Excited States and Reactive Intermediates

Photochemistry, Photophysics, and Electrochemistry

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Excited States and Reactive Intermediates

Photochemistry, Photophysics, and Electrochemistry

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FOREWORD

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PREFACE

MOLECULES IN THEIR EXCITED STATES and molecules of transient existence generated by photochemical stimulation or by other processes, such as electrochemistry, are rapidly drawing considerable interest and gaining importance. The excited state of a molecule is, in many ways, a new species different chemically from the ground state molecule and endowed with additional energy; it is often capable of chemical processes that are not possible in the ground state. The ability to do "test tube" experiments with such short-lived species is currently under intensive development.

The conference from which this book was developed addressed many of the techniques that may be used to probe these systems and dealt with the new chemistry that is being learned.

Approximately 160 participants took part in the Biennial Inorganic Chemical Symposium 1985. The participants came primarily from Canada and the United States; however, some came from as far as Japan, England, Belgium, Italy, East and West Germany, and The Netherlands, thus generating an international atmosphere. They heard the latest ideas in excited state photochemistry and photophysics, species at electrode surfaces, resonance Raman spectroscopy, electrochemiluminescence, photochemistry of organometallic and cluster species, and gas phase organometallic chemistry to name a few topics. Some fifty posters were also presented and the Chemical Abstracts Services displayed the latest in on-line searching.

Funding for the conference came from the divisions of inorganic chemistry of the American Chemical Society (ACS) and the Chemical Institute of Canada, the Petroleum Research Fund (ACS), the Natural Sciences and Engineering Research Council, York University, and eight industrial companies: Strem Chemicals Inc.; Merck Frosst Canada Inc.; Union Carbide Canada Limited; EG&G Canada Limited; Xerox Research Centre of Canada; Tasman Scientific Inc.; Guided Wave, Inc.; and Lumonics Inc.

I hope this volume will stimulate the readers to consider how they might also contribute to this rapidly growing area.

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INTRODUCTION

CHEMISTS HAVE BEEN CONCERNED predominantly with the chemistry of species that exist in their molecular ground state, often stable for an indefinite period. Structures can, in principle, be obtained by X-ray crystallographic methods, and physical data such as NMR, IR, and UV/VIS spectra can be obtained with conventional spectrometers.

The advent of lasers and electronic devices that can record extremely fast events has led to growing interest in the study of molecules in excited states, usually, though not exclusively, the lowest excited state. The detailed study of excited states is a field that is now growing rapidly and promises to deliver a fascinating new view of chemistry in the future.

Excited States: Characteristics

A molecule in its first excited state is, in a very real sense, a different molecule from the ground state of the species. It possesses additional energy and probably has a different structure, at least in respect to small changes in bond lengths and angles, and indeed may have a totally different stereochemistry. It has different electronic and vibrational spectra and clearly has a different chemistry. Such chemistry is referred to as *photochemistry* because it is accessed by a light absorption event. These excited state molecules commonly exist for time intervals ranging from picoseconds to microseconds, rarely longer, except when solids at cryogenic temperatures are being studied. Nevertheless, methods of analysis are available to probe the photophysics and photochemistry of these species even on such a short time frame.

Light absorption will not generally occur to the lowest excited state, but rather a series of excited states may become populated. These will generally decay rapidly (in picoseconds) to the lowest excited state. One can anticipate the even richer chemistry of these higher excited states, but their lifetime will usually—though not exclusively—be so short that this chemistry has no time to be expressed. Nevertheless, light emission and photochemistry may sometimes be observed from these higher energy levels. Special techniques such as ultra-short laser pulses (measured in femtoseconds) are becoming available to probe this chemistry (for example, on the time scale of bond breaking).

In general the lowest excited state will decay back to the ground state by one or more pathways, including radiationless *deactivation* (loss of excited state energy as heat to the surroundings), one or more photochemical reactions, or by *luminescence* (fluorescence or phosphorescence). The study of these processes leads to a better understanding of the electronic structure of the excited state.

In the short term, the value of such studies must lie in what we can learn about how chemistry changes when the quantum mechanical state of a molecule changes, and how the additional energy, distributed over the molecule, modifies its chemistry. In the long term, new industrially important processes may depend upon the use of excited state molecules.

With the exception of a few highly studied states, such as, for example, the redox active lowest metal-to-ligand charge transfer excited state (MLCT) in the $[Ru(bipyridine)_3]^{2+}$ cation, or the ligand field active ^2E state of Cr(III), we know relatively little about these excited states. An enormous body of knowledge is waiting to be explored.

