross sections for vibrational resonances can be much larger than those for non-resonant vibrational excitation. The study of the formation of resonances and of their subsequent decay has been a fertile ground for electron scattering experiments. In molecular plasmas, vibrational excitation, particularly when enhanced by resonances, is an important energy loss mechanism for the plasmas electrons in the low energy regime below 1 eV and thus impacts on the energy distribution function of the plasma electrons in a profound way.

Electronic collisions with polyatomic molecules are of fundamental theoretical importance in this context, because with many vibrational degrees of freedom and opportunities for interaction between excited electronic states, they offer a rich array of nonadiabatic processes which are still not completely understood. For example, a quantitative (and perhaps even qualitative) understanding of the low-energy electron scavenging reaction $e^- + SF_6 \rightarrow SF_5^- + F$, in which the temporary anion SF_6^- exists for many vibrational periods before it dissociates, is still beyond current computational and theoretical capabilities.

Knowledge of vibrational excitation cross sections is crucial for modeling plasmas. Being able to account for the distribution of vibrationally excited molecules is especially important given that dissociative attachment (DA) cross sections can be orders of magnitude greater upon electron impact on vibrationally hot than on vibrationally cold molecules. In many cases the vibrational excitation will be dominated by the decay of temporary anions. Modeling these processes theoretically is particularly challenging due to the coupling of the temporary anion state to the autoionization continuum and the necessity of treating nuclear dynamics over a wide range of geometries. A further complication is presented by the fact that many of the molecular

species present in plasmas are radicals, opening up the possibility that spin-orbit or Coriolis effects may be important.

II.2.2b Ionization

Ionization studies of molecules, free radicals, and even clusters are areas where experiments are now routinely carried out with accuracies of better than 15% for absolute total and partial ionization cross sections. Many of the earlier experimental pitfalls have been recognized and are dealt with in a quantitative fashion. By the end of 1999, absolute total ionization cross sections were available for almost 100 molecules, radicals, and clusters. Remaining experimental challenges are measurements of ionization cross sections out of excited states, ionization cross sections that are final-state specific, and a quantitative handle on the detection of product ions that are metastable and undergo dissociative decay reactions on a time scale of a few microseconds to a few tens of microseconds.

While there has been a considerable theoretical and computational effort directed at the electron impact ionization problem in the past few years, this effort has been largely confined to simple atomic systems. In fact, the very recent work of McCurdy, Rescigno and co-workers [II.13] has only now solved the electron-impact ionization problem involving the simplest imaginable atomic target, hydrogen. It is unclear whether their approach can be extended to other atomic targets or whether any of the other methods will prove practical for molecular targets. There are simple theoretical models, based on classical mechanics and high-energy Bethe-Born theory, that have recently been developed and appear to be capable of providing good data on the total electron impact ionization cross sections of ground state molecules (and atoms). These models are unfortunately less successful in treating ionization from excited states, which is important in many situations, such as ionized metal plasma vapor deposition (CMPVD), where a substantial percentage of the neutral population is in metastable states. The models are of little use in predicting energy sharing between scattered and ejected electrons, which is important in determining the electron energy distribution function. Moreover, such models cannot provide data on the relevant branching ratios in molecular ionization (i.e. partial ionization cross sections for the formation of the final ionic products such as parent ions and the variety of fragment ions). Indeed, the calculation of branching ratios remains a very difficult one for all electron scattering theories.

The "intermediate energy regime", ranging from approximately one to five times the ionization threshold, poses tremendous problems for *ab initio* theory, since the infinity of energetically accessible final states precludes us, in principle, from writing down a wave function that describes all possible scattering events. Moreover, perturbative methods based on the Born or distorted-wave approximation are only reliable at much higher energies. Nevertheless, the intermediate energy regime is an important region for practical applications, since many cross sections peak in this energy range.

In view of its obvious importance to any chemistry where electron collision processes occur, research on electron-impact ionization of molecules should be an important core component of any serious program in electron-driven chemistry. It will be important to see if the early successes of methods such as convergent-close-coupling, R-matrix with pseudo-states, time-dependent close-coupling or the direct grid methods can be extended beyond simple atomic systems and whether any of these techniques will be applicable to molecular targets. There is clearly a need for new computational methods in the field of molecular ionization. There is a rich, early literature on various methods based on the use of complex basis functions, Padé

approximants, analytic continuation and extrapolations from complex energies. In view of the fact that today's computer resources are vastly more powerful than anything envisioned at the time these methods were first proposed, they are worth a fresh look since, ultimately, the solution to the molecular ionization problem will depend on new methodologies.

II.2.2c Electron Transport

Electron-molecule collision cross sections (total, elastic, momentum transfer, rotational, and vibrational excitation cross sections) in the low energy regime from threshold up to a few electronvolts are of crucial importance in modeling low temperature plasmas. These cross sections play a critical role in determining electron transport properties, mobilities, and electron energy distribution functions.

In many applications, it is the total electron scattering cross section of an atom or molecule that is needed by the modelers. From a basic viewpoint, it can be said that we have only solved the electron scattering problem from a molecule, when all the individual measured and calculated cross sections for the various processes have been summed and add up to yield the "correct" total cross section. For some selected targets, total cross sections have been measured from a few meV to a few eV with a resolution of 1 meV and an accuracy of 5% [II.14]. Because total cross sections can be measured very accurately, they can serve as an important test of experiment and theory.

Angular differential cross sections (DCS) for elastic electron scattering from atoms and molecules and integrated cross sections derived from measured DCS are key quantities to comparing experiment and theory. Thus, benchmarking measured and calculated elastic cross sections for selected targets is of fundamental importance in evaluating the overall reliability of theoretical methods. Deriving angle-integrated elastic scattering cross section from measured DCS has been difficult until the recent advent of electron spectrometers which allow a rotation of the electron scattering angle by applying a small, well-controlled magnetic field [II.15]. This avoids the often difficult and unreliable extrapolation of small-angle and large-angle scattering data to respectively the backward and forward directions and enables the experimental mapping of the entire angular scattering range. This feature is invaluable for the experimental determination of accurate angle-integrated elastic scattering cross sections and momentum transfer cross sections.

Experimental studies of electron transport processes can be carried out in the form of very low-energy crossed-beams experiments or in the form of swarm experiments. Beam experiments at very low energies (from near-zero energy to a few eV) are very challenging and reliable crossed-beams studies in this energy regime are scarce. Swarm experiments, on the other hand, are comparatively straightforward to carry out: a pulse of low energy electrons is sent through a gas cell and the arrival time and temporal spread in the electron pulse after traversing the gas cell are measured. However, the difficulty lies in the interpretation of the experiments, i.e. in the extraction of collision cross sections. This is a particular challenge in the case of molecular gases with many competing low-energy loss mechanisms and certain a priori assumptions about the cross sections have to be made.

Although calculations in this energy range generally restricted to electronically elastic processes, it is essential to include target polarization and distortion effects if meaningful results are to be obtained. Features such as Ramsauer-Townsend minima, shape resonances and virtual states, which can dominate the electron-impact cross sections for molecular targets, are extremely sensitive to the incorporation of target distortion and, consequently, to the careful

balance of correlation differences in the N- and (N+1) electron systems. Although methods are available, they are computationally demanding. Moreover, the methods that have been developed are based on traditional configuration-interaction approaches. This problem has many similarities to the problem of accurately determining electron affinities in bound-state quantum chemistry. Some of the most promising approaches in this area are based on coupled-cluster methods and many-body perturbation theory, but little of this new technology has been incorporated into the collision methods. The low-energy regime is an ideal one in which to explore incorporating recent advances in quantum chemistry into the "continuum electronic structure" problem.

The potential of using Time-Dependent-Density Functional Theory (TD-DFT) and direct-calculation methods such as Green's function and Equations of Motion, each of which can describe the target at levels of accuracy including SCF, MPn, CI, and CC, presents other exciting possibilities. Using TD-DFT could provide an inexpensive way to describe target states, and hence it is possible that an inexpensive method for screening cross sections could be based on such a formalism. The direct methods could offer great computational savings in very accurate calculations. It remains an open theoretical question to determine how target state polarization would be treated in electron collisions using these methods.

II.3 Recent Advances in Theoretical and Computational Methods

Recent advances in electron scattering theory and in structure theory can be related to dramatic improvements in computers and computational power and to a lesser extent to the development of new theoretical methods and approaches [II.16,II.17].

II.3.1 Advances in Electron Scattering Theory

Several groups in the U.S. and abroad have made substantial investments in the development of computational methods for studying electron-molecule collisions. While the few successful methods (complex Kohn, Schwinger multi-channel and molecular R-matrix) that have been developed exhibit significant technical differences, they have many common features as well. They are all variational methods and make heavy use of the computational tools developed by quantum chemists to study bound-state, electronic structure problems. These methods have all been shown to be capable of providing accurate low energy cross sections for small target molecules and, in a few significant cases (such as Cl_2 and CF_4), the calculated cross sections have been benchmarked against experimental measurements. The R-matrix method has been used with sophisticated CI target wave functions and has provided highly accurate results for a number of diatomic molecules and molecular ions; a polyatomic R-matrix code has recently been developed. The complex Kohn method has been extensively developed and applied over the past decade and provided accurate collision cross sections (elastic and electronically inelastic) for a number of small polyatomic molecules used in plasma processing. The Schwinger multi-channel method has already been ported to several parallel platforms and has been shown to be capable of providing collision data on complex target gases (such as C_3F_8) and radicals where no other data exists. Because of the common underlying physics and the general algorithmic similarity, there is every reason to believe that the other advanced methods of studying low-energy electron collisions could similarly be adapted to parallel execution.

In the case of atomic targets, the numerical R-matrix approach of the Belfast group has been the basis of computer programs that have described a wide range of processes at low incident energies (below the ionization threshold). These programs are now used world-wide

and have formed the basis of several international collaborations, including most notably the international Opacity Project and the Iron Project.

There has also been significant new theory and methods development in the past few years. Traditionally, electron and photon collisions with atoms and ions have been described either by perturbative or non-perturbative methods, based upon the Born-series or the close-coupling expansions, respectively. Such methods are expected to yield somewhat reliable results in the limits of "high energy" (Born) or "low-energy" (close-coupling) scattering. The development of the "convergent-close-coupling" (CCC) approach has breached this gap and lead the way for other methods, such as time-dependent and other more direct approaches for the solution of the scattering equations. These methods account for the coupling between discrete and continuum target states and thus should (in principle) yield reliable results independent of the collision energy.

The computational study of electron-molecule collisions in important technological contexts is not merely a bright prospect, it is a current reality. There are many useful calculations that can be performed with currently available variational methods on a variety of technologically significant polyatomic species. These techniques have already been shown to be capable of providing highly accurate cross sections in a few important cases involving small polyatomic targets where experimental data was available for comparison. In many other cases, especially those involving reactive species and complex polyatomic target gases, theory has proved to be the "only game in town" and thus the sole source of critically needed collision data. While improvements to existing methodologies are under way, studies using existing codes will continue to be of immediate practical benefit.

There are practical limitations on what can be expected from current methods without substantial future investment. Nearly all calculations to date are fixed nuclei approximations. For very large target molecules, the calculations are currently limited to the use of simple target wave functions. Electronic excitation can be studied using only a small number of coupled states and the extent to which polarization effects, which are very important at energies below a few electron volts, can be accurately treated depends very strongly on the complexity of the target. An investment now will allow investigators to leverage existing methods and computational platforms to make an immediate impact on both plasma processing and environmental chemistry. Benchmarking against experimental measurements will be essential to bring the credibility that will be needed for a sustained future effort.

