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Edited by J.N.Bradley/ R.D.Gillard/ R.F.Hudson

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Preface

New knowledge in chemistry accumulates faster each year. Undergraduate courses in chemistry undoubtedly benefit from a judicious admixture of new material, and there is therefore always pressure for the content of courses to increase. Teaching staff often justify this by the statement that as new results appear, so new generalizations and themes emerge which help in accumulating and remembering chemical information. This statement is probably truer for experienced chemists, since to the undergraduate the new generalizations themselves represent an increased learning load. The same is true for graduates acquiring, by intensive study, detailed knowledge of a specialized area, who none the less wish to keep abreast of developments in other fields.

Unfortunately, too, the sources from which advanced teaching material must be taken are commonly aimed at an audience of experts who, very properly, do not expect elementary background material. The average review of modern work therefore starts at a level high above that of the non-specialist. This gap is a matter of concern to us and to many of our colleagues in other teaching institutions with whom we have discussed the problem of source material.

There is therefore a requirement for sources of information useful to and usable by undergraduates. To be useful, they must present information on areas of importance either not covered by standard text books or covered in too brief a fashion. The presentation must be highly explanatory, more so than is appropriate to review articles aimed at research workers in their own field, and must correlate information from related areas. This form of presentation may be at the expense of the quantity of information presented; these are essays, not comprehensive reviews.

These essays, then, attempt to provide genuine teaching matter for final year undergraduates, looking at the particular topics described. They embrace subjects that are possibly under-represented or cursorily treated in standard university texts, and we hope may be useful in informing the graduate chemist of developments across the whole range of chemistry.

Friedel said that "The purpose of instruction, particularly at higher levels, is less to convey matters of detail than to stimulate thought, not so much to pile fact on fact as to digest some of them well, less to slide round difficulties than to illuminate them, less to give faith in the infallibility of current methods and results than to point out their weaknesses, and thereby to cultivate critical attitudes and free inquiry, sound bases for the inquiring scientist." We hope that this series provides undergraduates and graduates with material which meets Friedel's suggestion, giving both an introduction into areas unfamiliar to them.

J. N. BRADLEY
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Problems in the photochemistry of transition metal compounds

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1. Introduction

In this essay, I discuss two examples to illustrate the general background against which inorganic photochemistry has developed in the last decade, when it has 'come of age' in terms of the sophistication both of the experimental approaches applied and of the theoretical and mechanistic discussion. That it took rather longer than organic photochemistry* to reach this level is not surprising in view both of the generally more complex description of the electronic states involved and of their generally greater number, resulting from the sets of *d* orbitals and electrons, the angular momenta of which may be permuted to give a proliferation of states and sub-states. It is to the adaptation of molecular orbital (MO) theory to crystal field situations that we owe our understanding of the spectroscopy (and hence the photochemistry) of metal complexes. Metal and ligand orbitals are combined (Fig. 1) to give the now familiar pattern, and the types of transition apparent in this scheme are as follows (referring to the labelling in the Figure).

1. 'Ligand-field' or, as they are also known, 'metal-centred' or '*d-d*' transitions. These will involve changes in population (or of spin, or both) of the *d* electrons among the *d* orbitals of the metal atom. They will be of low energy and either of relatively, or very, low extinction. It is this type of transition which is regarded as responsible for photochemical ligand-exchanges (substitutions) of complexes, particularly solvolyses, e.g.

$$[Cr(NH_3)_6]^{3+} \xrightarrow{h\nu} [Cr(NH_3)_5(H_2O)]^{3+} + NH_3 \qquad (1)$$

2. Ligand-to-metal charge-transfer transitions, denoted LMCT or as 'charge-transfer-to-metal' (CTTM). These are also very common, and can be written in general as follows.

$$\begin{tikzcd}
{[L_5{-}M{-}L]^{n-}} \arrow[rr, "h\nu"] & & {[L_5{-}M\ \ L^{\cdot}]^{n-}} \arrow[dl] \arrow[dr] & \\
& \text{cage recombination} & & \text{diffusion apart}
\end{tikzcd} \qquad (2)$$

---

* See S. T. Reid 'Essays in Chemistry' 1971, **2**, 93.