Excited State Quenching Reactions

An important facet of the chemistry of excited states is that additional energy confers upon the state both greater oxidizing power and greater reducing power, relative to the ground state. The greater reducing power originates in the higher energy electron that has been excited, while the greater oxidizing power resides in the hole created by the excitation of an electron. Electron transfer reactions may be observed by reaction of the excited state with an electron donor or acceptor.

Where the excited state luminesces, redox reactions with various species can be monitored by observing the quenching of excited state luminescence, or reduction in excited state lifetime, as a function of the concentration of quenching species (Stern-Volmer plot). In this fashion one can determine the rates of chemical reaction between excited state and quencher, and, using models such as those developed by Marcus or Angmon and Levine, determine various parameters such as free energies of activation and reorganization energies.

Because of the much greater driving forces potentially available in reactions between substrates and excited state molecules, difficult—but valuable—electron transfer reactions, such as the oxidation of water or chloride ion, may be accessed through excited state photochemistry. The question of how to separate hole-electron pairs generated in a quenching reaction, how to provide kinetic pathways to lead these two highly reactive species far apart from each another, and how to couple in some useful chemistry are currently of interest.

Of related interest is the problem of how far apart, in a fixed sense, an excited state and a quencher can be, and yet have electron transfer take place. Thus one can have quenching via a collision process, or by overlap of donor and acceptor orbitals at long distances. If the excited state and quencher are linked by a long conjugated pathway, quenching might be expected to take place. However, what about nonconjugated and through-space pathways, both of which can also lead to quenching? Such studies can lead to geometric information about proteins and impurity sites in crystal.

Some extremely fascinating oxidative addition-type chemistry is possible at cryogenic temperatures when metal atoms are irradiated in the presence of C-H and C-O bonds. Metal atoms are inserted, presumably via an excited state. This may well have significance for the activation of alkanes.

Some of the more interesting and valuable redox processes are multi-electron in nature, suggesting the utility of coupling a two- or many-electron event into an excited state process. The study of the excited state photochemistry and photophysics of binuclear and polynuclear (cluster) molecules is thus becoming of importance, and two-electron reactions are being identified.

The sensitization of semiconductors is a special example of electron transfer quenching and may prove to be very important. A photoexcited electron may, for example, be injected with high quantum yield into the semiconductor conduction band, to produce a photovoltaic device. The "hole" that is "left behind" may then perform some useful oxidation process.

Excited state quenching is not restricted to electron transfer processes, but may also occur by atom abstraction (for example, hydrogen atom abstraction), or by energy transfer to another species. In addition, the excited state energy may be used along a reaction coordinate leading ultimately to ligand loss or ligand exchange. New molecules may be formed by shining light upon the old. Organometallic photochemistry is particularly rich in providing unusual molecules after stimulation by light. The mechanisms and dynamics of such reactions are areas of serious study.

Indeed elucidation and understanding of the many processes that can occur upon light stimulation, and the chemical dynamics associated therewith, are major goals of current excited state chemistry.

Photoexcitation of biological molecules, proteins, and enzymes also has interest (such as watching a carbonyl group photodissociate from carbonyl heme and studying the chemistry of the resulting products).

Spectroscopy

As one might expect, various spectroscopies, especially electronic spectroscopy and resonance Raman spectroscopy, can provide detailed information about the electronic and vibrational nature of an excited state. Conventional electronic spectroscopy, absorption and emission, can provide information about the geometry and bond distances in excited states, while resonance Raman reveals the nature of the coupling between an electronic state and vibrational modes of the molecule.

Transient absorption spectroscopy, wherein one measures the electronic absorption spectrum of a molecule in an excited state, is still in its infancy, but the growing availability of ultra-high-speed, rapid-scan spectrometers augurs well for this area of spectroscopy. Thus one may, in the future, routinely probe excited state absorption spectra as well as ground state absorption spectra. The former can be expected to be as valuable in obtaining information about the excited state as is the latter for the ground state.

Time-resolved spectroscopies of various kinds have proven useful in probing the life of an excited state. As an excited state decays, perhaps through a chain of species, time-resolved spectroscopy (e.g., luminescence, excitation, resonance Raman) can provide data for these various steps. Such studies have led, for example, to the view that the first MLCT excited state in $[\mathrm{Ru(bipyridine)_3}]^{2+}$, is localized in one bipyridine ring rather than delocalized over all three rings.

Electrochemistry

Electrochemically generated chemiluminescence provides an unusual method for studying excited state energies. Thus, for example, an oxidant and a reductant can be generated at the same electrode (with alternating polarization), or at two closely spaced electrodes. Given appropriate energetics, the oxidant and reductant quench one another to generate an excited state rather than a ground state product, and luminescence may be observed.

