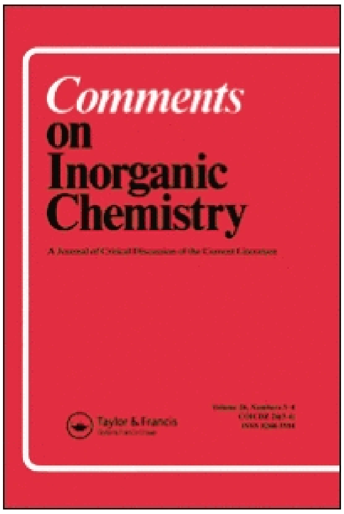

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Organometallic Photochemistry: The Study of Short-Lived Intermediates

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Organometallic Photochemistry: The Study of Short-Lived Intermediates

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The photochemistry of organometallic compounds is a new and exciting research area finding applications in synthetic and industrial chemistry. Photochemical processes involve the generation of molecules in excited states and the formation of highly reactive short lived intermediates. This Comment outlines the experimental techniques available for studying these transient intermediates and discusses the advantages and disadvantages of each one. The applications of these techniques to the study of fundamental photoprocesses are illustrated by a study of the photochemistry of $Fe(CO)_5$, $M(CO)_6$ [M = Cr, Mo, W] and $Mn_2(CO)_{10}$. The use of fast spectroscopy in the investigation of excited states of organometallics is also discussed.

Keywords: *organometallic, photochemistry, excited-state, transient intermediate, matrix-isolation, time-resolved spectroscopy*

INTRODUCTION

The photochemistry of organometallic compounds is a growing area finding applications in synthetic and industrial chemistry as well as being fascinating in its own right. Inherent in any photochemical proc-

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ess is the generation of molecules in excited states and the formation of highly reactive short-lived intermediates. One of the major problems facing any organometallic photochemist is how to study molecules in excited states and how to characterise highly reactive intermediates, many of which have lifetimes of picoseconds or shorter. It is the aim of this article to give a general critical discussion of the experimental methods used to study the chemistry of excited states and short-lived molecules. Attention is focused on the photochemistry of $Fe(CO)_5$, $M(CO)_6$[M = Cr, Mo, W] and $Mn_2(CO)_{10}$ as these serve as excellent examples of how the developments in experimental techniques have aided the understanding of fundamental photoprocesses.

The photochemistry of organometallic compounds can be subdivided into a number of categories of which the most important are:

1. *Ligand-field (LF) photochemistry*: Ligand-field transitions are localised on the metal centre and, in classical coordination complexes, are commonly referred to as metal-centred transitions. However, due to the high covalent character of metal-ligand bonds in organometallic compounds, the metal orbitals are affected significantly by the ligand and any metal-centred transitions have a significant perturbation on the metal-ligand bonding. Consequently, the LF photochemistry of organometallics, in particular those of having carbonyl ligands, is dominated by ligand labilisation.[1]

2. *Metal-to-ligand charge transfer (MLCT) photochemistry*: In one electron terms, an MLCT transition results from movement of an electron from a filled *d*-orbital on the metal to an empty π*-orbital on the ligand. The energy of MLCT transitions is dependent on the oxidation potential of metal atom, the reduction potential of the ligand and the charge separation caused by the transition. Since organometallic complexes are often easily oxidised it is not surprising that MLCT transitions are common. With the exception of associative substitution, MLCT transitions are not often found to lead to ligand labilisation. This is because MLCT transitions originate in a filled *d*-orbital, this not having a significant effect on the metal-ligand bonding. The study of the MLCT photochemistry of transition metal complexes has, to date, been focused on classical coordination complexes such as $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine)[2], but orga-

nometallic complexes are now receiving more attention due to the potential for the study and exploitation of non-dissociative processes.[3]

3. *Ligand-centred (LC) photochemistry*: Organic ligands which can be coordinated to metals have their own set of excited states. As a consequence, organometallic complexes have ligand localised excited states which are not too dissimilar to those of the free ligand. The energy of the LC excited state depends on the properties of the ligand such as the HOMO-LUMO energy gap and the singlet-triplet splitting. An example is $W(CO)_5$(pyridine) where the lowest absorption bands are at approximately the same position and have a similar extinction coefficient to the π-π^* transition of the free ligand.[4]

Although reference to all these photochemical processes will be made, comments will focus on the ligand-field photochemistry of organometallic complexes.