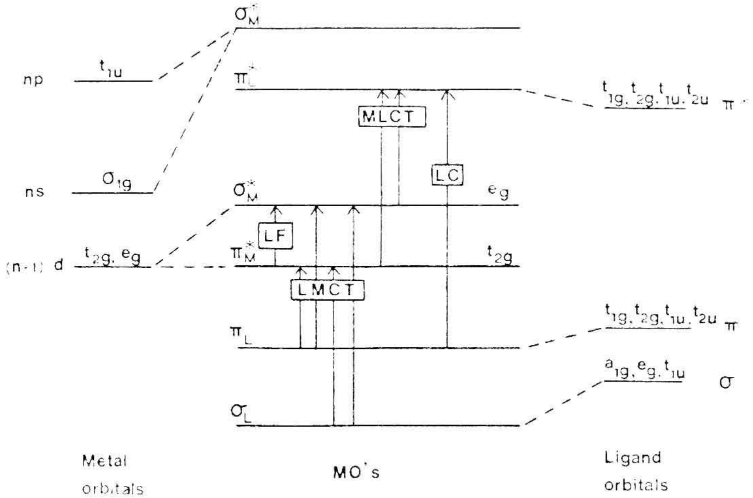
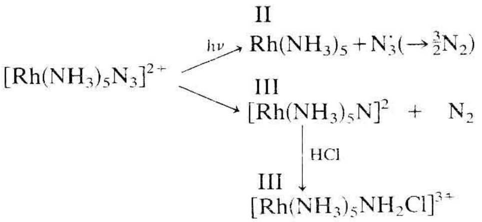


FIG. 1 Molecular orbital (MO) scheme for an octahedral complex: LF—Ligand-field transitions LMCT—ligand-to-metal charge-transfer MLCT—metal-to-ligand charge-transfer LC—ligand-centred transitions.

Usually M will be in an oxidized state and L will be a reducing ligand such as a halide or carboxylate ion. The ligand fragment can often be detected by flash photolysis [for example, as $X_2^{-\cdot}$ from halide complexes of cobalt(III)] or by electron spin resonance spectroscopy following irradiation usually in a rigid matrix but occasionally in solution (as with some carboxylate complexes of oxidizing metal ions). An interesting competitor with equation (2) has been reported by Basolo who finds azide ion coordinated to rhodium(III) to yield a coordinated nitrene on photolysis in an aqueous solution of HCl (1·0 mol dm^{-3}), viz.,

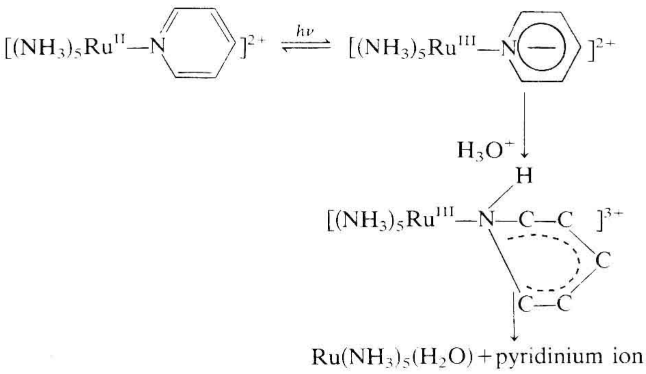


$$[Rh(NH_3)_5N_3]^{2+} \xrightarrow{h\nu} \overset{II}{Rh}(NH_3)_5 + N_3^{\cdot}(\rightarrow \tfrac{3}{2}N_2)$$

$$[Rh(NH_3)_5N_3]^{2+} \longrightarrow \overset{III}{[Rh(NH_3)_5N]^{2}} + N_2 \xrightarrow{HCl} \overset{III}{[Rh(NH_3)_5NH_2Cl]^{3+}}$$

3. Metal-to-ligand charge-transfer, denoted MLCT or as 'charge-transfer-to-ligand' (CTTL). This is rather rarer, requiring a reducing metal and an oxidizing ligand to be energetically accessible to near u.v.

light, but a nice example due to Endicott is shown in outline:



4. Ligand-centred transitions. These are typical of the ligand, and a simple example of a photochemical consequence of excitation of such a transition is provided by cis-trans isomerization, for example, of cis-4-stilbazole (4-styrylpyridine). In a sense, the presence of the metal ion is photochemically irrelevant here, and we shall pay no further attention to such cases.

$$[Ru^{II}(dipy)_2(\text{cis-4-stilbazole})_2]^{2+} \overset{h\nu}{\rightleftharpoons} [Ru^{II}(dipy)_2(\text{trans-4-stilbazole})_2]^{2+}$$

In making this particular classification of spectroscopic transitions, and hence offering a general rationalization of photochemical behaviour of inorganic complexes, one is making several assumptions, including the 'purity' of a transition and the non-overlapping character of adjacent transitions. Irradiating a single complex in its various different transitions using selected monochromatic light of the various appropriate energies often does segregate different types of photochemical reaction, but this segregation clearly breaks down in some instances. Even the photochemistry of the ligand-field bands has presented considerable difficulties, which are well-illustrated by the photosolvolyses of Cr(III) complexes. This is the first example I shall discuss.

