ELECTRONIC CHEMILUMINESCENCE IN GASES

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CONTENTS

I. Introduction ................................................. 1
II. A Hierarchy of Problems and Results ......................... 4
   A. Experimental ........................................... 4
   B. Light Yields ........................................... 5
   C. Emitter Identification and Analysis ...................... 8
   D. Dissociation Energies .................................. 9
   E. Reaction Mechanisms ................................... 11
      1. Alkali-Halogen Systems .............................. 11
      2. Group IIa Metal-Halogen Systems .................... 13
      3. Ba + N₂O → BaO* + N₂ Reaction ................... 14
III. Dynamics .................................................. 16
   A. The Nuclear Problems .................................. 17
   B. The Electronic Problem ................................ 20
      1. Symmetry-Allowed CL Reactions ...................... 22
      2. Dynamically Induced CL Reactions ................... 22
      3. Spin-Orbit Effects .................................. 26
   C. Interaction with Theory ................................ 31
IV. Epilogue ................................................... 34
Acknowledgements ............................................. 35
V. Tables ...................................................... 36
References .................................................... 49

I. INTRODUCTION

Electronic chemiluminescence (CL) in gases may arise through a variety of processes like recombination of atoms and radicals or its reverse, dissociation, and from chemical exchange (metathesis) reactions proper. I shall confine myself in this review to the discussion of exchange processes for two reasons: first, a great number of them have been discovered in recent years, primarily in the course of the quest for electronic transition laser systems, without having been comprehensively reviewed, and secondly, atomic and molecular recombination processes have already been adequately covered by previous reviewers of the CL field (Thrash, 1968; Carrington and Garvin, 1969; Carrington and Polanyi, 1972; Carrington, 1973; Golde and Thrush, 1975).
CL reactions are studied for a variety of reasons. As indicated, the possibilities of practical uses, such as chemical lasers in the visible (Wilson et al., 1977) or efficient chemical light sources in general (Cormier et al., 1973), as well as analytical applications (Mendenhall, 1977), have been dominant sources of impetus. Most appealing to the fundamentalist are the facts that they provide the simplest examples of reactions governed by more than one potential energy surface PES, and that the high information content of the CL spectra can be studied with relative ease. Much has become known about the dynamics of single PES reactions since the mid-fifties, but our understanding of the much more complicated non-adiabatic reactions is still in its infancy. It is an interesting historical fact that the chemiluminescent alkali–halogen reactions provided Michael Polanyi and his school (Polanyi, 1932) with the first paradigms for formulating many of the ideas of modern reaction dynamics which would three decades later (i.e. ≥ 1956, the beginning of the 'modern alkali age') bear fruit in the development of modern reaction dynamics. A timely monograph is being published by Davidovits and McFadden (1978) devoted to alkali reactions, in which McFadden (1978) reviews also the CL aspects relevant in the present context.

The orientation towards applications has resulted in a rich inventory of new CL reactions which are summarized in Tables I–XI of the Appendix. A few of them have been extensively investigated but less can lay claim to reasonably well-understood kinetics and dynamics, and even fewer have found the helping attentions of theorists.

In their recent articles, Carrington (1973) and Golde and Thrush (1975) have taken a deductive approach towards classifying CL processes, based on a hierarchy of theoretical concepts and models. Proceeding from the simplest and best understood case, the recombination of atoms along a single potential energy curve to recombination via curve crossing (the inverse of predissociation) and the equivalent recombination processes in three atomic systems, they showed that exchange reactions in triatomic, and to a much higher degree in polyatomic systems, were the most complex in terms of theoretical description as well as experimental accessibility. While adiabatic atom recombination can be analysed experimentally and theoretically with nearly ultimate rigour, only qualitative and general arguments can be advanced in the interpretation of multi-PES exchange reactions.

The central concept in CL reactions are ground- and excited-state potential energy surfaces (PES's, the subject of the present volume), whose symmetry, and with it their mutual strength of interaction, may change with internuclear geometry as described by group theory. The topologies of PES intersections and avoided intersections, mostly in triatomic systems, have been reviewed by Carrington (1974). The dynamical problem governed by three-atom PES's may in simple cases be amenable to (nearly) rigorous computational
solutions by trajectory surface hopping and other semiclassical techniques (Tully, 1976, 1977). Polyatomic systems, in contrast, are characterized by much higher vibronic state densities and, in general, by the absence of symmetry elements. Only in the presence of high barriers will symmetry considerations still be important since then the reaction will be confined to conformations of high symmetry, as Metiu et al. (1974) have shown. These circumstances cause the vibronic states to interact strongly over extended ranges of the multidimensional configuration space for which realistic and quantitative dynamical calculations become far too complex.

In contrast to the more recent of the above mentioned reviews, a more inductive point of view is taken here by organizing the chapters in terms of a hierarchy of questions that might arise in the course of typical CL studies. No attempts will be made to discuss a reaction exhaustively at any given point but different experimental facts of one system may be used to illustrate points of the systematic discussion. The first steps in characterizing a CL reaction, before questions of dynamic nature can be addressed, concern the chemiluminescence light yield, the spectroscopic emitter analysis, and the reaction mechanism, as well as molecular dissociation energies, an important by-product of the latter points. These are discussed in Section 11. Section II deals with dynamic interpretations of measurements. The nuclear and electronic rearrangements occurring in the course of a reaction are loosely classified into a nuclear and an electronic problem. The former concerns mainly the energy partitioning among nuclear degrees of freedom, while the latter deals with the coupling mechanism between reactant and product electronic states. Depending on the representation, reactions may be symmetry allowed, dynamically induced, or caused by spin–orbit interaction. In all three cases one can theoretically and experimentally distinguish electronic from nuclear or Franck–Condon-like components of the coupling terms. The experiments discussed under these headings include energy consumption and disposal among nuclear and electronic degrees of freedom, angular momentum consumption and disposal, specifically anisotropy effects of the reactant and product rotational angular momentum distribution, and angular distributions of CL products. Section IIIC on theory is necessarily brief: methods for obtaining ground- and excited-state PES's on the one hand, and the formal dynamical theory of multi-PES reactions and a variety of semiclassical models on the other, have existed for some years, practical difficulties however have prevented them from being applied to the point of a cooperation of theory and experiment. Statistical and information theory analyses represent the majority of efforts. The epilogue closes this review with some personal views on desirable objectives for future CL research.

The tables in the Appendix contain a compilation of electronically chemiluminescent exchange reactions in the gas phase, primarily covering the
last decade. The selection is personal and no claim of completeness is made.
I apologize to those authors whose work was not included either by oversight
or by practical limitations. The literature cited includes papers up to the
summer of 1978 as well as papers made available to me in preprint form.
I thank the authors of those references especially for their help.

II. A HIERARCHY OF PROBLEMS AND RESULTS

The aim of this chapter is to discuss, from an experimental point of view,
a hierarchy of problems one might encounter in the course of a typical CL
study, and to illustrate them where appropriate. Consider the flow diagram
Fig. 1. Independently of the experimental apparatus, i.e. regardless of whether
the CL phenomenon is observed as the bulk or in molecular beams, the
natural first questions concern the quantum yield \( \Phi \), i.e. what fraction of
reactive events produces CL emitters, and secondly the identification and
analysis of the emitter. One cannot embark on the dynamic interpretation of
the spectrum without having clarified the reaction mechanism. If the process
is bimolecular and vibrational structure of the emission spectrum is well
resolved, energy balance arguments can be used to obtain limits to the
dissociation energy \( D^0 \) of product or reactant molecules. The product internal
state distribution may then be obtained as the primary dynamic signature of
the system. The dynamical aspects are considered in Section III.

![Flow diagram](image)

**A. Experimental**

CL experiments combine well-established spectroscopic techniques for
detection, with bulk-flow (Polanyi, 1932; Felder and Fontijn, 1975, 1978;
West *et al.*, 1975), molecular beam (Fluendy and Lawley, 1973; Manos and
Parson, 1975, 1978; Redpath *et al.*, 1978), or ion beam techniques (Ottinger,
1976) for inducing the reaction and controlling the reaction parameters.
These methods, their applications, potentials, and limitations are sufficiently well known for this section to be brief and sketchy.

Our inventory of CL reactions has been dramatically expanded in recent years through the use of atomic and molecular reactants, neutral and charged, that are unstable under normal conditions. Radicals are obtainable by thermal dissociation or in discharges, and an arsenal of techniques common to high-temperature chemistry (Gole, 1976) is in use for evaporating even highly refractive metals. Traditional methods of resistance and electron bombardment heating have been supplemented by the shock-tube evaporation of metal powders (Johnson et al., 1974) report evaporation of refractives such as B, C, Ti, W, etc.) and by laser-vaporization of metal films (Utterback et al., 1976; Tang et al., 1976; Wicke et al., 1978). Exceptionally high metal vapour densities (typically $\sim 10^{15}-10^{20}$ cm$^{-3}$) have been obtained in the heat pipe oven (Hessel et al., 1975; Luria et al., 1976a,b).