Despite the availability of methods and codes for studying a wide range of electron scattering problems, it has become clear that very large problems of crucial importance in many applications cannot be tackled by the present generation computer programs. The treatment of hundreds and probably thousands of coupled channels clearly requires both major rethinking of the underlying theory and a complete and fundamental rewriting of the corresponding codes. The existing ensemble of computer codes assembled by the international community working in this area undoubtedly runs to many hundreds of thousands of lines, and the scale of the effort required is to replace it all. The new effort will have to be made in the context of modern quantum chemistry codes which will themselves have to be modified, possibly extensively, to provide the appropriate infrastructure for the simultaneous treatment of continuum and bound electron dynamics.

For collisions above the ionization threshold, there are still fundamental theoretical questions to be answered and accurate calculations of ionization cross sections are still only possible for simple atomic systems. Calculations of excitation cross sections that involve

Rydberg states pose significant technical problems for both atomic and molecular targets. And finally, the treatment of post-collision dynamics in polyatomic excitation, the elucidation of dissociation pathways and the determination of branching ratios is a grand challenge scale problem that will require an interdisciplinary effort involving quantum chemists, electron collision theorists and heavy-particle dynamicists before significant progress can be made.

II.3.2 Advances in Structure Theory and Computing

Dramatic improvements in computers have occurred over the past 20 years with the development of vector and vector/parallel computers, RISC architectures, powerful desktop computing, and, more recently, massively parallel computing systems based on lower cost RISC processors. With the availability of new high-performance computers, new algorithms and new theoretical methods have been developed to take advantage of the increased computational power. By combining workstation processors with good performance into massively parallel computing systems with distributed memory, it is now possible to attain on the order of a Teraflop of peak performance at reasonable cost. Furthermore, such computational power is no longer restricted to the sole use of specialized practitioners; access to high performance computing is becoming available to a much broader user community. Because of the dramatic increase in computational power and improved algorithms and software, computational chemistry can now be a partner with experiment in efforts to develop new materials and chemical processes. One can actually do computations with the required accuracy on molecular systems of real interest to experimental chemists across a broad range of the chemical enterprise.

Computational chemistry has, for many years, provided qualitative insight into chemical phenomena and guidance to experimentalists. During the past five years there has been a revolution in our ability to compute the thermodynamic properties of molecules from first principles. This revolution has resulted from a combination of factors. The first is the development of efficient computational implementations of coupled cluster methods to solve the n-body problem. The second is the development of a family of efficient, increasingly accurate basis sets, the correlation-consistent basis sets, for solving the coupled cluster equations. These basis sets provide a good solution to the one-body problem and have been made widely available through the use of modern World Wide Web technologies. The third is the continuing advancements in computer technology, both hardware and software, noted above. With current computer technology, it is possible to predict bond energies and heats of formation for molecules with 6 or fewer first row atoms, including fluorinated compounds of interest to plasma processing, as well as radicals and ions, to an accuracy of better than 1 kcal/mol. The range of molecules that can be treated will grow dramatically over the next several years as computer technology transitions to the teraflops capabilities of tomorrow and to the petaflops capabilities of the not-so-distant future.

There have been many other advances in addition to those discussed above. They include:

(1) new methods for computing, approximating, and eliminating the two-electron integrals $(ij|1/r_{12}|kl)$ in ways that scale nearly linearly with the physical size of the molecule rather than as the number of atomic orbitals, N, to the fourth power;

(2) the wide use of density functional theory (DFT) by chemists, the improvement of the computational methods of DFT and the invention of new functionals that permit electron correlation and exchange to be handled more accurately (DFT has a significant computational scaling advantage over traditional methods that treat electron correlation);

(3) major improvements in the efficiencies (including parallel implementation as well as strategies that permit near-linear scaling with system size) of theories that compute electron correlation energies, including the Møller-Plesset perturbation method, the configuration-interaction (CI) method, coupled-cluster (CC) theory, and multiconfigurational self-consistent field (MCSCF) theory;
(4) developments of theories designed to compute energy differences (e.g., electron affinities, ionization potentials, and excitation energies) and responses to external perturbations directly; and
(5) the effort to implement parallel computing techniques and to redesign existing methods to permit higher degrees of parallelization.

Although most of the calculations that are performed using modern electronic structure codes involve bound electronic states (they often involve scattering nuclear-motion states), it should be noted that most, if not all, of the advanced methods noted above have also been applied to electronic shape and Feshbach resonance states. In most such applications, only slight extensions to existing bound-state codes (e.g., to incorporate complex electronic coordinates for performing scaled coordinate calculations or to include box-normalized functions for stabilization calculations) have been necessary.

However, by making the remaining extensions of structure codes that would allow true *continuum* basis functions to be used, a complete interface between electronic structure theory and electron-molecule scattering can be realized. Among the methods noted above, the so-called Green's function (GF) or equations of motion (EOM) methods seem to be especially attractive for electron-molecule scattering because they focus directly on the interaction of the scattering electron with the molecular target. They thereby permit the scattering electron to be described in terms of continuum and localized orbitals while retaining conventional orbitals for the other electrons. Modern GF and EOM methods permit the target to be described in a highly correlated manner (i.e., not simply in a single configuration static-exchange picture) and thus produce an electron-molecule interaction that includes electrostatic, polarization, and correlation effects.

In light of the current revolution in scientific research arising from the rapid advances in computer power and computational methods and algorithms, particularly the development of massively parallel processors (MPPs), major advances towards the solution of many theoretical problems can be expected within the next few years. However, the novel architecture of the MPPs requires the rewriting of many codes for optimal use on such machines. Moreover, effective use of future teraflop-scale computers will require careful program design or redesign, even for methods that already deliver tens of gigaflops on today's architectures. Potential bottlenecks that will emerge in areas such as the user interface and I/O must be anticipated and addressed if detailed studies of large polyatomics, possibly encompassing many channels and/or nuclear geometries, are to become feasible. The porting of the Schwinger multi-channel codes to highly parallel MPP platforms represents a significant step. In the case of electron-atom scattering, substantial efforts are already underway along this direction, with special emphasis on the further development of the R-matrix codes. The current status of this work is summarized in a recent special issue of Computer Physics Communications [II.18].

II.4 Recent Advances in Experimental Techniques and New Instrumentation

The field of electron-atom and electron-molecule collisions has been continuously enriched by novel developments in AMO physics. For instance, the availability of tunable lasers in the 1960s started the area of laser spectroscopy. The techniques of laser spectroscopy were then

incorporated into collision experiments and they have now become an important part of many electron collision experiments. Presently, we are beginning to see the impact of techniques such as atom cooling and trapping on the studies of collision processes. The rapid development of trapping techniques and Bose-Einstein condensation will undoubtedly provide new techniques and methodologies for electron collision experiments. The comparatively easy availability of spin-polarized projectiles and targets is another example of a major advance in experimental techniques. In the 1970s, correlation and coincidence techniques, which had been developed earlier by the nuclear physics community, were introduced to the electron collision physics community and made a major impact on the level of detail with which the results of inelastic electron-atom collision experiments could be interpreted. There are many other such examples. A selection of perhaps the most striking recent developments of experimental techniques and instrumentation which had or may have a major impact on the way electron collision experiments will be carried out in the future is given below.

II.4.1 New Sources of Beams

New and improved sources of electron beams and atomic and molecular beams have opened up opportunities for new and more detailed experiments.

II.4.1a High-Resolution Electron Beams

Many aspects of the study of electron-driven processes depend on the availability of bright, high-resolution electron beam sources. Compared to light sources, electron beam sources are much more limited in terms of achievable brightness and energy resolution. Hence few experiments have been performed to date to investigate the rotational excitation of molecules, since the resolution of the incident electron beams has been insufficient to resolve rotational transitions in any molecule other than hydrogen and its isotopes (10 meV).

Two sources of electrons of very high energy resolution have been developed in the United States. One source uses Rydberg atoms to generate low-energy electron beams of extremely high energy resolution (in the range of μeV). Another source employs single-photon ionization of rare gas atoms. Two new sources of low energy (<<1eV) electrons have recently been developed in Europe using laser or synchrotron radiation to produce photoelectrons which are subsequently collimated into a high-resolution, low energy electron beam. These sources allow experiments to be performed at μeV and meV incident energies revealing rotational excitation cross sections and threshold phenomena at the onset of molecular vibrational excitation. Such experiments are also providing the first information on the interaction of electrons with molecules containing dipole moments. These interactions dominate low energy (<1eV) scattering and lead to extremely large total cross sections ($> 100 \times 10^{-16}$ cm^2).

II.4.1b Polarized Electron Beams

One of the most stringent ways to test state-of-the-art theories of electron-atom collisions is to do experiments with polarized electrons, either using them as projectiles or measuring the polarization of scattered electrons. Measurements of this type gave the first broadly compelling evidence for the validity of the convergent close-coupling (CCC) theory in calculating parameters for discrete excitation of simple targets [II.19]. They also showed the shortcomings of state-of-the-art R-matrix calculations for many-electron atoms [II.20]. Polarized electron technology has improved dramatically in the past 30 years. We mention here the most promising recent developments.

Much effort has been expended to develop "turn-key" sources of polarized electrons [II.21]. The current standard source is based on photoemission from negative-electron-affinity (NEA) GaAs. In highly specialized high-energy accelerator environments, such sources can provide hundreds of microamperes of electron current with polarizations approaching 75%. Their operation requires a high level of training and constant attention by a multi-person team. In situations where these conditions are difficult to achieve, simpler sources are required. One promising candidate is a source based on spin exchange collisions between electrons and optically-pumped rubidium (see Figure 2) [II.22]. This source does not require ultra-high vacuum conditions or extensive hardware. Optical pumping of the rubidium is accomplished with a standard dye laser. This source can thus be used in more typical laboratory situations. In first tests, it has produced several microamperes of electrons with 25% polarization, comparable to first-generation GaAs sources. This performance will probably be improved significantly, but the demonstrated specifications are adequate for many types of experiments.

Electron polarimetry has also seen recent promising developments. A crucial issue here is the efficiency with which polarimetric measurements can be made. High efficiencies allow analysis of processes with low differential cross sections, which often yield the most detailed physics information. The standard technique used is Mott scattering, and Mott polarimeters have become increasingly compact and efficient [II.23]. A recent development promising even smaller sizes and higher efficiencies, possibly approaching unity, is based on transmission of the electrons to be analyzed through thin films of iron having out-of-plane magnetization. Spin-"forward" and spin-"backward" longitudinally polarized electrons have different probabilities of being transmitted through these films, giving the device its analyzing power [II.24]. Another development is that of optical electron polarimetry, which is based on optical polarimetry of light emitted by atoms excited by polarized electrons [II.25]. This technique is inefficient, but it is extremely easy to implement and highly accurate. As such, it is most useful for analysis of primary source beams and the development of polarization standards.

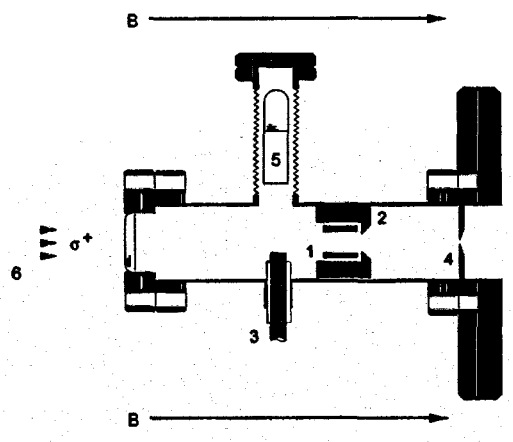


Fig. 2: Scale diagram of optically-pumped Rb electron spin filter showing 1) DC discharge cold cathode; 2) concentric anode; 3) high-voltage feedthrough for discharge power; 4) extraction aperture; 5) Rb ampoule; and 6) optical pumping light at 795 nm. Apparatus is immersed in a 100 Oe magnetic field.

