

GAS-PHASE
CHEMILUMINESCENCE
AND CHEMI-IONIZATION

GAS-PHASE CHEMILUMINESCENCE AND CHEM IONIZATION

edited by

ARTHUR FONTIJN

*Department of Chemical Engineering
and Environmental Engineering
Rensselaer Polytechnic Institute
Troy, NY 12180-3590*

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PREFACE

The phenomena of chemiluminescence (or more broadly chemi-excitation) and chemi-ionization have major similarities from a fundamental kinetic and dynamic point of view. However, since the former has primarily been investigated using optical spectroscopic techniques and the latter largely by mass spectroscopic (and other gaseous electronic) methods, the two phenomena have apparently never explicitly been discussed together in one volume. In addition to a number of review articles on each individual subject, several meetings and books have had chemiluminescence and bioluminescence as their theme; those have been dominated by condensed phase work. On the other hand, chemi-ionization is often discussed in the context of gaseous electronics, plasma chemistry, and combustion. It is the goal of this book to present a more unified understanding of the two phenomena.

This up-to-date overview is aimed at both workers in the field and at relative novices, such as beginning graduate students. Especially to aid the latter, the individual authors have been asked to include a brief review of their subject and to point out fruitful areas for future research. The introductory chapter should further help the non-specialist. While the field is primarily approached from a fundamental chemico-physical and physico-chemical direction, the practical significance of some of the findings is pointed out and in some places emphasized.

Both chemi-ionization and chemiluminescence have shown many interesting new developments in recent years. Compared to earlier discussions, where mechanistic aspects dominated, many of the papers here are aimed at understanding the reaction dynamics. The use of electron spectroscopy and of electronic and infrared optical spectroscopy of chemi-ions is beginning to provide an insight into the dynamics of their formation at a level of detail similar to that of neutral chemi-excitation. Two chapters on the chemiluminescence resulting from ion-molecule reactions provide a further bridge between the fields. Topics discussed include homogeneous reaction dynamics and kinetics, collisional ionization in laser fields, quenching and energy transfer, reactions in chemical lasers, upper atmospheric chemiluminescence, as well as electronic and vibrational excitation resulting from gas-solid interactions. The use of chemiluminescent reactions in environ-

mental monitoring and recent observations on chemi-ions in flames round out the subjects discussed.

Many of the individual chapters were presented in preliminary form at a symposium I organized for the Physical Chemistry Division of the American Chemical Society, held in Philadelphia in August 1984. To arrive at a well-rounded quality book, all chapters have been refereed and several additional chapters have been included.

I would like to thank the authors, referees and speakers for their contributions, which have made this book and the symposium such a worthwhile endeavor. Special thanks are due to Professor R.N. Zare, who kindled the interest of the publisher, and Professor D.W. Setser, who actively supported the idea of a symposium on chemiluminescence and chemi-ionization. I thank J.E. Mulson and A. D'Allesandro for their help with the organization. J. Hyatt superbly assisted in the preparation of the subject index.

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Arthur Fontijn
Rensselaer Polytechnic Institute
Troy, NY 12180-3590
U.S.A.

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INTRODUCTION AND OVERVIEW

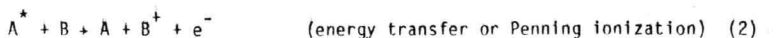
Arthur FONTIJN

Department of Chemical Engineering and Environmental Engineering,
Rensselaer Polytechnic Institute, Troy, NY 12180-3590, U.S.A.

The concepts chemi-ionization, associative ionization, Penning ionization, chemi-excitation and chemiluminescence are discussed with examples. The scope for the subjects is set and relations between the various chapters shown. To aid the non-specialist, references to authoritative earlier books and reviews are emphasized. A few areas of investigation, not discussed in detail in the following chapters, are briefly described here. Application aspects are pointed out.

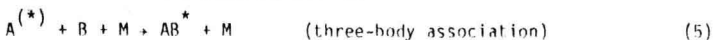
In earlier reviews^{1,2} chemi-ionization (CI) has been defined as "a process by which the number of elementary charge carriers is increased as a direct result of the formation of new chemical bonds". Chemi-excitation (CE) similarly may be defined as "a process by which excited species are formed as a direct result of the formation of new chemical bonds". Chemiluminescence (CL) is the process by which the excited species formed radiate. Even though CL is thus a secondary phenomena, and the prime interest from a fundamental chemical kinetic/dynamic point-of-view is the excitation process, the term chemiluminescence is almost universally used. Similarly, processes in which the excitation and ionization result from energy transfer, often from long-lived reaction intermediates, are frequently described as CI and CE or CL. In addition to papers obeying the more narrow definitions above, such work is included in this volume. However, the emphasis is placed on work in which the ionization and excitation result from a well-defined single reaction step in which a new bond is formed.