Reactants have been excited to metastable states by electron bombardment in a discharge (Brinkmann and Telle, 1977; Dagdigian, 1978; Kowalski and Heldt, 1978). Reactant state distributions have been varied thermally via the source temperature and by taking into consideration the internal state relaxation during the formation of supersonic beams (Redpath et al., 1978; Wren and Menzinger, 1975, 1979a). Lasers were used to state select reactants (Estler and Zare, 1978a), and to diagnose products (Pruett and Torres-Filho, 1977). We conclude by mentioning the direct photographic (or image-intensifier and optical multichannel analyser) observation of the CL angular distribution in crossed beam experiments (Siegel and Schultz, 1978).

**B. Light Yields $\Phi_{\text{CL}}$**

Foremost in the mind of the applications-oriented researcher (the laser builder and developer of chemical light sources) is the question of the CL quantum yield $\Phi_{\text{CL}}$. It is defined as

$$\Phi_{\text{CL}} = \frac{r_{\text{CL}}}{r_T}$$

the ratio of CL photon production rate to the rate of (reactive) consumption of reactants. In the special cases where both factors obey the same rate law equation (1a) reduces to

$$\Phi_{\text{CL}} = \frac{k_{\text{CL}}}{k_T}$$

the ratio of the corresponding rate constants. This is necessarily the case at sufficiently low pressures (the 'single-collision regime') for both terms to be bimolecular. The CL yield is to be distinguished from $\Phi^{*} = r^{*}/r_{T}$, the yield (or branching ratio) of electronically excited products regardless of whether they decay radiatively or not. In cases where 'reservoir states' are
produced with high efficiency $\Phi^*$, e.g. $\text{Ba} + \text{N}_2\text{O}$, $\text{Sm} + \text{N}_2\text{O}$, $\text{Sm} + \text{F}_2$, etc., the CL yield will be low under single-collision conditions but will increase substantially at higher pressures due to collisional intramolecular energy transfer to radiating states which entails a higher-than-second-order rate law for the rate of CL production $r_{\text{CL}}$.

Actual $\Phi_{\text{CL}}$ measurements may follow two methods based on equations (1a) and (1b) respectively. In *bulk-flow experiments* the rates of photon production (flux) and reactant consumption required in equation (1a) are measured directly. By working under pseudo-unimolecular conditions with one reactant in excess, the rate of reactant consumption is automatically given by the flux of the minor reactant, and the principal task remains the determination of absolute photon fluxes with a properly calibrated detection system (Black et al., 1974; Edelstein et al., 1974, 1975; Eckstrom et al., 1974, 1975; Field et al., 1974; Jones and Broida, 1973, 1974). A novel method for producing a calibrated light source has been reported by Lee et al. (1976) and Woolsey et al. (1977).

Equation (1b) forms the basis of quantum yield measurements in beam/gas experiments. Both factors in (1b) are obtainable from the dependence of the CL photon flux $I_{\text{CL}}$ on target gas density $n_{\text{BC}}$:

$$I_{\text{CL}}(n_{\text{BC}}) = k_{\text{CL}} n_A^p n_A^q$$

where $p$ and $q$ are the partial orders of the CL reaction. The density of beam particles in the plane of the detector obeys the (bimolecular) Lambert–Beer law

$$n_A(l) = n_A(0) \exp(-n_{\text{BC}} l \sigma_{\text{att}})$$

Here $l$ is the (effective) scattering path length and $\sigma_{\text{att}}$ the attenuation cross section. The dependence $I_{\text{CL}}(n_{\text{BC}})$ at low reactant densities gives the reaction orders $p, q$, and the initial slope (or curvature, as the case may be) yields $k_{\text{CL}}$ values. An upper limit of $k_T$ is given by $k_T \geq k_{\text{att}} \simeq \tilde{v} \sigma_{\text{att}}$, the rate constant for (reactive + non-reactive) attenuation of the (atomic) beam $A$, where $\tilde{v}$ is the average relative collision velocity. According to equation (3), $\sigma_{\text{att}}$ is obtainable either from $I_{\text{CL}}(n_{\text{BC}})$ at fixed $l$ or from $I_{\text{CL}}(l)$ at fixed $n_{\text{BC}}$ (Dickson et al., 1977).

To circumvent tedious detector calibrations relative $\Phi_{\text{CL}}^\text{rel}$ values are frequently normalized by a standard reaction (Yokozeki and Menzinger, 1976). Dickson et al. (1977) propose the $\text{Sm} + \text{N}_2\text{O}$ reaction as a standard (see Fig. 2) for which they measure a single-collision CL yield of $\Phi_{\text{CL}} = 0.0039$. The energy dependence of $\Phi_{\text{CL}}(\text{Sm} + \text{N}_2\text{O})$ has been reported by Yokozeki and Menzinger (1977a). An ingenious method yielding absolute $\Phi_{\text{CL}}$ of reactions of metastable metal atoms $M^*$ that eliminates detector calibrations has been reported by Dagdigian (1978). For the $\text{Ca}^*(3P) + \text{N}_2\text{O}$ reaction it yields $\Phi_{\text{CL}} = 0.10 \pm 0.03$ and $\sigma_{\text{CL}} = 6.2 \pm 1.7 \text{Å}^2$. 
The quantum yields of known CL reactions extend from the detection limit \( \Phi_{\text{CL}} \geq 10^{-8} \), e.g. for the ubiquitous autoxidation of organic material by the atmosphere (Mendenhall (1977)) to essentially unity. The majority of the gas-phase processes studied so far have disappointingly low \( \Phi_{\text{CL}} \lesssim 10^{-2} \). It is well to keep in mind that one deals in these cases with minor reaction channels (the proverbial 'tip of the iceberg'), which are of minor significance on a global scale. Nevertheless such processes inform us in a direct way about the system's excited PES's and they frequently display unusual kinetic and dynamic peculiarities.

Single-collision light yields of the order of unity are rare: a noteworthy exception is the reaction of alkali dimers with halogen atoms, e.g.

\[
\text{Na}_2 + \text{Cl} \rightarrow \text{NaCl} + \text{Na}^{*\cdot\cdot**}
\]  

(4) (Struve et al., 1975). In alkali-rich diffusion flames the overall quantum yield reaches \( \Phi_{\text{CL}} \sim 0.4 \) (Bogdandy and Polanyi, 1928). As the authors have pointed out, this requires a near unit quantum yield for the elementary processes which will be discussed later.

The reaction of group IVa atoms with oxygen donors, for instance \( \text{Sn}(^3P) + \text{N}_2\text{O} \rightarrow \text{SnO}^{*} + \text{N}_2 \) are likewise thought to produce predominantly excited triplet products \( \text{SnO}(a^3\Sigma^+, b^3\Pi) \)—based on adiabatic correlations (Donovan and Husain, 1970) and on experimental evidence (Wiesenfeld and Yuen, 1976; Felder and Fontijn, 1975, 1978).

The explanation for high CL quantum yields at thermal energies is usually found in the existence of adiabatic correlations to the emitter state, while diabatic transitions that are often required to reach the emitter state act as
the dynamical bottlenecks responsible for low $\Phi^*$ and $\Phi_{\text{CL}}$. A striking exception to this rule of thumb—the CL decomposition of tetramethyldioxetane into one $S_0$ ground state and one $T_1$ triplet acetone (Wilson, 1976)—has a plausible dynamical explanation which will be discussed in Section III.B.3. As mentioned earlier, consecutive reaction mechanisms may entail drastically pressure-dependent $\Phi_{\text{CL}}$. We merely point here to Fig. 2 and to the Sm $+ F_2 \rightarrow \text{SmF}^*$ reaction (Eckstrom et al., 1975; Dickson et al., 1977). The reactions between metal atoms (Ba, Sm, Al) and NF$_3$ (Eckstrom et al., 1975; Rosenwaks, 1976; Rosenwaks and Broida, 1976) are noteworthy for their high $\Phi_{\text{CL}}$ through a multistep mechanism involving metastable N$_2^*$. 

C. Emitter Identification and Analysis

The celebrated state resolving power of spectroscopic methods ideally endows CL studies with a maximum of product state information. This is represented by detailed rate constants $k_{ij}$ or cross sections $\sigma_{ij}$ for forming (e.g. diatomic) products in individual $|v',J',\varepsilon'>\rangle$ states and distributions over $m_J$ states, all of which we collectively label $|J\rangle$. The notation $i_f$ stands for reactant and product states, primes and double primes for upper and lower states of radiative transitions.