Polarized electron scattering will continue to play a leading role in the development of our understanding of electron-atom collisions, especially as more and more labs come on-line with polarized electron capability. On the other hand, the study of spin effects in electron-molecule collisions is a comparatively poorly developed field with only a few experiments performed [II.26]. Spin effects that are important in electron-atom collisions also apply to electron-molecule collisions. However, there are several features that render their study for molecular targets more difficult, such as the coupling of the electronic angular momenta including the spin of the target electrons to the rotation of the molecule. In general, quite different situations occur in inelastic electron-molecule collisions depending on the target angular momentum coupling as described e.g. by Hund's cases (a) – (d). For instance, the spin-orbit interaction of the entire system of continuum electron plus target electrons may be so small that it does not affect the collision process, in which case spin effects are only due to exchange independent of the angular momentum coupling case. A different scenario occurs in Hund's cases (c) when the spin and orbital motion of the target electrons couple to a total electronic angular momentum J which is the only well-defined angular momentum due to a very strong spin-orbit coupling. In this case, the target spin is no longer a good quantum number and the spin-orbit interaction of the continuum electron becomes important as well. A separate category of spin effect is realized in the interaction of spin-polarized electrons with chiral molecules. While chiral spin effects involving molecules with mainly low-Z constituent atoms are fairly small, more pronounced effects can be expected for targets containing high-Z atoms because of the chiral structure of the regular (non-parity violating) electrostatic force in conjunction with the spin-orbit force.

II.4.1c Bright Atomic Beams

The advent of laser cooling and trapping techniques and the rapid development of the associated technology in the past decade opened many new possibilities for highly controlled collision experiments. There are now several facilities, which are either operational or approaching operational status, where dense, slow and highly monochromatic atomic beams have been produced by the controlled use of laser radiation pressure to collimate, focus and slow a beam of atoms from a conventional source. These techniques have been applied to atoms in their ground states, e.g. the alkalis and to excited-state species such as the lowest-lying metastable excited states of the rare gas atoms. The latter cases are particularly interesting as they have been identified, both in this workshop and in other venues, as one of the critical areas for future research in electron-induced processes.

Metastable atoms, by virtue of their long lifetimes, large internal energies, and extremely large collision cross sections, can have a profound effect on the behavior of a low pressure discharge, even though they may be present only in small equilibrium concentrations. Their study, however, has been limited to only a few, albeit important experiments (mainly total cross section measurements), which have nonetheless highlighted substantial discrepancies with the best contemporary scattering theory. The main experimental limitation has been the difficulty to produce atomic beams of sufficient number density to enable detailed cross section studies. The new laser cooling techniques have resulted in metastable atomic beams with number densities 10-100 times that produced from conventional discharge sources, velocities as low as 100 m/s and a velocity spreads as small as 1 m/s. As these atoms contain substantial internal energy (>10 eV), they are readily detectable and new spectrometers employing large-area, position sensitive detectors are presently being developed. In these experiments, for instance, it will be possible to detect *scattered atoms* rather than scattered electrons and to do so with high angular and energy

resolution. As the recoil of the atom can be directly related to the energy and angle of the scattered electron and, in principle, all of the scattered atoms can be detected, a large number of electron scattering processes can be mapped at one time. These new experimental endeavors would not be possible without combining the latest technologies for "bright", monochromatic atomic beams and large-area position-sensitive detection techniques.

II.4.1d Radical Beams

The most common methods to generate target beams of species such as free radicals which are unstable and cannot readily be produced by evaporation of a solid target or by effusion from a commercially available gas cylinder involves either discharge sources or chemical preparation. Discharge sources through a stable feed gas e.g. CH_4 produces a variety of ionic species, most prominently singly charged ions including the CH_4^+ parent ion and the various fragment ions CH_3^+, CH_2, CH^+, C^+, and H+. When extracted from the discharge region and mass selected, a particular primary ion (e.g. CH_3^+) is then passed through a charge exchange cell where resonant or near-resonant charge transfer neutralizes a fraction of ions (typically ranging from a few tenths of a percent to a few percent). After removing the remaining ions from the beam and ensuring that excited-state species such as Rydberg atoms/molecules have a chance to decay, one can produce a more or less well-characterized neutral radical beam (here CH_3) which can then interact with an electron beam. The main disadvantages of this technique is the fact that the neutral beam may contain a distribution of vibrationally excited molecules which is far from room temperature ("vibrationally hot" molecules) and difficult to characterize quantitatively. Other "excited" species in the neutral radical beam may include long-lived metastables. Thus, all experiments using radical beam generated by charge transfer processes includes thorough and often time-consuming target beam diagnostics studies to ensure that one knows exactly the composition of the target beam.

Chemical preparation of particular radicals (e.g. ozone) is another common technique to produce radical target beams. This technique is limited to a few special cases, but these may be well-suited to benchmark theoretical calculations.

II.4.1e Ultracold Trapped Targets

A recent development in the field of electron-atom collisions is the use of ultracold trapped atoms as collision targets. In these experiments, a magnetic-optical trap, which consists of six cooling laser beams along the positive and negative x, y, and z directions and an inhomogeneous trapping magnetic field, is incorporated into the collision experiment. Typically, about 10^6 Rb (or Cs) atoms are trapped inside a volume of about 0.5 mm in diameter at a temperature of 1 mK. While the trap is turned off, a pulsed electron beam collides with the ultracold atoms and the recoiling atoms are allowed to escape from the trap. Measurements of the fractional trap loss due to the electron collisions yield the total scattering cross section. It is also possible to re-trap the recoiling atoms immediately after the electron beam has been turned off, so that the trap loss in the case of trapped Rb atoms is entirely due to the formation Rb^+ (and also Rb^{2+} etc.) ions which do not respond to the cooling laser for the Rb(5S $\rightarrow$ 5P) transition and cannot be re-trapped. In this fashion, one can measure the total electron-impact ionization cross section of Rb(5S) atoms, which is the sum of the partial ionization cross sections for the formation of Rb^+, Rb^{2+}, etc . Alternatively, the electron-impact ionization cross sections can also be measured by extracting the ions formed in the collision region using an accelerating voltage and detecting them with a suitable ion detector. For a given extraction voltage, the Rb ions

carrying a different charge reach the detector at different times. Thus, placing the detector a few centimeters from the trapped atoms allows one to isolate Rb^+ from Rb^{2+} and from other ions. It is also possible to carry out measurements of electron-impact cross sections involving excited Rb(5P) atoms as targets. Since all the trapped atoms are inside a small volume of 0.5 mm in diameter, nearly 50% of the Rb(5S) atoms can be pumped to the 5P level by saturated 5S → 5P absorption with a diode laser. Using such a nearly 50:50 mixture of Rb(5S) and Rb(5P) atoms as a target, one obtains the average ionization cross section for Rb(5S) and Rb(5P) which, in conjunction with the previously measured Rb(5S) ionization cross section yields the ionization cross section of excited Rb(5P) atoms.

The experiments described above illustrate some of the unique advantages of trapped atomic targets

- Since the trapped atoms are confined to a volume of 0.5 mm in diameter, which is much smaller than the size of the laser beam, it is easy to realize saturation absorption with a high and uniform fractional excitation using a diode laser. In contrast, the fraction of excited atoms produced by laser irradiation in a conventional atomic beam or static gas target is not only much smaller, but it is also non-uniform over the target volume because of the comparatively large target volume.
- In a standard collision experiment employing a crossed-beams geometry, it is necessary to measure the profiles of the intersecting beams and their mutual overlap in order to determine an absolute cross section. Measurements of beam profiles are difficult and tedious and introduce a major part of the systematic uncertainty of the experimental data. In trapped target experiments, by contrast, the target volume is so small that it represents essentially a point source at the center of the electron beam. Thus, absolute calibration only requires the electron current density at the center of the electron beam.
- Using trapped targets allows the determination of cross sections either by detecting the products of the collision process (e.g. Rb^+ ions in the case of an ionization experiment) or by measuring the trap loss. In the latter case, it is possible to vary the time delay between the end of the electron beam pulse and the timing of the trap (on, off), so that the resulting trap loss can correspond to cross sections for different processes. The cross section is simply given by the rate of the fractional trap loss multiplied by the electron charge and divided by the current density at the center of the electron beam. Since only the fractional loss is required, no absolute measurements of target number densities are necessary.

One can envision that in the future major efforts will be devoted to the wide-spread utilization of trapped-atom techniques for novel kinds of electron collision studies that take advantage of the unique properties of the trapped atoms. Expansion of trapping and cooling techniques to molecules will be explored and techniques will be developed to incorporate ultracold trapped molecular targets in electron-molecule collision studies. The recent success in trapping alkali-dimers marks the first successful step in extending the trapped-atom target experiments to molecular targets.

II.4.2 New Electron Spectrometers

One recent development that promises to extend the measurement of traditional differential electron scattering cross sections is the magnetic angle-changing spectrometer [II.15]. Conventional electron scattering experiments are limited in the range of scattering angles over which measurements can be made. This is because the physical size of both the electron source and the analyzer/detector impose unavoidable physical constraints at larger

scattering angles where the two devices would have to overlap in space in order for measurements to be possible. The new technique uses a highly localized magnetic field to effectively rotate the scattering geometry of an experiment by an arbitrary amount, typically 90°, with respect to the fixed position of electron source and detector. This enables measurements of electrons scattered in the backward hemisphere, in particular at 180°, to be made with the analyzer placed at a convenient angle of 90°.

This technique has enormous ramifications for the measurement of electron scattering processes. In many cases, scattering cross sections at backward angles can be substantial and of particular significance in the derivation of total and momentum transfer cross sections for applications in gaseous electronics. This technique will remove much of the uncertainty which is presently associated with the derivation of these important cross sections by extrapolating angular differential measurements to 180°. Examples of this sort of application have already appeared in the literature, e.g. measurements of elastic and inelastic differential cross sections for N_2 and N_2O. We expect further, extensive use of this technique in the near future. From a more fundamental aspect, collisions in the backward hemisphere provide a probe of particular aspects of the electron-atom(molecule) interaction Hamiltonian including the static interaction and exchange and correlation effects. As such they have the potential to provide a more complete test of contemporary scattering theory.

II.4.3 Lasers Techniques

The use of lasers and laser-based optical techniques in the experimental study of electron collision processes has dramatically increased in the past 15 years and has led to a variety of new developments which would not have been possible without lasers. Experiments that combine laser techniques with electron scattering techniques may be conveniently divided into two broad classes. In the first category, the laser is used to prepare the target in specific states prior to the electron scattering event, while in the second category the laser is so used to probe the products of the electron collision process.

II.4.3a Electron scattering from excited states

In many technological applications (e.g. gas discharges, lasers, pulsed power switches and MHD), electron interactions with targets in electronically excited states play an important role, but our knowledge of electron scattering from excited states is very limited. The few experiments that have been performed clearly show that cross sections for electron interactions with atoms and molecules in excited states tend to be considerably different from scattering processes involving ground state species. Cross sections from excited species tend to be larger than cross sections from ground-state species, but perhaps more importantly, the well-established energy dependence of excitation cross sections for ground-state excitation for optically allowed, optically forbidden, and spin-forbidden transitions is no longer valid when the target is an excited atom [II.27]. This indicates that the physics of the collision process is drastically altered when the target is in an excited state. Furthermore, dissociative electron attachment cross sections in molecular hydrogen change by orders of magnitude for different initial vibrational modes and DEA from optically pumped SO_2 shows new dissociation channels that open when the molecular target is in an electronically excited state [II.28].