2. Chromium(III)

Considering the energy levels for an octahedral complex of Cr(III) of O_h symmetry (Fig. 2), we have a set of quartet states ($S=\frac{3}{2}$) obtained by promoting one electron from a t_{2g} orbital to an e_g orbital and also a set of doublet states ($S=1$) obtained by 'pairing' the spins of two electrons. This situation, by analogy with organic photochemistry, prompts the construction of a Jablonski diagram (Fig. 3) in which the lowest energy state in

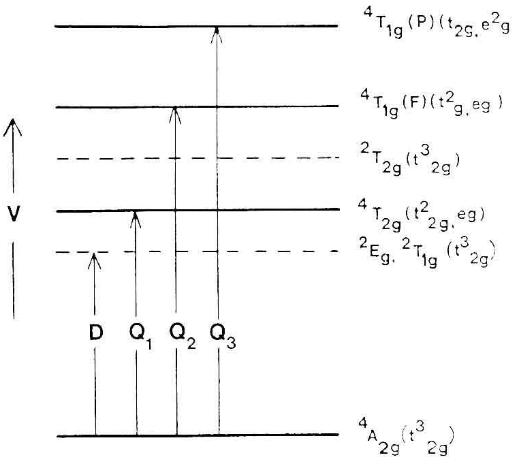


FIG. 2 Energy levels and transitions for Cr(III) in O_h symmetry: D—transition to lowest doublet state Q_1, Q_2, Q_3—transitions to first, second and third excited quartet states.

absorption, the ^2E_g state, is that into which all others will ultimately convert and which might well be regarded as the origin of all photochemical reactivity, rather as the lowest triplet state of organic molecules has been regarded. The lower of various states alluded to are often well-resolved in the spectra of Cr(III) complexes (Fig. 4), and can be selectively populated using monochromatic light. A further analogy with organic photochemistry is that the ^2E_g state can emit a long-lived phosphorescence, usually observed in rigid media at 77 K, but in some cases

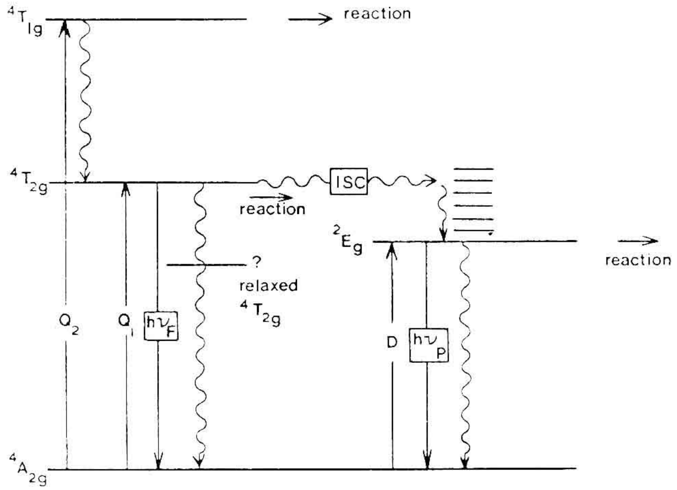


FIG. 3 Jablonski diagram for the lower excited states of octahedral Cr(III) complexes. $h\nu_F$ and $h\nu_P$ refer to fluorescent and phosphorescent processes and ISC to inter-system crossing.