The relation

$$I_{j'\varepsilon'} = A_{j'\varepsilon'}, N_{j'}$$

(5)

between the observed intensity $I_{j'\varepsilon'}$ of an (ideally rotationally resolved) spectral line and the steady-state emitter concentration $N_{j'}$ and spectral transition probability $A_{j'\varepsilon'}$, has been documented in detail by Nicholls and Stewart (1962), Albritton et al. (1980), and Manos (1976). This is done by writing the Einstein $A$-factor as

$$A_{j'\varepsilon'} = \alpha g_{j'}^{-1} v_{j'\varepsilon'} R_{\varepsilon'}^2 S(J'\Lambda',J''\Lambda'')$$

(6)

where $\alpha = 64\pi^4/3\hbar$ and $g_{j'} = 2J' + 1$ is the degeneracy of the emitter state. $v_{j'\varepsilon'}$ is the frequency of the spectral transition, $R_{\varepsilon'}^2$ the electronic transition moment evaluated at the $R$-centroid $\bar{R}_{\varepsilon'}$, $q_{\varepsilon'}$ the Franck-Condon factor, and $S(J'\Lambda',J''\Lambda'')$ is the (analytically given) Hönig–London factor (Herzberg, 1950) for the $J'\Lambda' \rightarrow J''\Lambda''$ transition where $\Lambda$ is the projection of the electronic angular momentum on the internuclear axis. Franck-Condon factors are calculated using standard computer programs (Zare, 1963, 1964; Jarmain and McCallum, 1970; Albritton et al., 1980) from the potential curves $V(R)$ derived from spectroscopic constants or from numerical RKR potentials. The necessity of extrapolating $V(R)$ to high quantum numbers beyond the range of validity of the input data may introduce substantial errors. Electronic transition moments are normally not known.
The possible errors associated with the usual assumption of an $\tilde{R}_{\nu''\nu'}$-independent $R_\gamma$ ought to be kept in mind.

The next step in relating an observed spectrum or equivalently the steady-state emitter population $N_{f'}$, to the desired microscopic rate constant $k_{fi}$ is to consider the kinetics of emitter formation and decay, including all competing loss channels. The latter include radiative and non-radiative intramolecular decay, drift out of the viewing range of the detector during the radiative lifetime, and collisional relaxation and quenching. This yields a relation between phenomenological and microscopic rate constants for CL radiation and an interpretation of the steady-state emitter concentration $N_{f'}$ in terms of the rate constants of all contributing processes (Carrington, 1961; Polanyi and Woodall, 1972; Redpath et al., 1978). The simplest case corresponds to a short-lived emitter (say $\tau_e < 10^{-6}$s) being formed at low enough pressures for single-collision conditions to prevail.

So far the CL emission has been assumed to correspond to well-known electronic band systems. Frequently however, previously unknown electronic states may be populated, or known electronic states may be formed with higher vibrotational excitation than under conventional excitation methods. Such spectra may represent new sources of spectroscopic information (Oldenburg et al., 1975; Dickson and Zare, 1978) or frustration, as the case may be.

D. Dissociation Energies

The energy balance of bimolecular CL reactions may provide convenient estimates of molecular dissociation energies (Zare, 1974; Gole, 1976). The method applies also to laser-induced fluorescence and complements $D_0^0(AB)$ determinations based on the study of chemical equilibria by mass spectrometric (Drowart and Goldfinger, 1967) and flame photometric methods (Gaydon, 1968). For a reactive event of the $(A + BC) \rightarrow (AB^* + C)_f$ type, energy conservation requires

$$E_T + \sum_i E_i + D_0^0(AB) - D_0^0(BC) = E'_r + \sum_f E'_f$$  \hspace{1cm} (7)

In accord with common usage in this context, primed quantities denote products, unprimed ones reactants. The available energy, i.e. the sum of reactant translational and internal energies and the energy released, given by the difference of the product and reactant bond energies, equals the product internal plus translational excitation. The $D_0^0$ value of either AB or BC could be determined exactly from (7) if all other factors were known. In praxi this is not the case and $D_0^0$ estimates can be obtained, based on a number of approximations and caveats which, although obvious, have in a number of cases bedevilled the application of this method: 1. The reaction
has to be bimolecular, a condition that is by no means guaranteed even in beam-gas (Jonah and Zare, 1971; Gole et al., 1977) experiments. 2. Since the product translation \( E'_p \) is generally unknown, this term is neglected and the highest product quantum state \( \left( \sum f_i E'_f \right)_{\text{max}} \) observable in the CL spectrum is used to derive an obvious inequality from (7) which provides lower and upper limit estimates for \( D_0^p(\text{product}) \) and \( D_0^p(\text{reactant}) \), respectively. The CL spectrum ought to be analysable for the highest quantum state, or else additional assumptions must be made. The quality of this approximation depends clearly on the \textit{a priori} unknown dynamics: if in a detectable fraction of emitters the total available energy is deposited as internal energy then the equality (7) is maintained in (9). In general, (9) gives only lower- (and upper-) limit estimates for \( D_0^p(\text{AB}) \) (or for \( D_0^p(\text{BC}) \)). 3. Matters are complicated since one is usually faced with a transvibronic distribution of reactants, and since the energy consumption, i.e. the distribution of states that actually do react, is frequently unknown. The consequence of translational and/or internal energy barriers to reaction has been pointed out by Thrush (1973), Preuss and Gole (1977a, b, c). One replaces the sharp values in (7) by the average translational energy \( \langle E_{T,i} \rangle^* \) at which state \( |i\rangle \) reacts and by the average internal energy \( \left\langle \sum_i E_i \right\rangle^* \) at which reaction \textit{actually} occurs, and noting that these are related to \( \langle E_T \rangle \) and \( \left\langle \sum_i E_i \right\rangle \), the unstarred averaged energies of all (i.e. reactive and non-reactive) collisions by (Menzinger and Wolfgang, 1969; Redpath et al., 1978; Preuss and Gole, 1977a, b):

\[
\langle E_{T,i} \rangle^* + \left\langle \sum_i E_i \right\rangle^* = \langle E_T \rangle + \left\langle \sum_i E_i \right\rangle + E_a \tag{8}
\]

where \( E_a \) is the (Arrhenius) activation energy, one finally obtains the desired inequality

\[
D_0^p(\text{AB}) \geq D_0^p(\text{BC}) + \left( \sum f_i E'_f \right)_{\text{max}} - \left\langle \sum_i E_i \right\rangle - \langle E_T \rangle - E_a \tag{9}
\]

for \( D_0^p \).

Applications of the method have been reviewed by Gole (1976), and I refer to that work for a data compilation. Discrepancies between CL and mass spectrometric \( D_0^p(\text{AB}) \) values (the latter lie usually lower) could in some cases be resolved by establishing the involvement of metastable reactant states. A good example is an ingenious experiment, reported by Estler and Zare (1978b), in which a pulsed metastable Ba beam was used to record time-resolved TOF-CL spectra in order to observe directly the \( E^*_f \)-distribution of reactive events, and to demonstrate the previously unrecognized involvement of Ba*\(^{3P}\) metastables. The earlier value of \( D_0^p(\text{BaI}) \geq 102 \pm 1 \text{ kcal/mol} \) (Dickson \textit{et al.}, 1976) is now corrected to \( D_0^p(\text{BaI}) \geq 72.9 \pm 2 \text{ kcal/mol} \),
which agrees well with mass spectrometric values (Hildenbrand, 1977, 1978). Dynamic interpretations of many experiments have likewise suffered from unrecognized metastable contaminations, although clues about their involvement have been recognized in some studies (Dubois and Gole, 1977; Gole and Chalek, 1976; Dickson and Zare, 1978; Rosenwaks and Broida, 1976). Small concentrations of metastables reacting with large cross sections (Brinkmann and Telle, 1977; Kowalski and Heldt, 1978; Pasternack and Dagdigian, 1978) may cause the small phenomenological $\sigma_{CL}$ of the overall system, which are traditionally interpreted as arising from ground-state reactants.

E. Reaction Mechanisms

Since radiative lifetimes for allowed electronic transitions lie in the $\tau_R \sim 10^{-9}-10^{-6}$ s range one expected originally that secondary collisions would not compete noticeably with radiation from a newly formed CL emitter at pressures below, say $10^{-2}-10^{-1}$ Torr. While this is usually the case for short-lived species, metastable intermediates have been found to play a crucial role in many systems. The additional fact that their internal excitation may endow them with much higher cross sections for secondary collisions than those which one is used to expect from their ground-state counterparts, is the reason for higher-than-second-order kinetics that are occasionally observed even in beam experiments at pressures well below $10^{-3}$ Torr, which were traditionally believed to define the single-collision regime (Wren and Menzinger, 1974; Yokozeki and Menzinger, 1976; Dickson et al., 1977; Brown and Menzinger, 1978; Kusunoki and Ottinger, 1978a). Bulk-flow experiments—typically in the $10^{-2}-10$ Torr range—are frequently affected by secondary processes, and dynamic interpretations of experiments of this type have to be taken with great care.

A great variety of kinetic schemes is possible, depending on the emitter formation via metathesis, energy transfer or recombination/dissociation, and on the first-order loss rates (radiation, intramolecular radiationless processes, diffusive loss, etc.) and collisional rates (quenching, energy transfer, etc.). Typical mechanisms have been considered by Gole et al. (1977). The three examples presented below are meant to illustrate some of these aspects.