A few groups have successfully used CW lasers to prepare atoms in excited (metastasble) states, so that cross sections for superelastic scattering processes (in which the scattered electron gains energy from the target) may be studied. Such experiments may be considered the time reversal equivalent of the more common electron/photon coincidence experiments pioneered in

the 1970s which proved to be invaluable experiments for the most stringent experimental tests of advanced scattering theories. The use of modern laser systems (diode and/or dye) coupled with supersonic gas sources provides the opportunity for the preparation of molecular systems in specific ro-vibrational states. When coupled with laser analysis techniques, it is possible to produce state-to-state electron scattering cross sections. The first experimental apparatus to determine such state-to-state cross sections is operational [II.29]. This field is only in its infancy, but it is likely to be a fertile area of study in the next ten years.

II.4.3b Laser Spectroscopy as a Probe of Electron Collisions.

Laser analysis techniques have been developed by the physical chemistry community to probe molecular photo-dissociation, surface desorption and reaction kinematics. The two most commonly used laser analysis techniques are Resonance Enhanced Multiphoton Ionization (REMPI) and Laser Induced Fluorescence (LIF). The first experiments have now been developed that use such techniques to probe the products of electron collisions with atoms and molecules. In addition to using LIF techniques to probe neutral molecular dissociation processes induced by electron impact, it should now also be possible to perform the truly state-to-state electron scattering experiments. Such experiments will provide a complete analysis of electron scattering from molecular systems that will allow discrete rotational, vibrational, electronic excitation and dissociation processes to be studied with unprecedented detail. When coupled with theoretical/computational advances, such experiments will finally allow the fundamental electron atom/molecule interaction potentials to be accurately derived, the "genome project" of electron collision research and an essential step in the understanding of electron-driven processes for technology and in the life sciences.

II.4.4 Detection of Products from Neutral Molecular Dissociation Processes

The important role of electron-induced neutral molecular dissociation processes and the challenge of the quantitative detection of the neutral ground-state reaction products has been stressed in section II.1a. Here we summarize some of the detection techniques that can be used to probe neutral ground-state species.

(a) Detection techniques that are not final-state specific:

(1) Quadrapole mass spectrometry using electron impact ionization (continuous or pulsed); rarely used in quantitative studies with the exception of appearance energy mass spectrometric studies in crossed beam arrangements.

(2) Vacuum Ultraviolet (VUV) photoionization in conjunction with mass spectrometry which is typically done in a pulsed time-of-flight (TOF) mode; has the advantage that all masses can be collected at once. Pulsed lasers whose wavelength range has been extended to the VUV by e.g. harmonic generation and four-wave mixing are typical photoionization sources. The Chemical Dynamics Beamline at the ALS, which uses the ALS to provide a broadly tunable, low resolution photon source with excellent brightness is a potentially powerful alternative light source.

The above techniques can be fairly easily quantified, so that branching ratios can be measured.

(b) Detection techniques that are state-specific (these techniques are usually pulsed):

(1) Laser-induced fluorescence (LIF) is the standard for ultrasensitive techniques, but limited to species with known radiative transitions. This technique is currently being used in single-

collision studies. It works well for diatomic fragments and for ground-state atoms. Extension of the wavelength range into the VUV is necessary for certain atoms which can be done by two-photon excitation, but with loss of sensitivity and increased complexity of the method.
(2) Resonance Enhanced Multiphoton Ionization (REMPI) is as good or better than LIF, but it sometimes requires more sophisticated (i.e. expensive) lasers and usually more than one laser. This techniques is currently being used in single-collision studies.
(3) Absorption techniques; for atomic fragments, direct absorption is often easy to implement and easily and quantifiable. Utilization under single-collision conditions is problematic because of low absorber sensitivity. The generation of the resonant light using lasers can be problematic and it is often more convenient to use a resonance lamp. Cavity Ringdown Laser Absorption Spectroscopy (CRDLAS) has potential because of its high sensitivity, but the technique is non-trivial to implement and involves the use of an optical cavity around the sample of interest.
(4) Resonant four-wave mixing techniques have much less sensitivity than the above listed techniques and require experience to implement.
(5) Rydberg atom TOF - in this scheme, lasers are used to excite an atom (always H atom up to now) to a high Rydberg state. The tagged atom, which has been produced by the reaction or photodissociation, recoils from the interaction region, drifts in a TOF and is field ionized and detected by a microchannel plate. Because the H atom is so light, it recoils very quickly from the partner fragment. The TOF spectrum of the H atom, which can be recorded with very high resolution, maps out the corresponding internal state distribution of the partner fragment. Thus, it gives state-specific data on the fragment through the speed distribution of the H atom. Very clever and very widely used by chemists these days. All of the above are state-specific and give loads of detailed information on the quantum states populated in the reaction or dissociation. They are all really tough to quantify, however, and getting absolute branching fractions is really tough. (The only exception might be direct absorption.)

II.4.5 The COLTRIMS Imaging Detection Technique

It is generally assumed that the experimental investigation of elastic and inelastic low-energy electron scattering from atoms and molecules is a rather difficult task because of, among other factors, the small solid acceptance angle of electron and nuclear fragment detection devices which are traditionally used in such experiments. The recently developed COLTRIMS imaging technique, however, provides a rather straightforward detection scheme which allows a nearly complete detection of all charged fragments with comparatively high momentum resolution for ion-molecule collisions and even for electron scattering experiments and renders such studies accessible to a more quantitative analysis.

In the COLTRIMS detection technique, all charged fragments are imaged by well-designed electrostatic or magnetic field configurations onto two position-sensitive detectors (one for positively charged fragments, the other one for negatively charged fragments). Neutral fragments are presently not detectable. Figure 1 below shows the schematics of an experimental set-up that employs the COLTRIMS technique. The positively charged ionic fragments are accelerated by a small extraction field (focusing lenses may be incorporated to enable a higher resolution in teh case of spatially extended reaction zones). In order to obtain a very good "time focusing" the ions must transvere through a drift tube region. The electrons are extracted towards the electron detector. A small axial magnetic field allows for an extended extraction region, thus still providing full solid angle detection. Even fast electrons (of kinetic energies of up to 25 eV) a large solid angle and a comparatively high time resolution can be obtained.

The determination of the position of impact of these fragments on the detector and the measurement of the flight time of each fragment allows the analysis of the momentum obtained intitally in the reaction process with comparatively high resolution (e.g. to better than about 10 meV in the case of electrons). The detectors have delay-line anode readouts which facilitates fast multi-hit detection (two hits in less than 10 ns can be resolved).

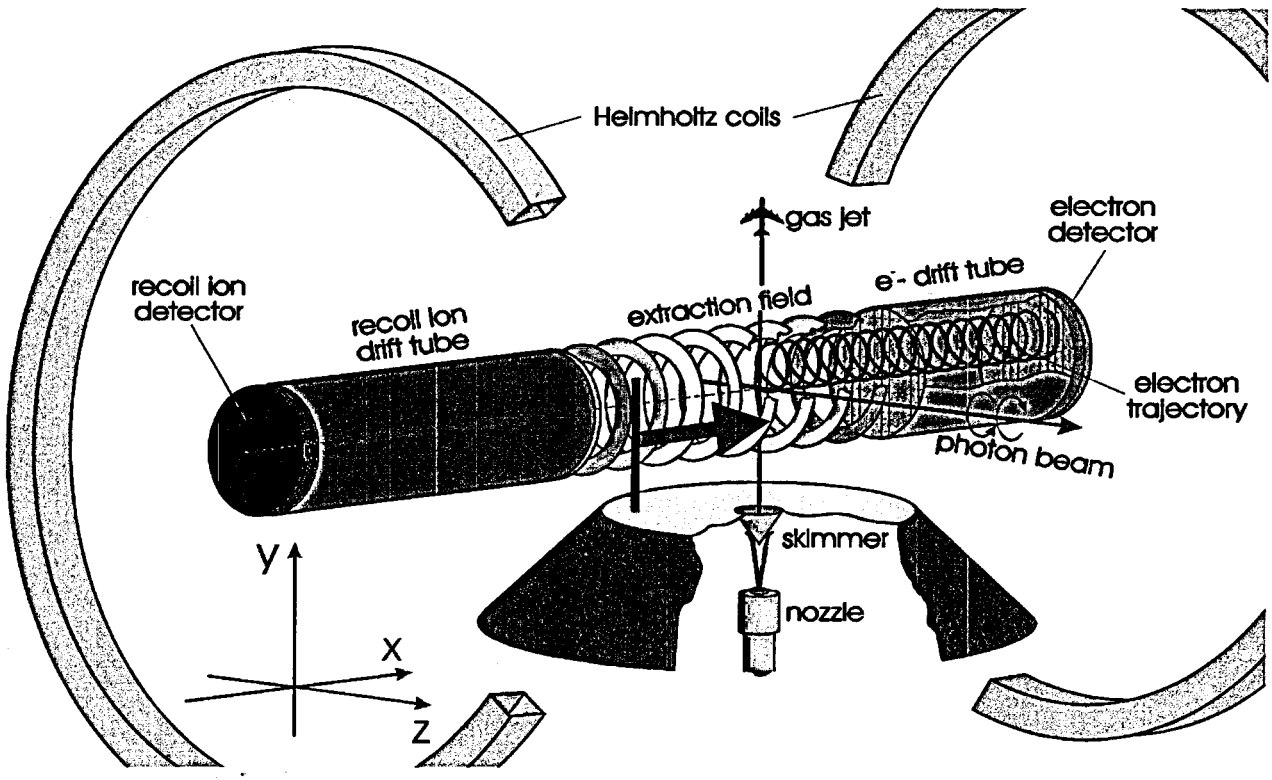


Fig. 3: Schematic diagram of the COLTRIMS set-up for electron-molecule collision studies.

In the case of electron collision studies at low impact energies (fig. 3), the electron source and thus the electron beam must be placed directly along the spectrometer axis (indicated by the thick blue arrow in fig. 3). One possible scheme employs a very thin wire mounted in the extraction region which is hit by a pulsed laser beam. This generates electron pulses of about 100 ps duration. The electrons are accelerated by a pulsed electric field which is directed towards the supersonic gas-jet of target species under study. A weak axial magnetic field ensures that the low energy electron beam travels exactly along the axis. The determination of the momentum of the scattered electrons is not affected by the magnetic field. The quantitative procedure for analyzing the electron and ion momenta in the presence of a weak magnetic field has been described in the literature [II.30].

The overall efficiency for e.g. single-electron detection is better than 60% of the full solid angle (4π). In the case of the coincident detection of two electrons (primary and secondary electron) and two charged ionic fragments, one still obtaines an overall detection efficiency of more than 1%, even in cases where a momentum resolution of about .2 a.u. is required.