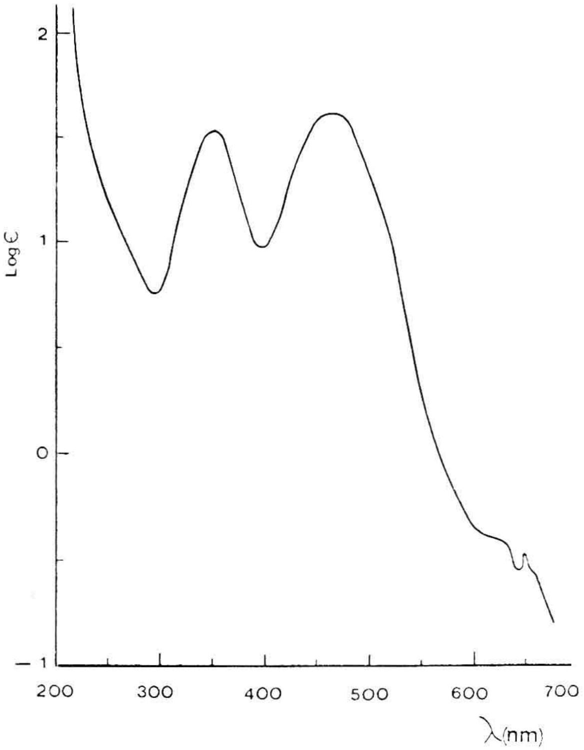


FIG. 4 Absorption spectrum of $Cr(NH_3)_6^{3+}$ in water, from M. R. Edelson and R. A. Plane, *J. Phys. Chem.*, **63,** 327 (1959). Compare the sharp but weak doublet band at ca. 650 nm with the broad but stronger quartet bands.

also measurable in solution. Finally, although the (forbidden) absorption of the ^2E_g band is very weak, direct irradiation in this band can be accomplished to produce photosolvolysis, and for reaction (1), irradiation in the bands *D* and Q yield values of 0·29 and 0·26 respectively, possibly implying efficient conversion from one of these states to the other.

This simple and attractive picture, however, has received much criticism in the last few years, of which the following is typical.

(i) In those cases where a *fluorescent* emission from the $^4T_{2g}$ state also occurs as in the hexakisureachromium(III) cation, $[Cr(urea)_6]^{3+}$, the emission is strongly red-shifted to an energy lower even than that of the phosphorescence (Fig. 5), which implies that the *relaxed* $^4T_{2g}$ state is lower, not higher, in energy than the ^2E_g state, and direct population of the latter may simply result in crossover to the quartet state. In other words, a Jablonski diagram based on absorption spectral energies is misleading, and it should more accurately refer to 'relaxed excited state'

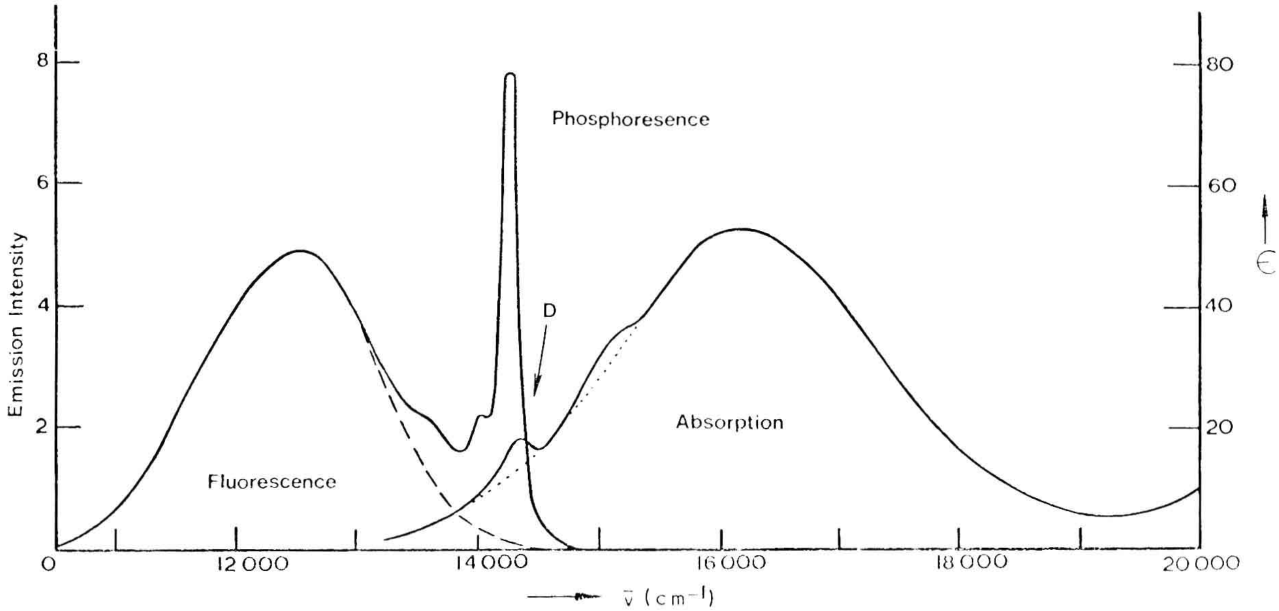


FIG. 5 Absorption (298 K) and emission (98 K) spectra of 0.03 M [Cr(urea)$_6$](ClO$_4$)$_3$ [from G. B. Porter and H. L. Schäfer, *Z. Phys. Chem.* (Frankfurt) **37,** 104 (1963)].