1. The Alkali–Halogen Systems

These deserve mention not only for their venerable history but also for the central role which reaction mechanisms play in the overall CL production. The discussion is kept brief since McFadden (1978) and the book edited by Davidovits and McFadden (1978) review this subject in depth. In skeletal
form, the mechanism of CL production from the reagents \((M, M_2) + X_2\), present at thermal equilibrium, is

\[
\begin{align*}
M + X_2 &\rightarrow MX + X \quad \text{primary reaction} \\
X + M_2 &\rightarrow MX + M^{*\text{**}} \quad \text{direct electronic excitation} \\
&\quad \rightarrow MX^\ddagger + M \quad \text{vibrational energy release} \\
MX^\ddagger + M' &\rightarrow MX + M'^* \quad \text{indirect (non-reactive) excitation} \\
&\quad \rightarrow M'X + M^* \quad \text{indirect (reactive) excitation} \\
M_2 + X_2 &\rightarrow MX + M^* + X \quad \text{atomic excitation (4 centre)} \\
&\quad \rightarrow MX^* + MX \quad \text{molecular excitation (4 centre)} \\
M + X + S &\rightarrow MX^* + S \quad \text{molecular excitation (atom recombination)}
\end{align*}
\]

From their well-reviewed (Polanyi, 1932; Laidler, 1955; Kondratiev, 1964; McFadden, 1978) 'highly dilute flame studies'—particularly from the fact that \(N_2\) buffer gas quenched the \(Na^*(2P)\) chemiluminescence faster than it quenched resonance fluorescence—Polanyi and coworkers were led to infer that the 'indirect excitation' pathway \((10) + (12) + (13, 14)\) involving the fast \(V \rightarrow E\) transfer \((13, 14)\) dominated over the direct mechanism \((10) + (11)\) (Beutler and Polanyi, 1928; Polanyi and Schay, 1928). This requires predominantly vibrational energy release in \((10)\) and it is the earliest evidence for such dynamically biased energy partitioning. Moulton and Hershbach (1966) substantiated the indirect mechanism by a triple-beam experiment, and showed that reactive \(V \rightarrow E\) transfer \((14)\) was substantially \((\sim 100 \times)\) faster than the non-reactive mode \((13)\). On a statistical basis one would have expected equal efficiency for both channels. Hershbach sees in this dynamical bias evidence for the importance of electron transfer in reactive electronic excitation. The complementary \(T \rightarrow E\) transfer was found to be much slower than \(V \rightarrow E\) transfer \((13 + 14)\) by Neoh and Hershbach (1975). Based on his qualitative PES's obtained from correlation considerations, Magee (1940) criticized the above-mentioned conclusion of the Polanyi school, and showed that the direct mechanism should even dominate the indirect one. More recent semiempirical \(M_2 X\) surfaces of Struve (1973) confirm some of Magee's early work. The crossed \(M_2 + X\) beam experiments of Struve et al. (1971, 1975) agree beautifully with this early inference by giving \(Na_2 + Cl \rightarrow Na^*\) cross sections of the order of \(10-100 \AA^2\). No self-consistent kinetic analysis has been given to date which would reconcile the early quenching results with the later evidence for the importance of both mechanisms \((10)-(15)\) in flame emission.

The early observation of highly excited alkali states \(M^{**}\) (Beutler et al., 1926) was originally also ascribed to vibrational-to-electronic energy
transfer (Schay, 1931) but again the beam experiments of Struve et al. (1975) exposed the direct excitation (11) as an important competitor, particularly since the (statistical) $M^{**}$ distributions from flow tube and beam experiments were in essential agreement.

The molecular $MX^*$ emission observed by Beutler et al. (1926), and later analysed and interpreted by Levi (1934) in terms of two- and three-body atom recombination (16), was eventually found to occur by a four-centre exchange step (15) (Oldenburg et al., 1974; Kaufmann et al., 1974a,b; Struve et al., 1975). The latter authors have also discussed a mechanism involving the rearrangement of a $M-M^+X^-X$ complex in which the central $M^+X^-$ plays the role of the chaperone in the recombination of the end-standing atoms to yield electronically excited $MX^*$.

2. The Group IIA Metal–Halogen Reactions

These reactions proceed by a number of competing channels:

$$M + X_2 \rightarrow MX^+ + X^- \quad \text{chemiionization} \quad (17a)$$

$$\rightarrow MX^*(X,A,B,C \ldots) + X^- \quad \text{monohalide formation} \quad (17b)$$

$$\rightarrow MX_2^* \quad \text{dihalide formation} \quad (17c)$$

With $M = \text{Ca, Sr, Ba}; X = \text{F, Cl, Br, I}$, this family of reactions differs from the homologous alkali systems primarily through the presence of an extra valence electron. In MX monohalides it occupies a non-bonding MO outside an alkali-halide-like core centered on the $M^+$ ion. Its excitation gives rise to the alkali-like Rydberg series of low-lying product states $A^2\Pi, B^2\Sigma^+, C^2\Pi$, etc., and to the low MX ionization potential, slightly less than that of the free metal atom M. This becomes manifest through the energetically accessible bimolecular CL and CI (chemiionization) channels (17b) and (17a) (Jonah and Zare, 1971; Menzinger, 1974a, 1974b; Diebold et al., 1977; Wren and Menzinger, 1979b).

The dihalides $MX_2^*$ also possess low-lying excited states. They may be visualized as originating from charge transfer from the doubly ionic ground state $X^-M^+X^-$ to the singly ionic excited states $X^*^-M^+X^-$. In MO language the lowest energy $MX_2^*$ excitations correspond to transitions from the highest $\Pi_g(b_2, a_2)$ orbitals to the lowest unoccupied (antibonding) $\tilde{\sigma}_g(a_1)$ orbital (Hayes, 1966; Gole, 1973; Gole et al., 1973; Yarkony et al., 1973). Although $MX_2^*$ can principally be formed via radiative two-body recombination (known to be rather ineffective), most of the $MX_2^*$ emission which dominates the CL spectra (except for $X = F$) at pressures round $10^{-3}$ Torr (Jonah and Zare, 1971; Menzinger, 1974a) obeys a third-order rate law, surprisingly even at pressures as low as $\sim 10^{-5}$ Torr (Wren and Menzinger, 1974, 1979c). This was originally explained by radiative three-body recombi-
nation involving the rapid stabilization of a long-lived $MX^*_2$ collision complex. A more recent finding (Wren and Menzinger, 1979c), namely the fact that the BaCl$^*_2$ intensity proves independent of N$_2$ pressure when N$_2$ is substituted as a stabilizing gas for Cl$_2$ in a beam/mixed gas (Cl$_2$ + N$_2$) experiment, is evidence against this route. A more likely mechanism involves the fast 'avoided harpooning' reaction of vibrationally highly excited ground state $MX^+$ ($X^2\Sigma^+$, $v \gg 0$):

$$M + X_2 \rightarrow MX^2 + X \quad (18)$$
$$MX^2 + X_2 \rightarrow MX^*_2 + X \quad (19)$$

Both mechanisms are consistent with the angular CL distribution, observed by Mims and Brophy (1977) to resemble roughly the M–X$_2$ centroid distribution.

Even the $MX^*$ channels, which were labelled bimolecular a moment ago when we had well-controlled beam experiments in mind, may develop mechanistic complexities at higher pressures (Eckstrom et al., 1975; Yokozeki and Menzinger, 1976), or when beam experiments suffer from a contamination by M$^*$ metastables. For instance the BaCl$^*$ ($C^2\Pi$) state has been observed in beam/gas (Jonah and Zare, 1971) as well as in flow tube experiments (Menzinger and Wren, 1973; Bradford et al., 1975), and thermochemical as well as dynamical interpretations have been attempted, although it is now recognized that for energetic reasons the $C^2\Pi$ cannot arise from ground-state reactants as written in (17b) but it must involve high-energy reactants such as Ba$^*$ metastables. Brinkmann and Telle (1977) and Kowalski and Heldt (1978) used metastable M$^*(3P)$ beams to show that their (symmetry-allowed) CL reaction with Cl$_2$ and HCl have near gas kinetic cross sections and that they produce MCl$^*$ states that are energetically precluded for thermalized ground-state reactants. This illustrates once again how minor contaminations by highly reactive species may confuse the issues by mimicking a slow reaction of the dominant component.

The simple electronic structure and the multiplicity of reaction paths (17a–c) which can be studied with relative ease make this reaction family the prototype CL systems which share many characteristics with others of greater complexity. Calculations of ground and excited-state PES's are well within present-day capabilities, as the initial. CaF$_2$ study of Yarkony et al. (1973) and the paper by Tully in this volume show. It appears highly desirable to pursue this matter since the prospect of narrowing the gap between experiment and theory is most promising in the present case.