References

[II.1] J.B. Corrigan, Chem. Phys. **43**, 4381(1965)
[II.2] H.F. Winters, J. Chem. Phys. **63**, 3462 (1975)
[II.3] S. Motlagh and J.H. Moore, Chem. Phys. **109**, 432 (1998)
[II.4] H. Helm and P.C. Cosby, J. Chem. Phys. **86**, 6813 (1987)
[II.5] H. Sugai et al., Contr. Plasma Phys. **35**, 415 (1995)
[II.6] P.W. Zetner et al., Chem. Phys. **124**, 453 (1988); M. Darrach and J.W. McConkey, J. Chem. Phys. **95**, 754 (1991)
[II.7] N. Abramzon et al., J. Chem. Phys. **113**, 2250 (2000)
[II.8] L.G. Christophorou (Ed.), "Electron-Molecule Interactions and Their Applications", Vols I and II, Academic Press, Orlando (1984)1984.
[II.9] H. Hotop et al., in "The Physics of Electronic and Atomic Collisions", L. J. Dubé, J. B. A. Mitchell, J. W. McConkey and C.E. Brion (Eds.), AIP Conference Proceedings 360, American Institute of Physics Press, Woodbury, New York (1995), pp. 267-278.
[II.10] B. Boudaïffa et al., Science **287**, 1658 (2000)
[II.11] L.R. LeClair and J.W. McConkey, J. Chem. Phys. **99**, 4566,(199)
[II.12] H.U. Poll et al., Int. J. Mass Spectrom. Ion Proc. **112**, 1 (1992)
[II.13] T.N. Rescigno et al. Science, **286**, 2474 (1999)
[II.14] D. Field et al., J. Phys. B **33**, 1039 (2000)
[II.15] F.H. Read and J.M. Channing, Rev, Sci. Instrum. **67**, 2372 (1996)
[II.16] For a current picture of state-of-the-art electronic structure theory, see "Modern Electronic Structure Theory", D. Yarkony (Ed.), World Scientific, Singapore (1995)
[II.17] For a comprehensive review of current theoretical methods being used in electron-molecule collision theory, see "Computational Electron-Molecule Scattering", W. Huo and F. Gianturco (Eds.), Plenum Pres, New York (1996)
[II.18] Computer Physics Communications, **114** (1998)
[II.19] I. Bray, Can. J. Phys. **74**, 875 (1996)
[II.20] B.G. Birdsey et al., Phys. Rev. A **60**, 1046 (1999)
[II.21] See, e.g., "Proceedings of the Workshop on Photocathodes for Polarized Electron Sources for Accelerators", M. Chatwell et al. (Eds.), SLAC Internal Report 432 Rev. April 1994
[II.22] H. Batelaan et al., Phys. Rev. Lett. **82**, 4216 (1999).
[II.23] H.-J. Drouhin et al., J. Magn. Mag. Mater. **151**, 417 (1995).
[II.24] T. J. Gay and F. B. Dunning, Rev. Sci. Instrum. **63**, 1635 (1992).
[II.25] T. J. Gay et al., Phys. Rev. A **53**, 1623 (1996)
[II.26] G.F. Hanne, "Spin Effects in Electron-Molecule Collisions", in "Novel Aspects of Electron-Molecule Collisions", K.H. Becker (Ed.), World Scientific, Singapore, 1998
[II.27] R.B. Lockwood et al., Z. Phys. D **24**, 155 (1992)
[II.28] E. Krishnakumar et al., J. Phys. B **29**, L657 (1996)
[II.29] L. Kaminski et al., Proc. 6th EPS Conf. At. Mol. Phys., Siena, Italy (1998), (C. Biancalana et al., Eds.), 4-77
[II.30] J. Ullrich et al., J.Phys. B **30**, 2917 (1997)

III. Low-Energy Electron Interactions and Clusters: Linking the Gaseous and Condensed Phases of Matter

Linking the gaseous and condensed phases of matter requires multidisciplinary and systematic investigations concerning how the microscopic and macroscopic properties of materials and the elementary processes involving electrons change as one makes the transition from isolated particle behavior in a low pressure gas to many body interactions in the condensed phase. A very useful review of previous work on linking the gaseous and condensed phases has been published [III.1]. To date there have been two main complimentary approaches to obtaining this linkage: (i) interphase and (ii) cluster physics and chemistry. In the former approach, a given reaction or property is studied as a function of the density and nature of the medium in which it occurs from the low-pressure gas to the liquid or solid. Traditionally, such studies begin at either end of the density range: from the solid (liquid) density to progressively lower densities and from a low-density gas (binary collisions) to progressively higher densities (multiple scattering regime). In the latter approach, the properties and reactions of a given species (atom or molecule) are studied as a function of its size (increased gradually by clustering), cluster shape and cluster composition. A unique feature of clusters is that they allow studies of the transition from large finite clusters to the bulk. Thus, one can determine the minimum cluster size beyond which the properties no longer vary and are essentially those of the bulk material.

III.1 Why Low-Energy Electrons

Low energy electrons are generated in gaseous and condensed matter by a multiplicity of mechanisms: energy transfer from high energy particles to atoms and molecules; absorption of light by neutrals and negative ions, collisions of excited and unexcited species with negative ions, electron-neutral collisions and injection from surfaces and interfaces. The reactions of low-energy electrons in dense matter often differ greatly from those in a low-pressure gas. In the latter case, the electrons are normally free and the collision mean free path l, is much longer than the electron de-Broglie wavelength. Whereas in the former case (i.e a dense medium), l is smaller than the de-Broglie wavelength and as the medium density increases the electrons become localized or delocalized in conduction bands. These differences associated with the solid media introduces changes in the symmetries of scattering resonances, polarization effects which can enhance resonance lifetimes, suppression of autoionizing states, removal of high n Rydberg states and new channels which involve reactive scattering of the ion and neutral (radical) products. ***The reactions of slow electrons are unique in that they help us unravel the structure of atoms and molecules, probe the structural and dynamical changes with the density and the nature of matter, and quantify the energetics and dynamics of basic reactions in matter.***

III.2 Electron-Induced Processes in Clusters

Dissociative electron attachment (DEA) often involves multi-electron core-excited resonances, which consist of an excess electron temporarily bound by the positive electron affinity of an electronically excited target molecule. These are generally two-electron, one-hole configurations that are classified as either Feshbach or core-excited shape resonances. Since the lifetimes of Feshbach resonances are typically $\sim 10^{-12} - 10^{-14}$ seconds, dissociation into stable anion and neutral fragments may result if the resonance is dissociative in the Franck-Condon

region and one of the fragments has a positive electron affinity. Single particle resonances can also lead to DEA or stable anion formation and thus DEA and resonances are important processes in many related areas, a fact, which is generally not yet widely recognized. It is thus a particular challenge to investigate how a DEA reaction in the gas phase is modified when (i) the molecule of interest is coupled to some environment and (ii) when in addition to ***free*** electron attachment electron transfer between ***bound states*** is also incorporated.

It is obvious that going from free molecules in the gas phase to different degrees of aggregation causes major changes as other effective channels to remove the excess energy become available [III.2]. In free molecular clusters (as produced, e. g., in supersonic beams), the general trend for the low energy transient negative ions (TNIs) is that associative attachment, i. e. production of the non-dissociated parent anion competes with DEA and can quench bond breaking. Aggregation thus generally decreases the reactivity (i.e. the ability to break chemical bonds) of low energy electrons due to the many additional pathways of energy dissipation. In addition to the possibility of generating relaxed gas phase parent anions, free clusters represent an ideal medium to study elementary processes in finite systems or in molecules under microsolvation.

As already mentioned, DEA in molecules is generally quenched under aggregation in favor of associative attachment. This is at least true for processes generating the lowest TNI accessible by free electrons, which is usually associated with the electronic ground state of the negative ion. For electronically excited resonances, however, the observations so far indicate considerable (giant) enhancements of DEA cross sections [III.3,III.4]. These enhancements can be up to several orders of magnitude and persist in the aggregate form [III.2].

References

[III.1] L. G. Christophorou, E. Illenberger and W. F. Schmidt (Eds.), "Linking the Gaseous and Condensed Phases of Matter; The Behavior of Slow Electrons", NATO, ASI Series, Plenum Press, New York (1993)

[III.2] E. Illenberger, Chem. Rev. **92**, 1589 (1992).

[III.3] R. L. Gordon et al., "Optically enhanced electron attachment by p-benzoquinone", Int. J. Mass. Spectrom. Ion Proc., **164**, 177 (1997).

[III.4] L.A. Pinnaduwage and L.G. Christophorou, Chem. Phys. Lett. **186**, 4 (1991)

IV. Electron-Induced Processes at Surfaces and Interfaces

The excitations produced by electron impact of molecular solids and condensed-phase targets include negative ion resonances, excitons, surface states and ionization (formation of free charge carriers). The typical energy distribution of electrons created in condensed phase targets or injected from surfaces is shown below in Figure 4.

The energy distribution of these secondary electrons generally peaks at a few eV, however, a considerable number have energies which extend out to > 50 eV. *These low-energy electrons must undergo multiple inelastic scattering events as they thermalize. If they are emitted from surfaces, they must also traverse the interfacial molecular layers prior to trapping or solvation.* The primary energy-loss channels for electrons with energies typical of the secondary distribution are ionization (electron-hole pair production in the condensed phase), direct electronic excitation and resonance scattering. The latter results in the formation of TNIs, which decay via electron autodetachment and dissociative electron attachment. DEA has been observed in many molecular solids, and many body interactions affect the energies, widths and lifetimes of the scattering resonances [IV.1,IV.2]. The lower portion of Figure 4 estimates the

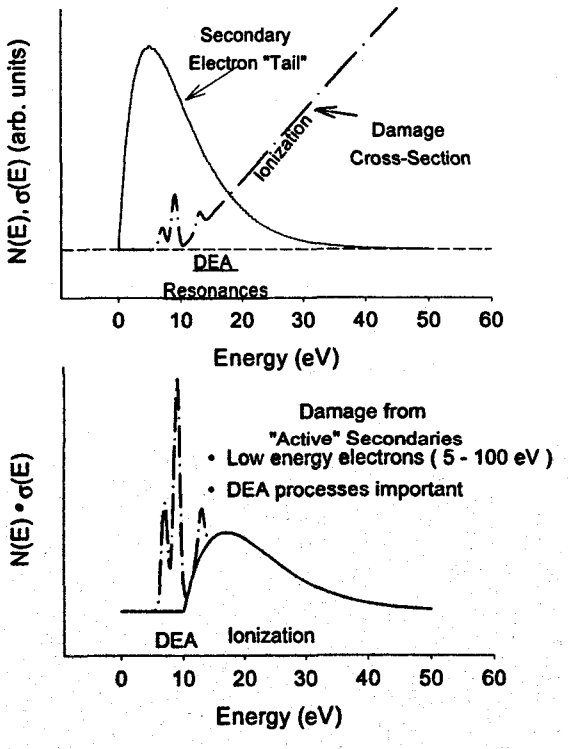


Fig. 4: Top Frame: Typical energy distribution of secondary electrons emitted from keV electron-beam irradiated insulators. Also shown are the estimated relative cross-sections for some of the main inelastic electron energy-loss channels that the secondaries undergo as they traverse the interface. Lower Frame: Estimate of the effective "damage" probability obtained by convoluting the energy-loss cross sections with the secondary electron energy distribution. The figure is from [IV.3].

effective "damage" probability of condensed layers of water due to ionization and DEA. It also demonstrates that interaction of low-energy electrons in a dense medium depends on the energy and "state" of the electron itself. Secondary electrons, which scatter inelastically with interface molecules also stimulate ion-molecule and reactive scattering events at an interface. The local potential and bonding configurations on surfaces or at interfaces can differ substantially from bulk configurations. Thus, the nature of excited states at surfaces can be altered due to changes in Franck-Condon factors associated with bond elongation of chemisorbed species. Configuration mixing with the electron density of the underlying substrate will also occur. Thus, electron impact dissociation cross sections can be greatly modified (enhanced or reduced) by the changes in the electronic structure and the local environment which is introduced by the interface.

Understanding and *controlling* the chemical and structural modifications which occur during and as a result of electron impact of surfaces and interfaces is critical in:

- the development of non-thermal processing technologies,
- the fabrication of semiconductor devices, nanostructured materials, and novel devices,
- assessing material stability and safety issues when dealing with mixed radioactive waste forms.

All of these key areas are of fundamental, technological, and environmental importance. Several of the underlying fundamental science issues which can help advance the progress in these key areas and which are or can be addressed by the communities studying electron-induced processes at surfaces and interfaces are discussed briefly in chapter V together with other applications.