Reactions of interest thus include

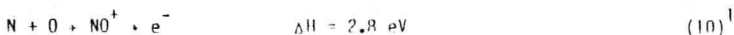




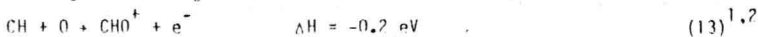
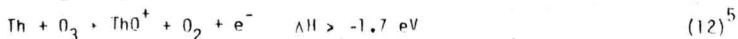
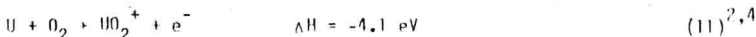
and their excitation analogues, such as



The (*) in these equations indicate that examples are known of reactions of these types both for excited and ground state species at thermal velocities. A relatively recent review discussing the competing channels for reactions of excited atoms is that by Donovan.³ Many exoergic reactions of ground state species are chemiluminescent, even at room temperature. By contrast ionization requires generally more energy, and most chemi-ionization reactions involve an excited reactant. There are however a number of associative ionization reactions known^{1,2} of ground state species, these include endoergic processes such as



observed in shock heated air at $T > 2500 \text{ K}$, exoergic reactions such as



and the alkaline earth atom/halogen molecule reactions discussed in the chapter by Menzinger. Reaction (13) is responsible for the formation of chemi-ions and electrons in hydrocarbon flames. It has also been observed in atomic oxygen reactions near 300 K .^{1,2,6} The free electrons from Reaction (13) are of interest in technology, e.g. in magnetohydrodynamic power generation, and can

[†]The parentheses in Reactions (3) and (4) indicate that these reactions may also lead directly to negative ions C^- ; they can be described as ion-pair formation processes.

act as an interference in radiocommunications with rockets.⁷ While Reaction (13) involving ground state $\text{CH}(X^2_{II})$ has been accepted as the dominant chemi-ionization reaction in non-sooting flames^{1,2} the chapter by Cool and Tjossem shows that the $\text{CH } A^2_{\Lambda}$ and $B^2_{\Sigma^-}$ states have rate coefficients for CHO^+ formation some 2000 times larger than the ground state, which raises the question of the importance of their reactions. The presence of these short-lived excited CH states in flames is known from their chemiluminescence and the problem is to determine the steady-state concentration ratios of the three CH species. In very fuel-rich sooting flames there is some evidence for another unidentified chemi-ionization reaction.^{8,9} Whether such ions can be significant in soot formation (an important practical combustion problem),¹⁰ remains to be established.

The most recent major development in chemi-ionization is that of laser-induced or enhanced chemi-ionization. Laser-pumping of a reaction intermediate, such as discussed by Cool and Tjossem, or of a primary reactant, is an important new but relatively straightforward method. However, direct pumping of the transient collision complex, as discussed in the chapter of Winn, is a fascinating development. The theory of chemi-ionization in laser fields forms a significant part of the contribution by Saha *et al.* Theirs, and the chapter by Yench, are the principal ones discussing current understanding of the theory of chemi-ionization. Yench has recently prepared an extensive review of Penning ionization.¹¹ In the present volume he also discusses the competition between Penning and associative ionization channels and gives an overview of the experimental techniques in use for observing these phenomena. Several of these techniques are further mentioned, where appropriate, in other chapters dealing with chemi-ionization.

In a wider context, we are not only interested in the competition between Penning and associative ionization, but also in the competition between reaction channels leading to ionized products and those giving rise to various electronically excited states and the ground electronic state of the product.

For one group of reactions, that between alkaline earth atoms (Be, Mg, Ca, Sr and Ba) and halogen molecules, this is extensively discussed here by Menzinger, who further compares the reactivities of the ground and metastable excited atom states. In Jordan's chapter a more general theoretical discussion of the competition between various reaction exit channels, i.e. of branching ratios, is given. The next step is the determination of the complete electronic, vibrational, rotational distribution of the original chemi-excited products, i.e. the nascent distribution. This problem is discussed in many places in this volume, especially in the chapters by Ottinger, Hamilton and Leone, Agrawala and Setser, and Prisant and Zare. Determination of such distributions from the observed chemiluminescence spectra tends to be a hard task. As two of these chapters deal with infrared chemiluminescence from vibrationally excited states and two with the more difficult deconvolution problem of emissions from electronically excited states, a good insight into the current approaches to the elucidation of nascent distributions is obtained. Determination of nascent product distributions provides a basis for comparison to theory. The many entries in the subject index on potential (energy) surfaces, simulated spectra, *ab initio*, classical, quasi-classical, etc. calculations testify to the current success in moving chemiluminescence from an observational field to one in the mainstream of the emerging understanding¹² of reaction dynamics.