3. The Ba + N$_2$O → BaO$^*$ + N$_2$ Reaction

This reaction is the best-studied member of a family of group IIa and IIIa metal atom reactions that have attracted attention since Jones and Broida
(1973, 1974) discovered the dramatic increase of the photon yield \( \Phi_{\text{CL}}(p) \) with pressure of an inert buffer gas—the principal indication for the involvement of non-radiating 'reservoir states'. The \( \Phi(p) \) dependence is very similar to that of the Sm + N\(_2\)O system, shown in Fig. 2 (Eckstrom et al., 1975; Dickson et al., 1977). Other systems with similar kinetic signatures have been reported (Eckstrom et al., 1974, 1975, 1977; Hsu et al., 1974a; Palmer et al., 1975). In his interesting 'case study', Field (1976) has concerned himself primarily with the kinetic and spectroscopic problems arising from the presence of long-lived precursors. He and Jones and Broida (1974) have elaborated on the pronounced spectral changes accompanying the increase of \( \Phi_{\text{CL}} \) with pressure: the highly structured, many-line low-pressure spectrum which has so far defied a complete analysis, changes into the well-known (\( A^1\Sigma^+ - X^1\Sigma^+ \)) band system as the buffer gas pressure is raised to \( \sim 0.1-1 \) Torr. Vibrational and rotational population anomalies in the (\( A-X \)) spectrum below 1 Torr coincide precisely with those rotational levels of the \( A^1\Sigma^+ \) state which are most strongly perturbed by the nearly \( a^3\Pi \) state (Field, 1974). This establishes the \( a^3\Pi \) state as a precursor, but cannot exclude possible precursors to \( a^3\Pi \) (Field et al., 1974). The \( a^3\Pi \) and \( A^1\Pi \) states have virtually the same spectroscopic constants and are strongly mixed by spin–orbit coupling (Field, 1974). For this reason any discussion of \( a^3\Pi \) as a precursor to \( A^1\Sigma^+ \) must also imply the same role for \( A^1\Pi \) (Hsu et al., 1974b). Kinetic modelling which includes as the crucial step the collisional transfer from a reservoir to the \( A^1\Sigma^+ \) emitter reproduces the measured \( \Phi_{\text{CL}}(p) \) very well but cannot distinguish between possible precursors (Pruett and Torres-Filho, 1977). Whatever their nature, they must be formed at yields approximating unity to account for the maximum CL yield \( \Phi_{\text{CL}}^{\text{max}} \sim 0.35 \) at \( p(\text{Ar}) \sim 10 \) Torr (Jones and Broida, 1973, 1974). Numerous kinetically equivalent pathways can arise from the interaction of at least five states of BaO (high \( v \) states of \( x^1\Sigma^+ \); \( ^3\Sigma^+ \), \( a^3\Pi \), \( A^1\Pi \) and \( A^1\Sigma^+ \)) since it is known that intramolecular energy transfer between mutually perturbing states is fast and may proceed at a rate exceeding that of rotational relaxation (Radford and Broida, 1963; Pratt and Broida, 1969; Gelbart and Freed, 1973). Much remains to be learnt about these aspects.

Wicke et al. (1975) have considered the possible involvement of metastable Ba*\(^3D\)) in the Ba + N\(_2\)O system but found it insignificant under normal conditions. The suggestion had been made that Ba* would provide a symmetry-allowed pathway towards \( a^3\Pi \) precursors. This would support the earlier view that the oxygen atom in N\(_2\)O behaves much like O\(^3P\)) (Field et al., 1974; Tully, 1974a). An alternative pathway towards \( a^3\Pi \), proceeding through an ion-pair complex will be discussed in section III.B.2 in connection with the excitation function measurements. Very efficient production of metastable M*\(^3P\)) occurs in ternary ((Mg, Ca) + N\(_2\)O + CO) flames (Benard et al., 1976, 1977a, b; Benard and Slafer, 1977; Eckstrom et al.,
by the following mechanisms:

\[
\text{Mg}^1S + N_2O \rightarrow \text{Mg}O^+ + N_2
\]  
\[
\text{Mg}O^+ + CO \rightarrow \text{Mg}^*(3P) + CO_2
\]

Whether \(\text{Mg}O^+\) is in the ground state or whether it is electronically excited is not clear. In either case addition of CO to \((\text{M} + N_2O)\) flames dramatically increases the CL yield through the reactions

\[
\text{Mg}^*(3P) + N_2O \rightarrow \text{Mg}O^*(A'\Sigma^+, B'\Sigma^+, a^3\Pi, 3\Delta)
\]

Here, \(a^3\Pi\) and \(3\Delta\) are produced adiabatically, while \(B'\Sigma^+\) requires diabatic transitions. Process (22) for \(\text{Ca}^*(3P)\) has been studied by Dagdigian (1978) in a beam-gas experiment.

In conclusion we note that the gross features of the mechanism involving precursors are understood, although detailed knowledge of all precursors and their mutual interconversions must await their spectroscopic analysis under typical reaction conditions, this is being attempted in different laboratories.

### III. DYNAMICS

The high product state resolution of chemiluminescence can be combined with the control over reactant conditions achievable by molecular beam and selective reactant excitation techniques to obtain, in principle, the ultimate state-to-state dynamical information symbolized by the transition probability \(P_{fi}\). Different experiments concern themselves with different subsets of, or averages over, the quantum numbers which are symbolized by the collective labels \(i,f\) as will be exemplified below.

Product and reactant attributes can be classified into scalar and vector quantities: energy disposal (product state distributions or specific rate constants) indigenous to the CL method and energy consumption (translational and internal energy dependences) are the most frequently studied aspects. More recently, directional information has begun to become available. This comprises angular distributions of CL products (Mims and Brophy, 1977; Siegel and Schultz, 1978) and angular momentum consumption (orientation dependence of reaction probability) and disposal (product alignment) (Estler and Zare, 1978a).

Before illustrating some of these points with examples from the literature, it appears useful to place them in a systematic scheme, together with the basic problems and theoretical tools that are currently available. This is done in Fig. 3.

The complete dynamical information displayed by the partitioning of the collisional invariants (energy, linear and angular momenta) is loosely and somewhat arbitrarily divided into a nuclear problem which deals with
rotation–vibration–translation aspects already familiar from single PES reactions, and into the *electronic problem* ('how does the system proceed from the reactant to product potential energy surface?') which is more specifically related to CL. Interesting aspects arising from the interplay of nuclear and electronic motion (failure of the Born–Oppenheimer separation) are incorporated into the electronic problem.

### A. The Nuclear Problem

This deals with the partitioning of the energy, linear and angular momenta describing the dynamic states of reactant and product nuclear motion. The total dynamic information is contained in total and differential detailed cross sections (or the equivalent rate constants) for populating states of nuclear motion in a given electronic level $|e'\rangle$. Total state-to-state cross sections ideally given by $\sigma(v',J',m'_j|E_T, v, J, m_j)_e$ contain *in praxi* a certain degree of reactant and product state averaging. Orientational effects, expressed by the reactant and product magnetic quantum numbers $m_j, m'_j$ are included here.

Examples will be discussed in this section and in the following one: differential CL cross sections have been measured for total CL emission (not spectrally resolved) although differential state-to-state cross-section measurements are in principle possible for long-lived emitters. The preceding lines merely summarize the observables of chemical reaction dynamics, where the specifically CL-oriented aspect deals with the electronic states $|e\rangle$ and $|e'\rangle$.

For reactions on a single PES, partial averages over the above functions
have been extensively studied by molecular beam and infrared chemiluminescence methods (Polanyi and Schreiber, 1974). By complementary classical trajectory calculations on suitable *ad hoc* or computed PES's one is able to rationalize the observations in terms of PES topology and kinematic constraints, Polanyi and Schreiber 1974; Kuntz, 1976). Although detailed cross sections (or rate constants and equivalently, product state distributions) of this type have been obtained for electronically CL reactions (Ottinger, 1976, 1978; Manos and Parson, 1975, 1978) little has been done to interpret them by dynamical calculations. If a limited goal was the interpretation of product $v'$, $J'$ distributions, purely classical trajectory calculations on a single *diabatic* PES that smoothly connects reactants with products, would be a promising approach. After all, the formation of a product internal state $|f\rangle$ is due to the accumulated forces acting on the nuclei along the entire reaction coordinate. It would be expected to be insensitive to localized diabatic interactions of PES's, unless they occur in regions where the forces on the nuclei (gradients of the PES's) are large.

The *kinetic energy dependence of the CL cross section* (total $\sigma_{\text{CL}}(E_T)$ or electronic-state-resolved $\sigma_{\text{CL}}(E_T)_{\nu}$) is relatively easy to obtain from the CL intensity measured at a fixed laboratory angle, compared to single PES reactions which require laborious normalizations and integrations of product fluxes over scattering angles. This simplification is due to the near-isotropic angular distribution of CL light, equivalent to the low degree of CL polarization (Jonah et al., 1972).