The future perspectives in the field of electron-driven processes must include interdisciplinary research between the different communities such as atomic molecular and optical physicists, surface physicists and chemists and scientists (such as radiation chemists) who are concerned with the fundamentals involved in the interaction of radiation with matter. Suggested future directions in electron-induced processes in clusters and at surfaces and interfaces include, but are not limited, to the following:

- A particularly fruitful area of study using clusters involves electron transfer between two components of a heterogeneous cluster following resonant capture by one compound. These studies should give insight to solution-phase electron transfer processes.
- Ion-molecule reactions (e.g. nucleophilic substitution reactions) following DEA at one component in a binary cluster may also occur and provides the opportunity to study reactions with oriented reagents.
- Giant enhancements in DEA cross sections such as though observed in the gas-phase have yet to be studied in a systematic way using cluster beams. Such enhancements may be exploited to develop very sensitive and selective schemes for detection of trace species.
- Stabilization of temporary negative ion states on surfaces and in solids may well enhance the importance of core-excited resonances relative to their contributions in the gas phase. At present, DEA from such states is much less explored than DEA from the low-lying "shape" resonances in which the "parent" neutral molecule is in its ground electronic state. Much more effort needs to be devoted to determining the properties of these resonances and their

influence on DEA cross sections. Again, studies of these effects for families of closely related compounds will be most beneficial.

- Post dissociation interactions and ion-molecule reactions between molecules adsorbed on the surfaces or embedded in molecular solids is beginning to attract interest from several communities. *Despite these efforts, there are no complete measurements of the absolute cross sections, product quantum-state distributions or threshold energies for electron-induced reactions on surfaces and interfaces.* The application of the quantum-state and time-resolved techniques developed to study gas-phase processes should prove to be particularly fruitful and will provide a pathway to study the dynamics of condensed phase cation-, anion- and radical reactions in unprecedented detail.
- An added advantage to studies on surfaces is the ability to control geometries and impact parameters. Because electron-stimulated desorption (ESD) processes occur on timescales short in comparison with molecular vibration and rotation, positive and negative ions fly off the surface in directions determined by the ground state bond orientation. Measurements of ESD ion angular distributions (ESDIAD) and momentum-resolved ESDIAD, can provide unique insights into the structure as well as dynamics of molecules in adsorbed layers.
- The electron standing wave technique is also a potentially useful technique, which can be developed into a useful surface spectroscopy technique based on electron scattering. The spatial variability of the wave amplitudes may also be exploited to pattern surfaces, probably on the mesoscale.
- Electron-induced patterning of surfaces using the Scanning Tunneling Microscope (STM) shows great promise and approaches using arrays of STM tips should be developed. STM manipulation of single molecules and/or nanostructures is important and may lead to novel devices.
- Though time-resolved studies can not be done with conventional electron sources, electron-driven reactions can be observed on the ultra-fast time scale using femtosecond laser excitations. This is due to the non-equilibrium distribution of electron energies created by the laser beam. These types of studies enhance our basic understanding of chemical processes on surfaces and clearly demonstrate the importance of non-thermal (electron-induced) reactions.
- Electron interactions with aligned or oriented molecules either in the gas phase or adsorbed at surfaces is a comparatively new area both experimentally and theoretically [IV.4]. It is also an area that allows to study the transition from processes in the gas phase to processes at surfaces. The use of incident polarized electrons and/or the measurement of the polarization of scattered electrons is crucial in such experiments. Polarized incident electrons can be used to measure the degree of alignment/orientation of the target molecules or one can probe, if aligned molecules produce a spin asymmetry in the scattering process.

References

[IV.1] L. Sanche, Scanning Microscopy, **9**, 619 (1995)

[IV.2] A.D. Bass and L. Sanche, Rad. Environ. Biophys. **37**, 243 (1988)

[IV.3] T.M. Orlando and D. Meisel, ACS Book Series, Symposium on the First Accomplishments of the Environmental Management Science Program (2000), in press.

[IV.4] K. Blum, in "Novel Aspects of Electron-Molecule Scattering", K.H. Becker (Ed.), World Scientific Publ., Singapore (1998)

V. Applications of Electron-Driven Processes

Electron interactions, with a variety of different species and in a variety of environments, play a key role in creating the energetic species that drive the chemistry in these environments. Electron collisions also figure importantly in a number of chemistries driven by secondary electron cascades such as processes in mixed radioactive waste or in the plasmas used to destroy undesirable compounds or remediate NO_x. For example, modeling chemical vapor deposition requires the knowledge of the mechanisms and rates of formation of hundreds of radical and ionic fragments. Because of the wide range of applications of electron-initiated processes in the gas phase, at surfaces and interfaces, and in condensed matter, this section out of necessity can only address a few selected areas of application in depth.

V.1 Plasma Processing

Plasma etching, deposition and cleaning are indispensable fabrication techniques in the manufacture of microelectronics components. The plasma equipment for these processes typically use partially ionized (fractional ionization less than 1%), low pressure (a few mTorr – 1 Torr) plasmas to provide activation energy to dissociate and ionize feedstock gases. The resulting radicals and ions interact with the semiconductor surface, either removing or adding material, to define the desired features or modify the surface. The high cost of developing both the plasma equipment and processes has motivated development of less empirical methods, and modeling/simulation in particular, to speed the time to market and to reduce costs. Following a National Research Council (NRC) report in 1991 which cited the need for science-based design of plasma processes [V.1], a modeling and simulation infrastructure was developed which can now address a wide variety of plasma tools and surface processes.

The application of this modeling infrastructure to industrially relevant problems has, to date, been limited by the availability of fundamental data (e.g., electron impact cross sections, reactive surface sticking coefficients) and validated reaction mechanisms. This situation was described in a second NRC report, "Database Needs for Modeling and Simulation of Plasma Processing" [V.2]. Table 1 taken from this report summarizes some examples of processes and their chemistries for which data bases were required in 1995. Since the report, other chemistries and types of processes have come to prominence for which databases are also required. This situation, where old chemistries/processes fall from favor and new chemistries/processes quickly come to prominence, is typical of the rapidly changing needs of the microelectronics industry. For example, Ionized Metal Physical Vapor Deposition (IMPVD) is a method whereby deep vias can be filled or lined with metals for interconnect wiring. At the time of the NRC report IMPVD was an inconsequential process. Now, IMPVD is an exceedingly important process, and so brings with it needs for cross sections for metals, their excited states and ions. This rapid change in priorities emphasizes the need for developing rapid, computational techniques to produce cross sections on industrially relevant time scales. The importance of Ionized Metal Physical Vapor Deposition (IMPVD) is creating a need for cross sections for electron collisions with metal atoms, particularly for electron impact on excited states and ions. Most of the atomic data made available from the Opacity and Iron Projects can already be used for modeling purposes at sufficiently low energies, and the accuracy for transitions involving many targets with low and intermediate nuclear charge Z ($Z < 30$) may be increased if necessary. For intermediate energies, the above mentioned CCC and the recently developed "R-matrix with pseudo-states" (RMPS) methods have shown to give very reliable results for a few benchmark cases, and so have time-dependent close-coupling (TDCC) approaches. Both excitation and ionization can be treated in

these methods. Due to the computational demands, however, their application is currently restricted to simple quasi-one and quasi-two electron atomic targets that can be described in a non-relativistic model.

Table V.1: Examples of Processes and Their Chemistries for Which Databases are Required

Application	Cited in NRC Report (Including Fragments)	Gases Recently Coming to Prominence
p-Si Etching	Cl_2, Br_2, HBr, O_2, N_2	BCl_3, HCl
SiO_2 Etching	CF_4, CHF_3, C_2F_2, O_2, N_2, CO, Ar	c-C_4F_8
SiO_2 Deposition	SiH_4, O_2, N_2O, Ar, TEOS,	SiF_4
Metalion PVD		Cu, Al, Ti, Ba, W, Sr
Reactor Cleaning		NF_3, COF, COF_2

The databases (cross sections and rate constants) that support this modeling infrastructure are complete for only a small subset of the gas chemistries of interest. Fluorocarbon compounds (i.e., $C_xH_yF_z$) with admixtures of rare gases and O_2 are typically used for etching of crystalline silicon and silicon dioxide. Chlorine containing gases (e.g., Cl_2, BCl_3) are typically used for poly-silicon and metal etching. With the exception of CF_4 and to a lesser extent Cl_2, the electron impact and ion transport databases for these compounds are fragmentary, as is the database for reactive sticking coefficients of their radicals with the polymerized surfaces typically encountered in actual etching reactors. Since the majority of new plasma tools operate at low pressure and high plasma densities, the feedstock gases are highly fragmented, in some cases over 90% dissociated. These conditions emphasize the need for electron impact dissociation cross sections and cross sections for fragments of the feedstock gases.

The required accuracy of the database varies with the intended use. For example, to optimize the uniformity of plasma generation in an etching reactor, it is not necessary to employ the gases which will be used in the actual etch process. It is, however, important to use well-characterized gases whose behavior can be accurately modeled and which are representative of classes of the process gases. For example, well-characterized cross section sets might be required for a highly attaching easily dissociated gas mixture and a weakly attaching gas mixture which is largely undissociated. On the other hand, when "screening" large numbers of different chemistries, the required accuracy may not be as critical as being able to compare many different chemistries. Hence there are needs for both *ab initio* and semi-empirical methods for developing databases. The first maximize accuracy and are expensive, and the second rapidly produce databases at the cost of some degree of accuracy.

Because of the paucity of reliable experimental data for most of the relevant processes, it is important for producers of the calculated cross sections to closely collaborate with plasma equipment and process modelers who will use the data. By incorporating the data into the plasma models and reproducing experimentally observed plasma behavior (e.g., plasma density vs. gas mixture at constant power), one can obtain a "working" validation of the cross section sets. One area in which calculations can make an especially valuable contribution is the characterization of replacement gases with lower greenhouse potential than those currently used in the semiconductor industry. Although the need to identify such replacements is increasingly pressing, most of the candidate gases are as yet poorly studied experimentally. Calculations

using existing methodology can provide elastic and momentum-transfer cross sections for such gases, as well as excitation cross sections for the lowest-lying electronic states. Together with selective theoretical studies of dissociation on excited-state potential surfaces, calculations of this kind would aid in identifying the most promising gases for more detailed characterization.

V.2 Plasma Remediation

The ability of non-thermal, low-temperature plasmas (LTP) to destroy relatively low concentrations of volatile organic compounds (VOC's) at atmospheric pressure is well known. Interest in these technologies has grown recently due to the increase in global pollution control and environmental remediation activities [V.3]. These LTP processing techniques generally involve either high energy electron-beam irradiation or electrical discharge methods. In the latter case, examples using pulsed corona, dielectric barrier, capillary, hollow cathode, surface, and packed-bed corona discharges have all been reported. All of these techniques rely upon the fact that electrical energy can produce electrons with much higher average kinetic energies than the surrounding gas-phase ions and molecules. These energetic electrons can interact with the background gas to produce highly reactive species (i.e. radicals, anions, cations, and secondary electrons) that will preferentially destroy pollutants (VOC's).

Low-temperature plasmas are particularly attractive for treatment of low-level waste concentrations and for dealing with compounds that resist treatment by standard chemical means. One important class of these compounds is halogenated compounds such as carbon tetrachloride (CCl_4), trichloroethylene (C_2HCl_3) and hexaflouroethane (C_2F_6). The destruction and treatment of such compounds is particularly important since some of the chlorinated solvents were used for decades in a wide variety of processing applications. For example, CCl_4 has been used extensively in the chemical processing of irradiated nuclear materials [V.4]. At the Department of Energy's Hanford site in Washington State, several hundred thousand gallons of liquid CCl_4 were discharged over the 40+ years of plutonium production. Presently, the most contaminated spots contain ~ 8000 ppb of CCl_4 in the groundwater which greatly exceeds the drinking water standard of 5 ppb.

Remediation of large inventories of halogenated solvents clearly relies upon the development and deployment of effective and efficient treatment methods. In packed-bed coronas, the high frequency of surface collisions involving reactive and/or energetic species suggests that surface mediated processes could also effect the overall plasma efficacy. The synergism between the electron-induced plasma chemistry and surface reactions can be exploited in the treatment of waste streams as well as in reduction of nitrogen oxides in highly oxidative combustion exhaust streams. Such an approach is being developed for the treatment of diesel and automotive exhaust emissions and thus, technologies involving electron-molecule scattering may help in the reduction of urban pollution from non-stationary sources.