Another important problem which continues to receive major attention is to establish how different forms of reactant energy influence chemical reactivity.^{13,14} One aspect of this problem, on which information has begun to become available in recent years, is that of spin-orbit excitation. It is discussed in several chapters, particularly those by Dagdigian and Alexander. The subject is not peculiar to chemiluminescence studies, but chemiluminescence offers a particularly convenient way for studying it. It is advantageously complemented by laser-induced fluorescence observations on ground and metastable states.

Most work on gas-phase chemiluminescence has been concerned with reactions between electrically neutral species. Ion-molecule reactions require other experimental techniques, which often are not readily adaptable to optical observations.^{15,16} However, the energetics of many of these reactions is such that excited ionic and neutral products can reasonably be expected. Indeed excited intermediate products have been invoked to explain some of the observations, and the decrease in appearance potential values of neutral products can be used to determine the degree of their excitation. Experimental difficulties involved in attaining electronic and vibrational chemiluminescence spectra from ion-molecule reactions have been overcome. Ottinger and Leone, in their respective chapters, give an overview of their work in this area. Light emission aspects of ion reactions are further discussed by Bowers.¹⁷

The experimental techniques for studying chemiluminescence are discussed in several places in the appropriate chapters. Additionally, gas-phase chemiluminescence is used as a diagnostic tool in laboratory kinetic and fluid dynamic experiments, in studies of the upper atmosphere and for monitoring of trace gases such as air pollutants. Such applications have been described in earlier reviews.^{18,19} More recent developments related to the atmosphere are discussed in the chapters by Ogryzlo and Stedman.

There are further practical aspects to the study of chemi-excitation and chemiluminescence. Thus observations on excited species resulting from surface catalysis, discussed here by Halstead *et al.* and by Halpern and Kori, may be expected to contribute significantly to the understanding of catalysis and hence to be of major importance to chemical industry. Another subject of current research is the feasibility of a purely chemical electronic transition laser (CETL) operating in the visible or uv part of the spectrum. Chemical lasers are devices in which the excited species at the upper laser level result from a chemical reaction.[†] Chemical lasers operating on ground

[†]Excimer lasers²⁰ involve an electronically excited reactant, produced by an electrical discharge, and are usually not considered to be CETLs.

electronic state vibrational transitions have been in existence for some time, e.g. hydrogen halide lasers.^{21,22} The chapter by Agrawalla and Setser discusses the energy distribution in reactions leading to vibrationally excited hydrogen halides. However, only one CETL has been demonstrated thus far: the oxygen-iodine laser which emits at 1315 nm, i.e. in the near infrared.^{23,24} The first step toward developing a CETL is to find a reaction capable of producing a population inversion of a level of an electronically excited state with respect to the ground state or a lower excited state.^{21,22} Hence a chemi-excitation reaction with a large branching ratio for formation of a particular excited state could provide an inversion. Excited states with a radiative lifetime on the order of 10^{-5} to 10^{-3} s are preferred.²⁵ Shorter-lived states are not desirable because the rapid rate of radiation would lead to inadequate concentrations of products in the upper excited state and longer-lived states have too low a probability for stimulated emission. Thus chemiluminescence, as distinct from chemi-excitation, is a nuisance effect in an actual device by decreasing the concentration of excited species available for stimulated emission. Nonetheless high chemiluminescence quantum yields, i.e. the fractional number of photons emitted per molecule reacted, are a convenient indication of large branching ratios when searching for suitable reactions. Because of energy transfer effects, such as quenching, the quantum yield gives a lower limit to the branching ratio. Especially a large number of metal atom oxidation reactions have been investigated because of their high exoergicity with respect to ground state production and hence energy available for excitation. Some such reactions are discussed here by Menzinger, Dagdigian, Jordan and Gole. The observations prior to 1980 have been summarized by Menzinger²⁶ and Fontijn and Felder²⁷. Quantum yields generally have been disappointingly low. One major exception is²⁸



for which a quantum yield has been measured of 0.53 ± 0.26 . Some previously