Product alignment or an anisotropic distribution of the rotational angular momentum vector manifests itself through anisotropic CL polarization. This may arise in beam experiments through the anisotropy of the initial collisional angular momentum $L$ with respect to the collision axis, and through its propagation into product rotation $J'$. Maximal $J'$ alignment is expected in the presence of kinematic constraints, e.g. in a system of the type $\text{HL} + \text{H} \rightarrow \text{HH} + L$, where the exit collisional angular momentum is constrained by the low product reduced mass ($\text{H}, L = \text{heavy and light groups}$). In any case, averaging due to product rotation (Zare, 1966) reduces the degree of CL polarization $P$ to a low value. Jonah et al. (1972) have shown this to be maximally $P \leq 0.3$ for a simple dynamical model and an idealized beam-gas experiment. This has been verified for $\text{Ba} + \text{NO}_2$ and for $(\text{Tl}, \text{In}) + \text{I}_2^*$ by Jonah et al. (1972) and by Estler and Zare (1978a) respectively.

Quantitative information about *product orientation* (the $m'_r$, distribution) is obtainable from polarization measurements. Rotationally resolved spectra are required since the degree of polarization depends on the type—$P$, $O$, or $R$ branch—of the rotational transition. While this is very promising in principle, the high spectral resolutions required are seldom achieved and the method has consequently not yet been applied. Case et al. (1978) have
Fig. 4. (a) Laser-induced chemiluminescent spectra for $\text{Tl} + \text{I}_2^*$ → TlI$^*$ as a function of the angle $\theta$ between the metal beam axis and the polarization vector of the linearly polarized exciting light. (b) Variation of the chemiluminescence signal with angle $\theta$ for $\text{Tl} + \text{I}_2^*$. The data demonstrate a preference of collinear over perpendicular collisions. From Estler and Zare (1978). Reprinted, with permission, from *J. Ann. Chem. Soc.*, 100, 1323. Copyright by the American Chemical Society.
given a theoretical analysis of the more general problem of determining the moments of the rotational angular momentum distribution from polarized resonance (e.g. laser-induced) fluorescence data. They have also shown that two-photon resonance fluorescence experiments yield more information (12 moments of the $J'$ distribution) than one-photon CL measurements, capable of providing only the distribution's second Legendre moment.

More promising than the disposal aspect is the study of *angular momentum* (i.e. $m_J$) consumption in CL reactions. Aligned reagents may be prepared, apart from selecting them as usual by their deflection in inhomogeneous magnetic and electric fields (Fluendy and Lawley, 1973), by optical pumping with polarized laser light (Feofilov, 1961). Recently, Estler and Zare (1978a) have studied the dependence of the reaction probability on reactant orientation in the laser-induced CL reactions

$$M(\text{In, Tl}) + I_2^0 (B^3 \Pi) \rightarrow MI^* + I$$

in a beam-gas experiment. The CL intensity varies with the angle $\theta$ between metal beam and the polarization vector of the exciting light as shown in Fig. 4. Since the distribution of molecular axes in the pumped and rotating molecules is peaked along $\theta = 0^\circ$ for ‘parallel’ $I_2(B \leftarrow X)$ transition, it is clear from Fig. 4 that reaction (23) prefers collinear over $C_{2v}$ collisions.

Extensions of this technique to other systems and to more detailed experiments (e.g. translational energy dependences and product state resolved experiments) promise new insight into the detailed structure of steric factors.

B. The Electronic Problem

The electronic problem may be described by the question: ‘How does the reacting system reach the electronically excited product state?'. More fundamentally it is concerned with the coupling mechanism or the term in the total molecular Hamiltonian responsible for the transition to the observed product electronic state $\epsilon'$.

Symmetry rules (e.g. Wigner–Witmer, spin conservation, and Woodward–Hoffmann rules (Herzberg, 1967; Metiu et al., 1978) provide on the one hand, a guide as to which reaction channels are expected to be fast, and on the other hand, when symmetry rules appear violated, they give a classification scheme for the symmetry-allowed respectively forbidden nature of the observed process. Interactions between more than one PES are traditionally described in the adiabatic (Nikitin, 1974) or various diabatic representations (Smith, 1969). More recently, the *quasi-adiabatic* representation (O'Malley, 1971) has found some acceptance, last but not least for its inherent conceptual simplicity in formulating and classifying the transition amplitudes $T_{ji}$ in *concerted* multi-PES reactions (Metiu et al., 1978). Briefly, quasi-adiabatic PES's (QAPES) are designed so as to exclude specifically the possibility of
nuclear rearrangement on any one of them, i.e. there are reactant and product QAPES’s which intersect in the interaction region. Reaction is considered as an electronic transition between reactant and product QAPES’s, and symmetry rules can be derived in analogy to optical selection rules. Metiu et al. (1978) have shown that, given the approximate molecular Hamiltonian

\[ H = H_{el} + H_N + H_{SO} \]  \hspace{1cm} (24)

whose components are the total electronic Hamiltonian \( H_{el} \), the nuclear kinetic energy \( H_N \), and the electron spin–orbit interaction \( H_{SO} \), the total transition amplitude, whose square modulus is the transition probability from reactant \( |i\rangle \) to product state \( |f\rangle \), may be approximately expressed as

\[ T_{fi} = T_{fi}^{el} + T_{fi}^{N} + T_{fi}^{SO} \]  \hspace{1cm} (25)

Each component is the matrix element of a term in the Hamiltonian operator (24) between quasi-adiabatic reactant and product vibronic states, e.g. \( T_{fi}^{el} = \langle f | H_{el} | i \rangle \).

By making Franck-Condon and subsidiary approximations these component \( T \) matrix elements can be further decomposed into the products of a nuclear (Franck-Condon) \( q_{fi} \) and an electronic factor \( R_{fi} \)

\[ T^{OP}_{fi} = q_{fi} R^{OP}_{fi} \]  \hspace{1cm} (26)

The very simple factorization based on equations (25) and (26), is summarized in Fig. 3. The usual symmetry rules (e.g. of the adiabatic state correlation, or Woodward–Hoffmann type) serve only to predict whether the electronic \( R_{fi}^{el} \) term is Large or not, regardless of the corresponding Franck-Condon factor. For a concerted reaction to be fast both the electronic transition moment and the Franck-Condon factor must be large. An example for the controlling influence of the nuclear factor is given below.

Dynamically induced reactions (zero \( T_{fi}^{el} \), non-zero \( T_{fi}^{N} \)) arising from the breakdown of the Born–Oppenheimer approximation are further separated into radially and rotationally induced (Russek, 1971):

\[ T_{fi}^{N} = T_{fi}^{N,rad} + T_{fi}^{N,rot} \]  \hspace{1cm} (27)

Traditionally radial coupling is taken to be the dominant term in low-energy scattering, since in the adiabatic representation the rotational matrix element, coupling states of different electronic angular momentum \( \Lambda' = \Lambda \pm 1 \) is weighted by \( vb/R^2 \) where \( v, b, R \) are radial velocity, impact parameter, and interparticle distance (Barat, 1973). It remains to be seen whether rotational coupling in reactive collisions is really as unimportant as is usually assumed to be the case.

Whenever the total electronic spin is not conserved in a reaction, or when fine structure components exhibit different reactivities or are formed in non-statistical amounts, then spin–orbit coupling \( T_{fi}^{SO} \) plays a special role.
1. Symmetry-allowed CL Reactions

A good example for a symmetry-allowed CL reaction (large $T_{ji}^{\text{el}}$) involving orbitally degenerate reactants is the previously discussed dialkali–halogen process (equation 2.11). The high CL yield at thermal energies is mainly due to the adiabatic correlation of the one reactant component with excited $^2P$ products (Magee, 1940). The actual situation is much richer, since among the many observed excited $M^{**}$ states (Struve et al., 1973, 1975) only the lowest $^2P$, which also contributes heaviest to the light yield, correlates adiabatically with reactants. The higher energy and minor channels do require diabatic transitions.

A related process, in which all reactant components correlate adiabatically with excited products (Wiesenfeld and Yuen, 1976) is the

$$\text{Sn}(^3P_J) + \text{N}_2\text{O} \rightarrow \text{SnO}^*(a^3\Sigma^+, b^3\Pi) + \text{N}_2$$

(28)

reaction (as well as its Pb analogue, to be discussed below). The high CL quantum yield $\Phi \lesssim 0.5$ (Felder and Fontijn, 1975, 1978) and its pressure dependence are consistent with (28) as the dominant channels. The CL yield does not reach unity since reaction is slow (Wiesenfeld and Yuen (1976) have measured $k = 5 \times 10^{-13} \text{ exp} - 4000/RT \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), the radiative lifetimes long, and product quenching fast. Although the vibrational energy dependence of (28) has not been studied, one may expect in analogy with the $\text{BaO} + \text{N}_2\text{O}$ reaction (see below) that the $\text{N}_2\text{O}$ bending vibration may play an important role. This would be an example for the influence of Franck–Condon overlap (26) on the rate of a symmetry-allowed reaction.