In addition, one can extend the concept of chemical destruction to chemical synthesis in plasmas. For example, controlled oxidation of alkanes is one of the "Grand Challenges" of industrial chemical research because of the tendency of the oxidation process to lead to the thermodynamic sink products, CO and CO_2. The ability to specifically control the site and amount of oxidation would enable the use of cheap feedstocks (simple alkanes and alkenes) to make a wide range of intermediates for further synthetic changes. In order to develop new industrial-strength processes that are more energy efficient and produce less waste, new types of technologies need to be developed. One such technology which is being investigated is the gas phase corona reactor (GPCR). The phenomena of significantly enhanced reaction rates in a gas

phase plasma raises the potential of utilizing a non-equilibrium plasma for chemical synthesis reactions. Only ozone formation has to-date proven economic and several other plasma-assisted volume chemical reaction processes are currently being explored in terms of their economical feasibility e.g. in the petrochemical industry. It is generally recognized that plasma reactions feature the advantage of producing high energy active species which can produce different reaction pathways than those available through traditional thermal activation. However, the reaction pathways have, so far, not been controllable and have consumed too much power. Computational research would significantly enable this field to become more competitive with traditional synthesis methodologies.

V.3 Applications to Atmospheric Science and Astrochemistry.

Electron scattering is providing useful information for the applied research community far beyond the previously mentioned plasma processing and environmental applications. For example, an extensive European initiative was started to re-visit the issue of electron interactions with those molecules playing a key role in stratospheric ozone depletion. Preliminary research has led to the discovery of new coupling mechanisms between the upper stratosphere and the lower ozonosphere. Electron energy loss spectroscopy has provided the first conclusive evidence for the bound nature of low-lying electronic states of the ozone molecule (which is an important criteria for understanding ozone chemistry in both the stratosphere and urban conurbation), and has demonstrated possible isomerization reactions on aeronomic ice surfaces. The work of Allan et al. [V.5] appears to have established the metastable character of at least two low-lying states of ozone. These states can act as n energy sink and their role in ozone depletion mechanisms may have to be re-evaluated by atmospheric modelers.

Electron scattering experiments also provide new information on the role of ozone (and some other moleucles) on the processes in the Earth's ionosphere. The D-layer, at altitudes between about 60 km and 90 km, is of particular interest, since it is the region of importance in radio communication. It is also the critical region in the interaction between the ionosphere and the lower stratosphere where terrestrial ozone chemistry is dominant. The processes in the D-region are dominated by negative ion formation and their reactions. The recent work of Senn et al. [V.6] demonstrated the existence of a rather large and very sharp peak in the O^- formation from O_3 by DEA at or close to zero impact energy, which, in turn, results in an O^- rate constant considerably higher than what was derived from earlier experiments. This has consequences far beyond a simple adjustment of one of many rate constant in the codes employed in the modeling of the processes in this region of the atmosphere. It would indicate the possibility of a direct coupling mechanism between the lower ionosphere and the Earth's ozone layer and thus predict that alterations in global ozone concentrations may affect terrestrial radio transmissions.

Electron spectroscopy will also play an important role in understanding the spectroscopy and dissociation pathways of molecules in planetary atmospheres (other than the terrestrial atmosphere) and within the interstellar medium. Electron-driven processes on surfaces (ices and/or dust grains) are also likely to be an important field of research in both atmospheric science and astrochemistry where heterogeneous chemistry has been demonstrated to be a dominant process in molecular formation and reactions.

V.4 Non-Thermal Processing

An obvious fundamental goal of surface scientists is to control the reactivity and properties of surfaces since such advances would have major impacts in catalysis, materials

engineering and the development of fabrication and processing technologies. Attempts to control chemical processes at the fundamental level using electronic excitations have been reported using the Scanning Tunneling Microscope. For example, one of the most exciting developments in this area is the use of STM to cleave specific (e.g., Si-H bonds) bonds on surfaces and as a technique of "writing" at nearly atomic resolution on surfaces [V.7]. There has been considerable speculation as to the specific mechanism by which the emitted electrons cause the bond cleavage, with the production of repulsive electronically excited states, direct vibrational excitation of the ground state, and formation of temporary anions (which upon decay produce the highly vibrationally excited ground state) all having been proposed. High quality calculations could play a valuable role in establishing the relative importance of the various mechanisms, which, in turn, would aid in establishing the optimal conditions for use of the STM method for patterning surfaces. Theoretically, these processes present the challenge of accurately treating the influence of the neighboring surface atoms on the dissociation dynamics of surface bonds. Exciting examples of nanoscale manipulation or ***single-molecule engineering*** using the STM have also been reported [V.8].

Other attempts to control chemical processes at the fundamental level using electronic excitations have been reported which take advantage of quantum mechanical interference effects between the incident electron wave and the elastically scattered wave [V.9]. The electron wave induced interference patterns result in spatially selective removal of surface adatoms or molecules and may be useful for mesoscale patterning of surfaces. Another useful technique that involves selective electronic excitation is surface photochemistry. Recent results using ultra-fast laser excitations show the importance of electron scattering since the laser intensities (pulsed power) typically involved create very high densities of non-thermal electrons. The multiple scattering events these electrons undergo can stimulate reactions prior to thermalization. For example, electron-mediated desorption and oxidation of CO on Ru(0001) has been demonstrated using femtosecond infrared laser pulses [V.10]. The desorption is caused by coupling of the adsorbate to the phonon bath of the ruthenium substrate, *whereas the oxidation is caused by hot electrons!*

V.5 Electron-Induced Processes in the Environment

The study of chlorofluorocarbons (CFC's) is a subject of widespread scientific and public interest. Because of industrial activities, CFC's, mainly $CFCl_3$ (CFC-11) and CF_2Cl_2 (CFC-12), have been emitted into the atmosphere and cause depletion of the ozone layer via production of reactive chlorine atoms from photodissociation. It is generally accepted that heterogeneous reactions (e.g., on surfaces of ice particles in polar stratospheric clouds) play a key role in this process. Other gas phase and heterogeneous processes where thermal and non-thermal activation of CFC's are of importance include environmental clean-up and dehalogenation of CFCs, plasma etching in semi-conductor processing, understanding toxicity of CFCs in the presence of electron donors such as anionic enzymes, and CFCs as electron scavengers in solid-state chemistry and high-voltage breakdown. *A major challenge is to characterize and understand how low energy electrons induced dissociation of CFCs adsorbed on surfaces, in particular, when coadsorbed with water.* Measurements indicate that dissociation of CFCs by non-thermal processes (electron bombardment) is greatly enhanced by coadsorption [V.12]. Recent experiments have also shown orders of magnitude enhancements for the electron attachment to halogenated hydrocarbons adsorbed or embedded in multilayers of Kr [V.11]. The underlying mechanisms for the enhancements are related to lifetime and charge transfer effects. Progress has been made in adapting semi-empirical treatments of the gas-phase process (for diatomic molecules) to the

problem of DEA in these more complex environments and respectable agreement with experiment has been achieved in some cases [V.13].

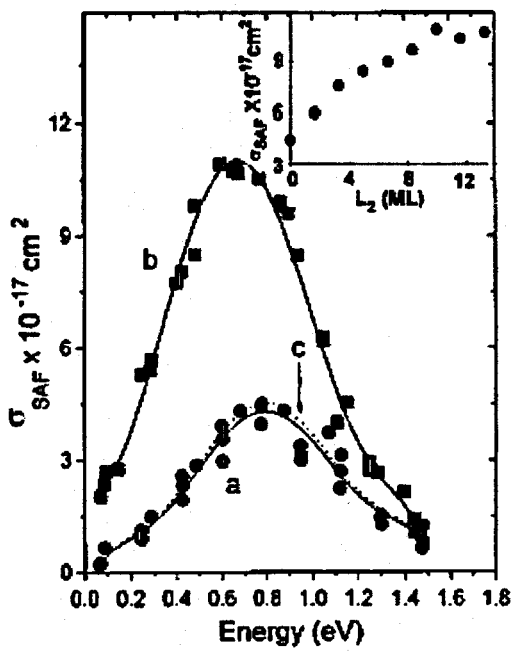


Fig. 5: Variation of the cross section for negative ion formation with incident electron energy for CF_3Cl deposited onto the surface of a 13-ML-thick film (a). Cross section with 13-ML-thick Kr film overlayer added. The figure is from [V.11].

Mixed (radioactive/chemical) wastes present in underground storage tanks contain complex mixtures of sludges, salts, and supernatant liquids. These "mixtures", which contain a wide variety of oxide materials, aqueous solvents and organic components, are constantly bombarded with energetic particles produced via the decay of radioactive ^{137}Cs and ^{90}Sr. The high-energy particles produced during these decay events lose energy mainly via interaction with the effective electron density of the "atomic" targets. *These "primary" energy loss events eventually lead to the production of copious numbers of secondary electrons whose inelastic scattering ultimately determines the chemistry which occurs.* Low-energy electrons are ubiquitous in radiation environments and initiate many processes and chemical reactions. Currently, there is a vital need to understand electron interactions with water, organic and inorganic species present in radioactive mixed waste storage tanks since these processes can (i) produce mixtures of toxic, flammable and potentially explosive gases (i.e. H_2, N_2O and volatile organics) (ii) degrade organics and reduce hazards associated with nitrate combustion reactions and (iii) alter the surface chemistry of insoluble colloids in tank sludge, influencing sedimentation and the gas/solid interactions that may lead to gas entrapment. Understanding the inelastic scattering of low-energy electrons with molecules such as water is also important with respect to the safe interim and long-term storage of spent nuclear fuel (SNF). Thousands of tons of metallic uranium SNF remain in water storage. For example, the Hanford site K-basins hold 2300 tons of SNF, much of it severely corroded [V.14]. Plans have been proposed to remove this fuel and seal it in overpack canisters for "dry" interim storage, for up to 75 years awaiting permanent disposition. Chemically bound water may remain in cracks and bound to surfaces and interfaces even following proposed drying steps. Safety concerns are related to the non-thermal

production of potentially explosive mixtures of hydrogen and oxygen gas in storage canisters. Studies on water thin-films indicate that dissociative electron attachment resonances [V.15] and the decay of excited states [V.16] created directly or via ion-electron recombination can lead to the direct production of molecular hydrogen. Unfortunately, the relative importance of these channels (dissociative electron attachment and dissociative recombination), ionization and reactive scattering of radicals and hot atoms on the production of molecular hydrogen and oxygen in SNF canisters have not been fully resolved. This is largely due to the fact that the theoretical and experimental information available on electron-driven processes in the gas, condensed and interfacial phases is insufficient to develop models which adequately describe waste issues.

V.6 Nanostructures and Electron-Emitting Devices

Understanding the electron- and photon-induced processes in nanoparticles is very important in electrocatalysis and photocatalysis. Nanodevices are being constructed with nanoparticles and nanostructures, which can be used as novel sources of low-energy electrons. Particularly useful technologies based on metal-insulator-metal devices and nano-fabrication techniques [V.17] are being developed which may have enormous impacts on the study of electron-induced processes on surfaces and interfaces. These devices can be spatially (nanometers) and energy (only a few meV) resolved electron sources and should prove useful in selective excitation of molecules. These devices can also be assembled in arrays and may prove useful as gas processing technologies.

The realization of nanometer-scale resolution necessary for the exploitation of novel quantum effects in new electronic and optical devices will also be achieved using lithographic techniques, many of which are electron-beam based. The importance of this continuing effort to "shrink" circuits and the role of electron-induced processes is summarized in "*Nanolithography: A Borderline Between STM, Electron-Beam, Ion-Beam, and X-ray Lithographies*", Gwentili, M., Dor,drecht, Boston: Kluwer Academic Publishers (1994).