CONTENTS

1

Excited States of Mononuclear and Dinuclear Chromium(III) Complexes

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Excited states of Cr^{3+} complexes were explored by single crystal spectroscopy at low temperatures. In the dimeric $[a_4Cr(OH)_2Cra_4]^{4+}$ the sharp ^2E single excitations were used to determine orbital exchange parameters. Out-of-plane interactions are dominant. The complex $CrCl_6^{3-}$ was studied in two exactly octahedral crystal environments. Broad-band $^4T_{2g} \longrightarrow {^4A_{2g}}$ luminescence with a great deal of fine structure was observed. The equilibrium geometry of the luminescent $^4T_{2g}$ state is a distorted octahedron with an equatorial Cr-X elongation of 0.1 Å and a small axial compression.

Luminescence from Cr^{3+} complexes, both in the solid state and in solution, is a widespread phenomenon. The great majority belong to type a) in Figure 1, where the luminescent state is ^2E and the optical transitions are sharp. The well-known ruby emission is a prototype for this situation. In a weaker ligand field the situation b) in Figure 1 is approached, the $^4T_2$ state becomes competitive with ^2E as the luminescent state. The $^4T_2$ emission, corresponding to a spin-allowed d-d transition, is vibronically broadened. Pure $^4T_2$ luminescence from Cr^{3+} has been observed in halide and oxide coordinations (1). Intermediate situations with both ^2E and $^4T_2$ emissions are also known.

The ^2E and $^4A_2$ states both derive from the $(t_2)^3$ electron configuration. The two states have approximately the same chemical bonding and thus the same equilibrium geometry. The resulting sharpness of the corresponding optical transitions in absorption and emission at low temperatures provides a great deal of information about the nature of the excited ^2E state. In the case of dinuclear Cr^{3+} complexes very useful information about the exchange coupling can be obtained from a detailed study of the singly and doubly excited ^2E dimer states (2). The reason lies in the intraconfigurational nature of the ^2E excitations, which greatly simplifies the theoretical ap-

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proach to the problem. It is possible to deduce the dominant orbital contributions to the net exchange from an analysis of the energy splittings in the excited states which result from exchange interactions. This information about the mechanisms of exchange is not accessible by studying the ground-state properties alone. We will give an illustration of this type of study in the first part of this paper.

The $^4T_2$ state derives from the $(t_2)^2(e)^1$ electron configuration and is therefore displaced with respect to $^4A_2$ in the diagram of Figure 1b. Exploring the nature of the $^4T_2$ state, in particular its equilibrium geometry with respect to the ground state, is chemically and physically relevant. In the low-field situations of Figure 1b $^4T_2$ is the excited state with the longest physical lifetime. Its photochemical relevance is thus enhanced. The broad-band $^4T_2 \longrightarrow {}^4A_2$ luminescence lies in the near infrared (NIR). Solid state materials with broad NIR luminescence are of current interest as possible candidates for tunable lasers (1) as well as "solar concentrators" (3). In the second part of this paper the potential of crystal luminescence spectroscopy to investigate excited state properties will be illustrated for $CrCl_6^{3-}$.

Superexchange in bis(μ-hydroxo)-bridged chromium (III) dimers

Optical spectroscopy is a valuable complement to magnetochemical techniques for the study of exchange effects in polynuclear paramagnetic complexes. A recent review was given in Ref. (3). Dinuclear Cr^{3+} complexes have received a great deal of attention, mainly because of the sharpness and thus the high information content of their $^2E \longleftrightarrow {}^4A_2$ transitions. The complexes $[a_4Cr(OH)_2Cra_4]^{4+}$, where $a = NH_3$ or a_2 = en, have been studied in great detail(5,6). They will serve as illustrative examples of the types of effects which are observed and the conclusions which can be drawn.

When both ions of a Cr^{3+} dimer are in the electronic ground state, the exchange interaction can be represented by the well-known Heisenberg Hamiltonian

$$\hat{H}_{ex,g} = -2J_{ab}\,\vec{S}_a \cdot \vec{S}_b \qquad (1)$$

One of the main aims of magnetochemical studies is a determination or estimate of the exchange parameter J_{ab}.