energies. Such thermally equilibrated excited states have been denoted 'thexi' states. Their energies are not as readily located as are those of the ^2E_g states, however, because both absorption and emission bands are broad and the relevant energy, that of the 0–0 transition, is located at the intersection of these two broad bands, a point which is, in many instances, very near to that of the ^2E_g state. The latter is usually well-defined energetically, both absorption and phosphorescence bands being quite sharp (Fig. 5), in accordance with the negligible change in nuclear configuration (the framework of the complex ion) on simply changing the spin multiplicity of the ground state.

(ii) The phosphorescence of hexamminechromium(II) ion, $[Cr(NH_3)_6]^{3+}$, is quenched by added hydroxide ions, but the quantum yield of reaction (1) is barely affected by this treatment, which implies that the phosphorescent ^2E_g state is not the photoreactive state.

(iii) The phosphorescence of hexacyanochromate(III) $[Cr(CN_6)]^{3-}$ in solution in dimethylformamide is quenched by water and di-oxygen, but the photochemical reaction is relatively unaffected.

(iv) The quenching of the phosphorescence of the Reineckate ion, $[Cr(NH_3)_2(NCS)_4]^-$, by energy transfer to $[Cr(CN)_6]^{3-}$ leaves 50% of the photochemical solvolysis (loss of NH_3) unquenched.

(v) Referring to the energy level diagram of Fig. 6; the photoaquation of the cyano-complex $[Cr(CN)_6]^{3-}$ is sensitized by pyrazine and xanthone triplets, but not by the triplets of Michler's ketone or the tris-2,2'-dipyridylruthenium(II) ion, $[Ru(dipy)_3]^{2+}$; however, the latter does sensitize the phosphorescence of $[Cr(CN)_6]^{3-}$, implying that efficient sensitization of the ^2E_g state is insufficient for chemical reaction to occur. In the case of $[Cr(CN)_6]^{3-}$ at least, it appears that the $^4T_{2g}$ state is that responsible for photoreactivity. A further salient point is that the triplet level of Michler's ketone is of the order of the energy of the $^4T_{2g}$ state of $[Cr(CN)_6]^{3-}$ (as indicated in absorption) but nonetheless fails to sensitize it.

Fleischauer, Adamson and Sartori have proposed that excitation of an octahedral complex compound of O_h symmetry produces a $^4T_{2g}$ state of initially the same geometry (as the Franck-Condon principle would suggest): this can then relax vibrationally either to emit or to cross to a doublet state (in a rigid medium) or (in a fluid medium) to undergo a more comprehensive geometrical relaxation to give the photoreactive 'thexi' quartet state.

The photoreactions of six co-ordinated octahedral complexes with true O_h symmetry, $[ML_6]^{3+}$, generally show a wavelength independence of quantum yield, implying that rapid internal conversion for upper quartet states to the lowest quartet state is efficient. However, in the case of