References

[V.1] "Plasma Processing of Materials: Scientific Opportunities and Technological Challenges", National Research Council, National Academy Press, Washington DC (1991)

[V.2] "Database Needs for Modeling and Simulation of Plasma Processing", National Research Council, National Academy Press, Washington DC (1996)

[V.3] R. A. Frosch, Sci. Am. **283**, 180 (1995)

[V.4] D.L. Illman, Chem. Eng. News, **71**, 9 (1993)

[V.5] M. Allan et al., J. Chem. Phys. **105**, 5665 (1996)

[V.6] G. Senn et al., Phys. Rev. Lett. **82**, 5028 (1999)

[V.7] T.-C. Shen et al., Science **268**, 1590 (1995)

[V.8] B. C. Stipe et al., Science **279**, 1907 (1999)

[V.9] M. T. Sieger et al.,, G. Schenter, and T. M. Orlando, Phys. Rev. Lett. **82**, 3348 (1999)

[V10] M. Bonn et al., Science **285**, 1042 (1999)

[V.11]. K. Nagesha and L. Sanche, Phys. Rev. Lett. **78**, 4725 (1997)

[V.12] Q.-B. Lu and T. Madey, Phys. Rev. Lett. **82**, 4122 (1999)

[V.13] L. Sanche, A. D. Bass, P. Ayotte and I. I. Fabrikant, Phys. Rev. Lett. **75**, 3568 (1995)

[V.14] Record of Decision: "Management of Spent Nuclear Fuel from the K-Basins at the Hanford Site", Richland, Washington DOE/ROD-6450-01-P (1996)

[V.15] G.A. Kimmel and T.M. Orlando, Phys. Rev. Lett. 75, 2606 (1995)
[V.16] G.A. Kimmel and T.M. Orlando, Phys. Rev. Lett. 77, 3983 (1996)
[V. 17] A. A. Driskill-Smith et. al., App. Phys. Lett. 75, 2845 (1999)

VI. Educational Opportunities

Experimental students studying electron-induced processes, e.g. observing the effects of electron collisions with molecules in a variety of environments, learn a wide range of topics. Students design, build, and put together varied modern apparati, a process during which they learn to operate and understand lasers, electron and atomic beam systems, discharge systems, metal vapor systems, electronics and computer interfacing, and computer control and process simulation. The students will be exposed to state-of-the art research instrumentation used in atomic, molecular, and optical physics, chemical physics, plasma physics, surface science, and condensed matter physics. They will learn to integrate knowledge and expertise from different sub-fields of physics and chemistry, work in teams as well as independently, establish communication and interpersonal skills, and mature to becoming first-rate scientists.

When integrated with the appropriate coursework, the intense apprenticeship of graduate and postgraduate work in the area of electron-driven processes greatly benefits the development of a well-trained pool of skilled future scientists and engineers in the US who will be ready to continue the tradition of their discipline in an academic teaching and research environment, in an industrial research and development laboratory, as an entrepreneur, or in a National Laboratory.

There is a growing need for scientists and engineers who are skilled at working together in teams to solve complex problems that are inherently multidisciplinary. Studies of electron-driven processes are ideally suited for training students at all levels (undergraduate, graduate, postdoctoral) in this mode of research. Theory will require a new generation of computer codes which will necessarily combine algorithms from different areas of computational chemistry/physics and will have to be designed to perform well on parallel processing computers. Furthermore, the systems to be studied are important in a wide range of applications, including modeling of plasma processing in fabrication of electronic devices and modeling of atmospheric chemistry. On the computational side, it will be necessary to develop computer programs that more closely integrate state-of-the-art algorithms from the electron scattering and electronic structure communities. Moreover, for tackling complex systems (e.g., polyatomics with a large number of energetically accessible states) it will be necessary to develop software that effectively exploits parallel processing platforms. Building that software will require students and postdoctoral fellows with individual expertise in scattering theory, electronic structure methods, and software methods for parallel computers to work together in teams that may include chemists, physicists, applied mathematicians, and computer scientists. The synergy of such efforts allows for the development of the highest performing software with the best algorithms and the longest in-use lifetime. Thus, the participants working on these projects would gain valuable experience in working in teams. This experience, combined with the skills and knowledge about computer architectures that they will acquire, would help prepare them for a range of jobs in the computer modeling/simulations area.

The students involved in the theory and computation aspects of electron-driven processes will, by necessity, learn the techniques of massively parallel computation and modern visualization technology. In addition, the numerical algorithms that they will develop and the ones they will adapt from other areas will be at the forefront of the transformation of high-end computational science to massively parallel computing. Modern computer science is transforming not only the tools but the practice of computational science. A new generation of graduate students has appeared who consider the proper graduate curriculum to be a combination of computer science and physics. Those students will be in high demand in areas outside of the

sub-disciplines of physics in which they do their thesis work, and there is no better training for them than work in the theory of electronic collisions in the gas and condensed phases.

Research in the area of electron-driven processes offers exceptional educational opportunities for undergraduate students to become involved directly in the various aspects of the research. Undergraduates can contribute to all aspects of electron-driven processes from the laboratory to the terminal. This experience prepares students well for graduate school and industry. Electron-driven processes provide an ideal instructional environment for undergraduates who may undertake a variety of tasks. With proper guidance, the may assist in the design and building of pieces of an experimental apparatus, analyze and evaluate data, or write computer software, interface experiments to computers and run computer simulations. A critical mass of undergraduates in the laboratory often creates an environment where they will teach each other the skills needed to tackle tasks, such as using programming languages, operating equipment, and developing data acquisition and measuring processes. Laboratories benefits from undergraduate student involvement for a number of reasons – this has been recognized, for instance, by the National Science Foundation (NSF), which has been running a rather successful Research for Undergraduates (REU) program in the form of dedicated REU sites and supplements to individual grants to enable the research participation of undergraduates in research projects funded by the NSF.

VII. Summary and Conclusions

Electron interactions with molecules, clusters, surfaces and interfaces are at the center of many applications in areas ranging from radiation chemistry, environmental chemistry, stability of waste repositories, plasma-enhanced chemical vapor deposition, plasma processing of materials, novel light sources, and even in the life sciences. Yet, the level of understanding of electron-initiated processes at the microscopic level is rather fragmentary. It is safe to say that the level of understanding of electron interactions with molecules in the gas phase far exceeds our insights into electron interactions with clusters, surfaces, and interfaces. Nonetheless, there are still many aspects of the interaction of an electron with a molecule in the gas phase under well-defined single conditions that have received little or no attention.

It is apparent from this report that major progress in the future in the area of electron-driven processes must include interdisciplinary research between different communities such as atomic, molecular, and optical physics, surface physics and chemistry and the physics and chemistry that is concerned with the interaction of radiation with matter. It is also apparent from this report that significant future progress can only be achieved if experiment, theory, computation, and simulation work hand in hand and coordinate their respective efforts. This collaborative effort must involve (i) case studies of selected species or families of species, (ii) benchmarking between selected measured and calculated cross sections and other quantities, (iii) experimental and/or theoretical verification of the predictions of computer simulations, and (iv) studies along well-defined sequences and for species with similar properties and/or structure.

For the experimentalist studying electron-molecule interactions in the gas phase, the most challenging area of future endeavor is the study of molecular dissociation processes following excitation of higher-lying repulsive states. Such studies must include a complete mapping of the spectrum of dissociation fragments, i.e. a quantitative determination of the branching ratios leading to various combinations of final products including neutral ground-state fragments, excited fragments, and positively as well as negatively charged ionic fragments and studies of the kinetic energy distributions of the various fragments. The quantitative detection of neutral ground-state fragments poses perhaps the biggest experimental challenge. Experimental techniques and detection schemes (pulsed as well as cw) that have been developed and successfully used e.g. by chemists in reaction dynamics studies must be adapted to single-collision conditions and incorporated into crossed-beam experiments. Other future challenges include, but are not limited to (i) experiments involving targets in well-characterized ro-vibrational states such as vibrationally "hot" molecules in well-defined vibrational states, (ii) studies of targets in states other than the electronic ground-state, (iii) quantitative investigations of the routes and the time scales of the decay of high-lying excited states, and (iv) experiment in the presence of intense fields.

Future directions in experimental studies of electron-induced processes on clusters, at surfaces and at interfaces need to address the important question of how gas phase concepts have to be modified as the targets become larger, more complex, and interactions between adjacent molecules become increasingly stronger. Some promising areas include:

- Electron transfer between two components of a heterogeneous cluster
- Studies of giant enhancements in DEA using cluster beams which may lead to the development of very sensitive and selective schemes for detection of trace species
- Stabilization of temporary negative ion states on surfaces and in solids which may enhance the importance of core-excited resonances relative to their contributions in the gas phase

- Post dissociation interactions and ion-molecule reactions between molecules adsorbed on the surfaces or embedded in molecular solids; the application of the quantum-state and time-resolved techniques developed to study gas-phase processes should prove to be particularly fruitful and will provide a pathway to study the dynamics of condensed phase cation-, anion- and radical reactions in unprecedented detail.
- Electron-induced patterning of surfaces using the Scanning Tunneling Microscope (STM) shows great promise for the manipulation of single molecules and/or nanostructures
- Observation of electron-driven processes on the ultra-fast time scale using femtosecond laser excitations
- Electron interactions with aligned or oriented molecules either in the gas phase or adsorbed at surfaces using incident polarized electrons and/or a measurement of the polarization of scattered electrons

While there have been remarkable calculations for a number of diatomic and a few polyatomic molecules that treated this problem with varying levels of success, they have in general not taken advantage of many of the developments in bound-state quantum chemistry of the past fifteen years. The difficult electronic continuum problem for polyatomics has been formulated outside the context of bound state electronic structure, and components of modern quantum chemistry technology have been grafted onto it.

Another major observation that emerged from the discussions at the workshops is the simple statement: *It makes no sense to build the next generation of electron scattering codes and theories outside the context of the rich bound state quantum chemistry infrastructure of codes and approaches which now exists.* Moreover, the problems associated with electron driven

Table VII.1: Summary of Theoretical/Computational Challenges

Area/Problem	**Fundamental Questions**	**Scale of Calculations**
Electronic excitation	Do close-coupling expansions converge?	Very large, equal to largest quantum chemistry
Dissociation	What are the branching ratios and dynamics on excited polyatomic surfaces?	Largest, larger than current reactive scattering
Dissociative Attachment and Dissociative Recombination	What is the importance of multidimensional effects in nuclear dynamics?	Largest, but even more complicated than simple dissociation
Ionization	There is no known formulation that is practical for molecules	Very large, even atomic calculations tax current computers
Electron transport	The N and N+1 electron correlation problems are not optimally described by conventional CI methods	Large
Condensed phases/ Interfaces	How can gas phase methods be extended to condensed media?	Largest, at least of the scale of the largest materials calculations now contemplated

chemistry cannot be solved by any other theoretical approach. These two communities must collaborate to address these questions, or they will not be answered. In both the major areas of application discussed below, there are issues of timeliness as well as of accuracy of the required results. The consensus is that only a broad collaboration between the quantum chemistry and electron scattering theoretical communities, which produces a new approach to this problem from the existing theoretical components, can successfully produce results on a relevant time scale.

Finally, it has become clear that the scale of computer resources required for these calculations rivals that of any quantum chemistry application to the bound electronic states of even very large molecules. The complications of simultaneously treating the continuum and bound electrons, even for targets with less than ten atoms, will stress the largest massively parallel computers currently available in the world. The extension of these calculations to the condensed phase is a daunting computational task. It is as great as any that has been contemplated for the future computational resources that are likely to exist as massively parallel computers extend to tens of thousands of processors.