Reactions which are symmetry forbidden and slow can be greatly accelerated by electronic excitation to states that correlate adiabatically with the emitting products (Donovan and Husain, 1970). Examples are the CL reactions of metastable $^3P$ alkaline earth metals:

$$M^*(^3P) + (\text{HCl}, \text{Cl}_2) \rightarrow \text{MCl}^* + (\text{H}, \text{Cl})$$

(29)

studied by Brinkmann and Telle (1977) and Kowalski and Heldt (1978) and $\text{Ca}^*(^3P) + (\text{O}_2, \text{CO}_2) \rightarrow \text{CaO}^*$ studied by Pasternack and Dagdigian (1978). The reaction

$$\text{I}_2^*(B^3\Pi) + \text{F}_2 \rightarrow \text{IF}^*(B^3\Pi(O^+)) + \text{IF}$$

(30)

however is symmetry forbidden both for ground state $\text{I}_2(X)$ (Valentini et al., 1977) and for the $\text{I}_2^*(B)$ state. It is somewhat of an exception since it occurs readily as written (Engelke et al., 1977).

2. Dynamically Induced CL Reactions

Numerous cases of dynamically induced, diabatic CL reactions are known. A particularly illustrative example for present purposes is $($Ba + $\text{N}_2\text{O})$. 
From direct photographic observation of the angular CL distribution, Siegel and Schultz (1978) have inferred the BaO*(A'\Pi) state, which incidently does not correlate adiabatically with reactants, to be the primary emitter. The excitation function measured at two N₂O vibrational temperatures is shown in Fig. 5 (Wren and Menzinger, 1975, 1979a). The pro-

**Fig. 5.** Chemiluminescence excitation functions for Ba + N₂O \rightarrow BaO*, measured at two N₂O vibrational temperatures (assumed to be equal to the nozzle temperature). The dashed curve represents the BaO* (A'\Pi) product state density. From Wren and Menzinger (1975, 1979a).

**Fig. 6.** Chemiluminescence excitation functions for the endoergic Pb + N₂O \rightarrow PbO*(B, v = 0) reaction. The dashed curve is the product state density as drawn by the authors. From Wicke et al. (1978). Reproduced by permission of the North Holland Publishing Corp.
nounced CL enhancement by vibrational excitation is believed to be due principally to the \( v_2 \) bending rather than the \( v_3 \) asymmetric stretch vibration. The strong increase of electron affinity upon \( \text{N}_2\text{O} \) bending (linear ground state) combined with the data, Fig. 5, suggests that formation of the ion pair \( \text{Ba}^+\text{N}_2\text{O}^- \) initiates the reaction, followed by rearrangement to the observed products. Whatever the promoting mode and the emitter, we have here a clear example for the importance of the Franck-Condon factor in (26) vibrationally enhancing the CL cross section by increasing the overlap between reactant and product nuclear wave functions.

Numerous CL reactions of transition metals with oxygen donors, and of \( \text{O}^+, \text{N}^+, \text{C}^+ \) ions have been studied (Manos and Parson, 1975, 1978; Ottinger, 1978), the majority requiring non-adiabatic transitions. The ion-molecule CL studies of Ottinger and his group are well chosen since they deal with relatively simple reactions involving atoms of the first and second row of the periodic table for which more is known about the relevant PES's (e.g. the \( \text{CH}_3^+, \text{N}_2\text{O}^+, \text{NH}_3^+, \text{CO}_2^+ \) systems) from electronic structure calculations and general MO arguments as well as from other scattering experiments, than for most neutral-neutral CL processes. Furthermore the available energy range is broad, and vibrational and rotational state distributions have been determined, apart from CL excitation functions, for most of the reactions given in Table XI. Out of these, large CL cross sections exceeding prior expectations \( (\sigma_{\text{CL}} > 1 \text{Å}^2) \) were found only for the \( \text{N}^+ + \text{hydrocarbon} \) reactions. The reviews by Ottinger (1976, 1978) of these studies, particularly (1976), contain more detail than the individual papers.

An example for which some aspects of the PES's are reasonably well understood (Liskow et al., 1974) is the \( \text{C}^+ (2P) + \text{H}_2 \) reaction (Appel et al., 1975), for which an extended state correlation diagram, taken from Ottinger's detailed (1976) discussion, is presented in Fig. 7. The lowest energy pathways

![Fig. 7. Extended adiabatic state correlation diagram for the C\(^+\) + H\(_2\) \rightarrow CH\(^+\) + H reactions, obtained from symmetry considerations and electronic structure calculations. The state energies are drawn for complexes of slightly distorted (C\(_s\)) complexes of approximate (C\(_{2v}\), D\(_{av}\), C\(_{nv}\)) symmetries. Solid and dashed lines correspond to states of \(^A'\) and \(^A''\) symmetry, respectively. Reproduced, with permission from Ottinger (1976).](image-url)
to CH⁺(A¹Π) are seen to involve the lowest A' + A'' surfaces, from which adiabatic transitions to the product state occur during the exit phase of the collision. It is evident that only the A' pathway will be significant at low collision energies.

Interesting product state distributions shown in Fig. 8 were found for

![Graph showing vibrational and rotational state distributions of CO⁺(A²Π) products of the reaction indicated.](image)

**Fig. 8.** Vibrational and rotational state distributions of CO⁺(A²Π) products of the reaction indicated. (a) The vibrational distribution; (b) rotational distributions in three vibrational states (v' = 0, 5, 10). The best fit of the vibrational band contours was obtained with the distribution characterized by Tᵣ = 45,000 K. The Tᵣ = 14,000 K curve gave an unacceptable fit. Reproduced, with permission from Ottinger (1978).
the C⁺ + O₂ → CO⁺ (A^2Π) reaction (Ottinger and Simonis, 1975; Ottinger, 1978). The monotonically decreasing but non-statistical P(ν') seems to be evidence for short-lived, bound CO₂⁺ intermediates. The rotational distributions P(J') in different ν' are of the Boltzmann type, truncated for angular momentum restrictions, and characterized by extremely high rotational temperatures T_r ≈ 45,000 K (average J ≈ 80)! This corresponds to ~ 50% of the reactant orbital angular momentum L predicted by the Langevin model and suggests the repulsive decay of a non-linear complex (Miller et al., 1967). Other interpretations cannot however be excluded. As usual, a more than qualitative interpretation of these high-quality data is not possible unless theory meets experiment halfway.

3. Spin–orbit Effects

The effects of spin–orbit interaction on electronic transitions are discussed in two complementary pictures. One is appropriate in the limit of weak S–O coupling, where the conventional adiabatic PES's, or eigenfunctions of the electronic Hamiltonian H_e, determine the dynamics of systems containing only light nuclei. The other applies to strongly S–O coupled, heavy systems which are more conveniently represented by the eigenfunctions of (H_e + H_{SO}) called spin–orbit surfaces (SO-PES) to distinguish them from the former.

When a molecular system is described by a given approximation, the 'switching on' of a new interaction, or reduction of some symmetry, may cause two (diabatic) terms which previously did not interact and crossed at some geometry, to become adiabatically interacting at and in the neighbourhood of an 'avoided crossing'. This is illustrated in Fig. 9 where two non-interacting adiabatic terms of \( ^3\Sigma \) and \( ^1\Pi \) symmetries are caused by \( H_{SO} \) to mix. The pair of new interacting (non-crossing) terms share the remaining good quantum number \( \Omega = \Lambda + \Sigma = 1 \) and are both labelled 1. In this sense a transition between Russell–Saunders states \( ^3\Sigma \) and \( ^1\Pi \) can be 'induced' by the LS coupling operator. Both types of PES's can be dynamically coupled by radial \( T_{\text{rad}}^{N;r} \) and those of differing electronic angular momentum (\( \Lambda \) or \( \Omega \)) by rotational \( T_{\text{rot}}^{N;r} \) coupling. It is therefore not surprising that fine-structure states may dynamically steer the non-reactive and reactive properties of atoms and molecules, since they correlate with different SO-PES's. The same holds, of course, by microscopic reversibility for their production in non-statistical amounts. Examples of preferential consumption and disposal of S–O energy have been studied experimentally as well as theoretically for non-reactive and reactive collisions.

Regardless of CL, the following prototype studies come to mind: The most elementary examples deal with elastic scattering. The different interaction potentials of rare-gas ions in their two fine-structure states R⁺(\(^2P_{1/2}\),
Fig. 9. Schematic diagram illustrating how two intersecting adiabatic B–O surfaces (dashed lines) of different symmetry \( ^1\Pi \) and \( ^3\Sigma \) are coupled by the S–O operator in the S–O representation, giving rise to a new set of non-intersecting SO–PES's (solid curves) labelled 0 and 1 respectively by the new quantum number \( \Omega = \Lambda + \Sigma \). Note that the \( ^3\Sigma \) B–O state splits into a 1 state which does and a 0 state which does not interact with the 1 state originating from \( ^1\Pi \).