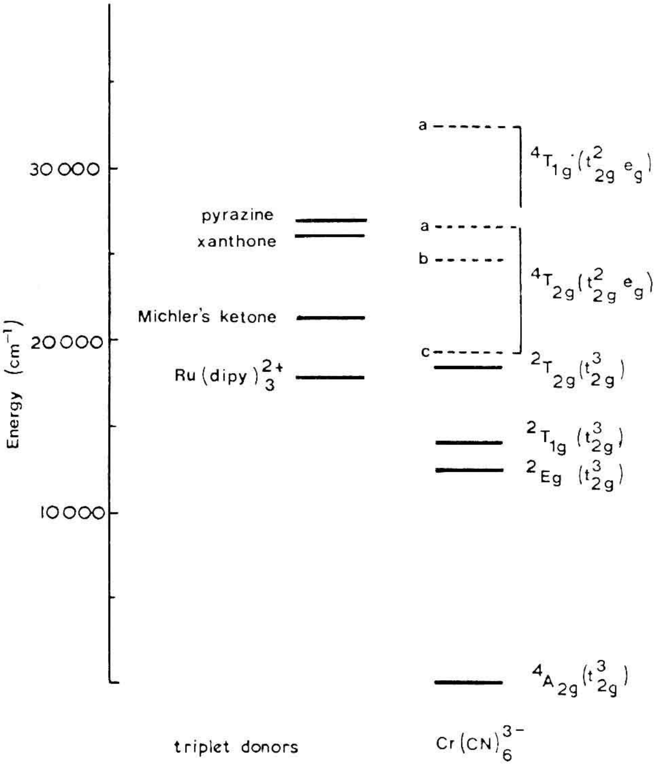


FIG. 6 Energy levels of triplet donors and $Cr(CN)_6^{3-}$. a refers to positioning of band maxima, b and c to the estimated upper and lower limits of the 0–0 level of the $^4T_{2g}$ state (from N. Sabbatini and V. Balzani, *J. Amer. Chem. Soc.*, **94**, 7587 (1972).

complexes with mixed ligands, the ratio of quantum yield, ϕ, for the departure of two different ligands does show a dependence on the wavelength of the light used for irradiation. For example, with *trans*-$[Cr(en)_2(NCS)Cl]^+$, loss of both chloride ion and isothiocyanate ion (so called because it is bonded to chromium through its nitrogen atom) is wavelength-independent from 365 to 549 nm, but while loss of ethylenediamine (en) does not occur on irradiation in the strong ^4E band at 549 nm, it *is* displaced on irradiation at 365, 404 and 464 nm, i.e. it appears that the second excited quartet state is responsible for photoaquation of ethylenediamine, but the first excited quartet state for those of chloride and thiocyanate.

Clearly, opinion has moved in favour of the quartet states as the source of the photochemical reactivity of complex compounds of chromium(III), but the role of the doublet state has not been completely excluded in every case, and we may expect continued interest in this area for some years, not least in the rates and yields of non-radiative energy-wasting processes.

3. Metal carbonyls

The second problem, which is now being attacked on several points, is that of the photochemistry of the Group V1A hexacarbonyls and their monosubstituted derivatives. So much has been done here that I can only outline the main experimental approaches, and the differing kinds of information that these produce, as a demonstration of the activity in mechanistic inorganic photochemistry. Very many cases have now been established by Strohmeier (1964) and others of the following photo-substitution in solution ($M = Cr$, Mo, W) where S is a molecule of the solvent.

$$M(CO)_6 + S \xrightarrow{h\nu} M(CO)_5S + CO \tag{3}$$

Where S is capable of coordination to M, then the product can be isolated and characterized. One question of interest relates to whether the loss of carbon monoxide and the coordination of the solvent molecule S are concerted or whether reaction proceeds via a labile pentaco-ordinate species, $M(CO)_5$, which then reacts further with solvent. The existence of such a pentacarbonyl metal moiety, $M(CO)_5$, was first demonstrated in experiments where hexakiscarbonylmetal(O) was photolyzed in a rigid, glassy alkane matrix at 93 K. The new, well defined absorption bands which were observed in the carbonyl stretching region of the infra red spectrum were assigned to the new species $M(CO)_5$, together with the $2135\ cm^{-1}$ band of free carbon monoxide. These bands disappeared when the cold matrix was allowed to warm: starting material was then recovered in 70% yield. In donor matrices, such as 2-methyltetrahydrofuran (MTHF), the product is believed to be the solvate, i.e. $M(CO)_5\,MTHF$. The geometry of the unstable $M(CO)_5$ is now generally held to be square-pyramidal (C_{4v}) rather than trigonal-bipyramidal (D_{3h}). Subsequent matrix isolation work has involved considerable use of inert-gas matrices and u.v. as well as i.r. spectroscopic measurements, developments including, (i) the observation of photoreversal of reaction (4) utilizing light of

$$M(CO)_6 \xrightarrow{h\nu} M(CO)_5 + CO \tag{4}$$

longer wavelength, (ii) the sequential loss of further CO molecules, reactions (5) and (6)

$$M(CO)_5 \rightarrow M(CO)_4 + CO \tag{5}$$

$$M(CO)_4 \rightarrow M(CO)_3 + CO \tag{6}$$