When one of the ions is in the ^2E state we have a singly excited dimer state, and the exchange interactions can be represented by

$$\hat{H}_{ex,e} = -2\sum_{i,j} J_{a_i b_j}\,(\vec{s}_{a_i} \cdot \vec{s}_{b_j}) \qquad (2)$$

where i and j number the singly occupied t_2 orbitals. $J_{a_i b_j}$ are orbital exchange parameters, which are related to J_{ab} by

$$J_{ab} = \frac{1}{9} \sum_{i,j} J_{a_i b_j} \qquad (3)$$

The simplicity of equation (2) results from the fact that both the $^4A_2$ and the ^2E state correspond to a half-filled t_2 shell in the strong-field limit. As a consequence the ^2E excitations are pure spin-flip transitions. More complicated expressions for the exchange Hamiltonian result even for the case of orbital changes within the $(t_2)^3$ configuration ($^2T_1$, $^2T_2$ excitations). On the basis of equation (2) it is possible to determine the individual orbital parameters from a knowledge of the experimental energy splittings in the singly excited ^2E dimer state. The dominant orbital pathways of the exchange coupling can thus be derived. In the title complexes we distinguish between in-plane and out-of-plane orbital interactions, as shown schematically in Figure 2. With a Cr-Cr separation of approximately 3.0 Å and a CrOCr angle of 100° it is not a priori clear which of the two is dominant. The question was recently resolved by a spectroscopic determination of the exchange splittings (5).

Figure 3 shows that, as a result of exchange splittings, there is a great deal of fine structure in the ^2E, $^2T_1$ region of the 6K single crystal absorption spectrum of $[(NH_3)_4Cr(OH)_2Cr(NH_3)_4]Br_4 \cdot 4H_2O$ (abbreviated $[NH_3]Br_4 \cdot 4H_2O$). The temperature dependence of the low-energy part of the spectrum is shown for $[(en)_2Cr(OH)_2Cr(en)_2]Br_4 \cdot 2H_2O$ (abbreviated $[en]Br_4 \cdot 2H_2O$) in Figure 4a. On the basis of the observed polarizations and temperature dependencies the dimer transitions can be assigned. The exchange splitting pattern of the ground and excited state emerges (Figure 4b). Under very high spectral resolution the dimer transitions in $[NH_3]Br_4 \cdot 4H_2O$ were found to consist of several sharp lines. This "zero field splitting" is illustrated in Figure 5. It provides an additional handle for the assignment of the dimer states.

As elaborated in detail in Ref. (5) there are two principal intensity mechanisms for dimer excitations. The single-ion mechanism is based on the combined action of spin-orbit coupling and an odd-parity ligand field potential at the Cr center. It is by this mechanism that spin-forbidden transitions obtain their intensity in mononuclear complexes. The pair mechanism, on the other hand, is restricted to exchange-coupled systems. It leads to the selection rules $\Delta S = 0$, $\Delta M_S = 0$, where S, M_S characterize the dimer states. The single-ion mechanism also allows transitions with $\Delta S = \pm 1$ and $\Delta M_S = \pm 1$. In addition, both mechanisms lead to orbital, i.e. symmetry selection rules. In order to make full use of the latter in the assignment of dimer states it is essential to have single crystal data.

The fact that the crystals used in this study are primitive triclinic proved to be an advantage rather than a disadvantage. All the dinuclear molecules are lined up parallel in the crystal, and it was found that the crystal extinction directions in the relevant wavelength range more or less coincide with the molecular symmetry axes (6). In higher symmetry crystal systems one often encounters the problem that it is difficult or impossible to extract molecular po-

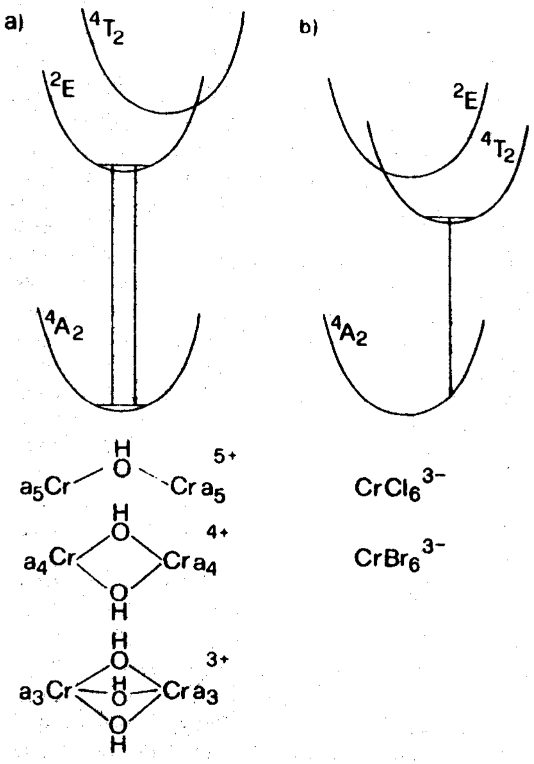
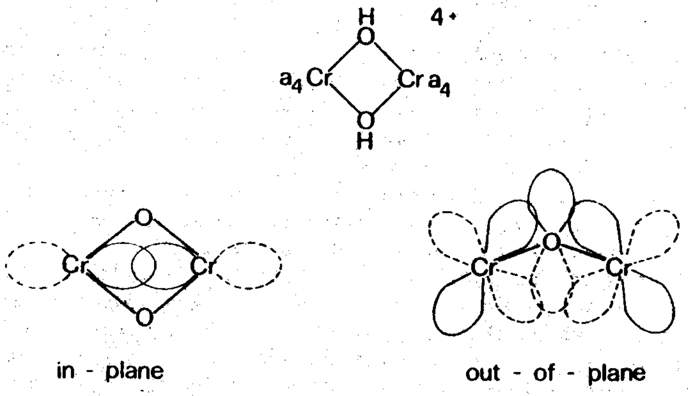