\( ^2P_{3/2} \) with their parent atoms endows them with unequal transport properties, as drift tube measurements of their mobilities have shown (Helm, 1976). PES's for \( F( ^2P_{3/2, 1/2}) + H_2 \) have been computed and studied by Tully (1974b) and Jaffe et al. (1975). In the related system \( Br( ^2P_{3/2}, ^2P_{1/2}) + HI \rightarrow HBr + I, \) Bergmann et al. (1975) have observed that ground-state \( Br( ^2P_{3/2}) \) reacts rapidly while electronic excitation to \( Br( ^2P_{1/2}) \) even inhibits the reaction! Similar selectivity and specificity has been observed in the following CL processes. The reactions of metastable \( Hg*(6^3P_{0,2}) \)

\[ Hg*(6^3P_{0,2}) + X_2 \rightarrow HgX*(B^2\Sigma^+) + X \]  

have been found by Krause et al. (1975) and Hayashi et al. (1978) to proceed primarily via the \( Hg*(6^3P_2) \) component. The reactive cross section of \( Hg*(6^3P_0) \) is roughly a tenth of the former, presumably due to the existence of a barrier in the corresponding SO–PES.

Of particular interest to the chemical laser community are processes (photodissociation, energy transfer, exchange reactions) that generate halogen (especially iodine) atoms with inverted fine-structure populations. As an example we mention the reaction

\[ F + HI \rightarrow HF + I( ^2P_{3/2, 1/2}) \]  

for which Burak and Eyal (1978) find the production rates for \( I*( ^2P_{1/2}) \) and \( I( ^2P_{3/2}) \) to be non-statistical and approximately equal (Dinur et al., 1975;
Dinur and Levine, 1975). A chemically pumped electronic transition laser with > 4 mW output power operating on the 1315 nm intermultiplet transition of I(2P) has been recently reported by McDermott et al. (1978). It is based on rapid E–E energy transfer

\[
O_2^*(1\Sigma_g^+) + I_2 \rightarrow O_2(3\Sigma_g^-) + 2I(2P_{3/2})
\]

(33)

\[
O^*(1\Delta_g) + I(2P_{3/2}) \rightarrow O_2(3\Sigma_g^-) + I^*(2P_{1/2})
\]

(34)

In retrospect, the S–O effects in the relatively strongly S–O coupled systems mentioned so far are not surprising, since the multiplet surfaces are well separated, and their dynamical coupling is weak.

By contrast, the pronounced S–O effects observed in the light systems characterized by weak S–O coupling are more instructive since they are much less obvious.

A reaction of great complexity (5 atoms) whose numerous kinetic and energy partitioning aspects have been studied in some detail, is

\[
\text{NO}(2\Pi_{3/2}; v) + O_3(v_1 v_2 v_3) \rightarrow \text{NO}_2^* + O_2(3\Sigma_g^-)
\]

(35a)

\[
\text{NO}(2\Pi_{1/2}; v) + O_3(v_1 v_2 v_3) \rightarrow \text{NO}_2^* + O_2(3\Sigma_g^- 1\Delta_g 1\Sigma_u^+)
\]

(35b)

As written in terms of two separate reaction channels, equations (35a, b) already anticipate results to be discussed below. Thermal rate constants are known for both channels (Clough and Thrush, 1967) and their dependence on reactant vibration has been studied by laser excitation. As one would expect, NO vibration which does not lie along the reaction coordinate, is relatively ineffective in promoting reaction (Stephenson and Freund, 1976). Excitation of the O_3(001) asymmetric stretch mode, followed to a certain, unspecified, degree of intermode relaxation (Hui et al., 1975), enhances both channels (Braun et al., 1974; Kurylo et al., 1974, 1975; Gordon and Lin, 1976) by reducing their activation energies (Moy et al., 1977). This acceleration by O_3^+ vibration exceeds prior expectations, but translational energy is even more effective.

The excitation functions have been measured in a beam-gas experiment by Redpath and Menzinger (1971, 1975) and by Redpath et al. (1978). Their most relevant finding in the present context was the (indirect) observation (Redpath and Menzinger, 1975) that the two relatively closely spaced (ΔE = 121 cm⁻¹) fine-structure components of NO(2Π_{1/2, 3/2}) are capable of channelling the reaction as written in (35), i.e. of causing the upper 2Π_{3/2} state to give predominantly electronically excited NO₂*, and ground-state 2Π_{1/2} to give NO₂. The fact is unexpected that at collision energies ~ 10 times in excess of the fine-structure splitting dynamic coupling of SO-PES’s appears negligible. A direct test of the f.s. reactivities by fine-structure selecting the NO beam in a deflection experiment is within reach and is being attempted by Stolte (1978). The CL excitation function for the
NO($^2\Pi_{3/2}$) state was found to be well approximated by $\sigma_{3/2}(E_T) = C(E_T/E_0 - 1)^n$ in the threshold region $3.0 > E_T > 6$ kcal/mol, where the threshold is $E_0 = 3.0 \pm 0.3$ kcal, $C = 0.163$ Å² and $n = 2.4 \pm 0.15$. At higher $E_T$, $\sigma_{CL}$ rises faster ($n > 2.4$) than in the threshold region. A puzzling feature of reaction (35) is the failure to observe excited $O_2$ ($^1\Delta_g$ and $^1\Sigma_g^+$) which are both energetically accessible and favoured by adiabatic correlations (Gauthier and Snelling, 1973). Implications of this fact have been discussed in the light of general features of the $O_3$NO PES's (Redpath et al., 1978).

A second example for pronounced S–O effects despite weak coupling is the thermal cleavage of tetramethyldioxetane into predominantly $S_0$ ground-state

$$\begin{align*}
O--O & \xrightarrow{E_a \sim 2.5 \text{ kcal}} O + O^* \\
\sim 50\% \ S_0 & \sim 49\% \ T_1 \\
\sim 1\% \ S_1
\end{align*}$$

acetone and $T_1$ triplet acetone. It is a prime example for highly efficient production of excited states in a blatantly spin-non-conserving reaction (Turro et al., 1974; Wilson, 1976). Process (36) is isomorphic with the (cyclobutane $\rightarrow$ 2 ethylene) reaction in that formation of excited products is enforced by orbital symmetry (Woodward–Hoffmann rules). This is illustrated by the schematic diabatic correlation diagram Fig. 10 showing the $S_0$ ground-state PES with the symmetry-enforced high barrier towards decomposition into $2A$ on the $S_{0,p}$ product surface and the intersecting $T_1$ triplet and $S_1$ singlet PES's. Configuration interaction will strongly mix the singlet surfaces as indicated by the large circles, but S–O coupling of the $S_0 \times T_1$ and $S_{0,p} \times T_1$ surfaces is very weak as symbolized by the small circles. The high triplet yield can be understood in terms of a model developed Tully (1974a, 1975) and Zahr et al. (1975), to explain the fast quenching of $\text{O}(^{1}D)$ by $\text{N}_2$. Applying it to the present case, the isolated $S_0$ molecule, vibrationally excited above the threshold $E_T^0$ is imagined to pass many times through the $S_0 \times T_1$ intersection and has a small probability, say $P_{ST} \sim 10^{-3}$, at each passage to make a transition to $T_1$. After $P_{ST}^{-1} \sim 10^3$ such passages, the transition will have occurred with unit probability. The same model is believed to explain, by a long-lived $\text{BaSO}_2$ complex (Behrens et al., 1976), the rapid, spin-non-conserving (but not chemiluminescent) process

$$\text{Ba}(^{1}S) + \text{SO}_2(^{1}A_1) \rightarrow \text{BaO}(^{1}\Sigma^+) + \text{SO}(^3\Sigma^-)$$

that has been first reported by Smith and Zare (1975). Dioxetanes have been activated (a) thermally (Wilson, 1976), (b) collisionally by $T \rightarrow V$ transfer
Fig. 10. Schematic diabatic correlation diagram for the decomposition of tetramethyl-1, 2-dioxetane into ground-state and electronically excited (triplet $^3A^*$ and singlet $^1A^*$) acetone. The small circles represent the weak spin-orbit interaction of the singlet $S_0$, $S_{0,p}$ with triplet $T_1$ surfaces. The big circles symbolize the strong configuration interaction of the singlet states $S_0$, $S$, and $S_{0,p}$, which causes the transitions between diabatic surfaces to be facile. Thresholds for the slow $S_0 \rightarrow T_1$ transition and the fast $S_0 \rightarrow S$, transition are labelled $E_{S0}^T$, $E_{S0}^S$ respectively. Redrawn from Brown and Menzinger (1978).

(Brown and Menzinger, 1978), (c) chemically by transiently forming a dioxetane from $O_2(1\Delta_g) +$ alkene (in the bulk: Bogan et al. (1975, 1976), and in crossed beam: Alben et al. (1978)), and (d) photochemically by infrared $S_0 \rightarrow S_0$ (Haas and Yahav, 1977, 1978) or by direct $S_0 \rightarrow S_1$ absorption (Lechtken and Turro, 1973; Smith et al., 1977).

The collision-induced dissociation (b) of tetramethyldioxetane by a variable energy xenon beam (Brown and Menzinger, 1978) shows a threshold for CL production in nice agreement with thermal activation energy and, more interestingly, a marked increase in photon yield as the collision energy is raised and the amount of vibrational energy deposited in the dioxetane molecule increases. With reference to Fig. 10 this signals the opening of a