Figure 1. Luminescent states of Cr^{3+} complexes.



in - plane

out - of - plane

Figure 2. Exchange interaction pathways in $[a_4Cr(OH)_2Cra_4]^{4+}$ complexes.

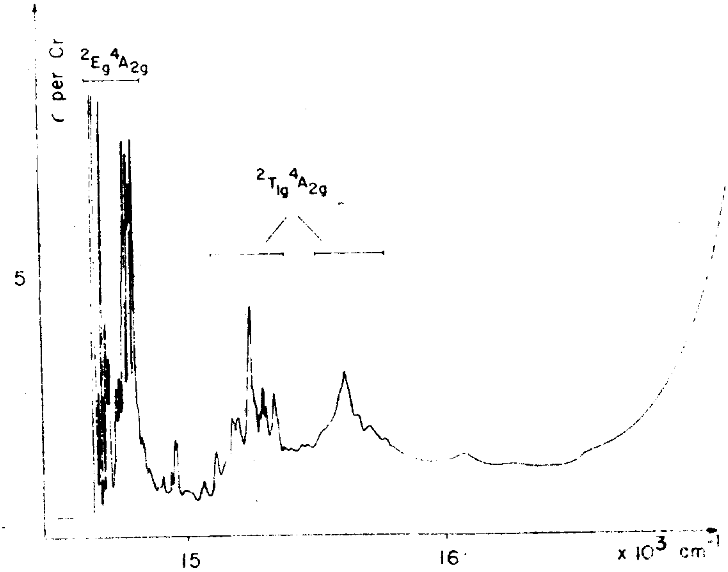


Figure 3. Single crystal absorption spectrum of $[NH_3]Br_4 \cdot 4H_2O$ at 6K in the $^2E/^2T_1$ region. "Reproduced from Ref. 5 - Copyright 1982, American Chemical Society".

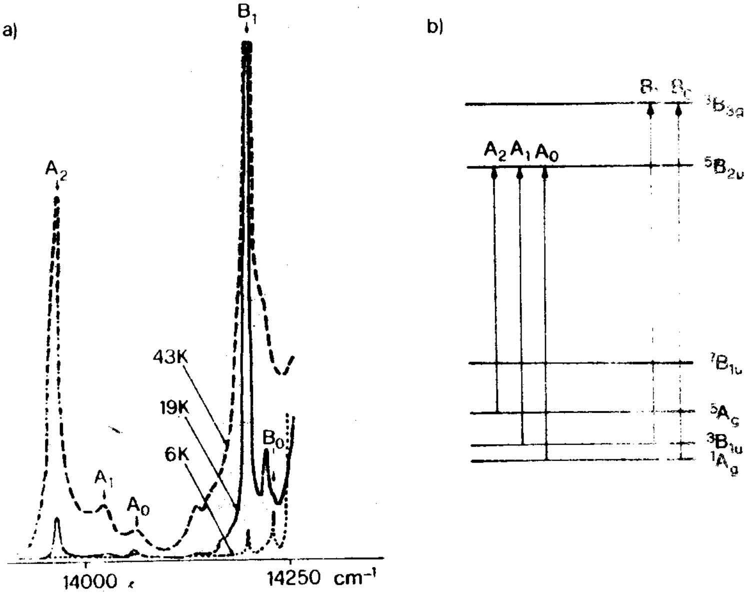


Figure 4. Low-energy dimer excitations of $[en]Br_4 \cdot 2H_2O$. "Reproduced with permission from Ref. 4. Copyright 1985, Reidel Publishing Company."