SPECTROSCOPY IN ORGANOMETALLIC PHOTOCHEMISTRY

Despite the fact that UV-vis spectroscopy is used routinely in inorganic chemistry it has severe limitations when applied to organometallic species. Typically, the visible or UV spectrum of either gas- or solution-phase organometallic compounds are broad, featureless and relatively insensitive to the structure of the compound.[5] Information can, however, be obtained by vibrational spectroscopy, in particular infrared (IR). The number, pattern and position of the IR absorptions gives information about molecular structure.[6] This is especially useful in the case of carbonyl compounds due to the very intense IR bands exhibited, both the band pattern and intensity being reproducible using simple force-field models.[7] Additional information can be obtained by isotope labelling experiments.[8] The mixed isotope carbonyl complex $M(^{12}CO)_{x-y}(^{13}CO)_y$ has more IR active bands than $M(^{12}CO)_x$ alone, and the number and frequency of these new IR bands is often sufficient to determine the number of carbonyl groups in the molecule and sometimes its qualitative structure.[9] Indeed, in certain cases, these data can even provide accurate estimates of bond angles.[10]

Matrix Isolation

(A) Outline

One way to record spectra of short-lived metal carbonyl species is to increase their lifetimes by *matrix isolation.*[11] This is achieved by isolating a stable metal carbonyl species in a large excess of an inert solid, the matrix, and then photolysing the sample to generate the desired intermediates. Typical solid host materials are glassy media such as hydrocarbons at liquid nitrogen temperature (77 K)[12] or frozen inert gases such as nitrogen or noble gases, this requiring temperatures in the region of 10–20 K.[13] More recently, cast polymer films have been used.[14] While in the solid environment, bimolecular reactions are limited, provided that the sample is at sufficiently high dilution, and the low temperatures greatly reduce the probability of unimolecular decomposition. As a consequence, once trapped within the matrix, the lifetimes of the reactive intermediates, which exist only transiently under standard conditions, are greatly extended and can be studied using a range of conventional spectroscopic techniques, the most important being IR.[15] Techniques such as electron spin resonance (esr),[16] magnetic circular dichroism (mcd)[17] and laser-induced fluorescence (LIF)[18] have also been applied successfully to matrix trapped organometallic species. More recently, Mössbauer and even NMR and photoelectron spectroscopy have been used.[19,20]

(B) Applications

Matrix isolation has found great application in the determination of geometry and electronic structure of metal carbonyl intermediates as is illustrated in the cases of $Fe(CO)_5$ and $Mn_2(CO)_{10}$.

UV photolysis of $Fe(CO)_5$ in low temperature matrices results in progressive CO loss, yielding $[Fe(CO)_4]$,[21] $[Fe(CO)_3]$,[22] $[Fe(CO)_{2\text{ or }1}]$[22] and, eventually,[23] iron atoms.

$$Fe(CO)_5 \xrightarrow{h\nu} [Fe(CO)_{5-n}]\ \{n = 0 - 5\}$$

Using $^{13}C^{16}O$ and $^{13}C^{18}O$ isotopic enrichment in conjunction with IR spectroscopy and force-field calculations, $[Fe(CO)_4]$ has been shown to have a C_{2v} geometry in the ground state.[24,25] Bond angles have been calculated from IR absorption intensity measurements and are found to be ~ 145° and ~ 120°, varying slightly, but not significantly, between matrices.[24] These values are close to those predicted from approximate[26] and *ab initio*[27] molecular orbital calculations and from density functional calculations[28] for a d^8 ML_4 complex with a *triplet* electronic ground state. Consequently, iron tetracarbonyl should be paramagnetic. This has been confirmed by mcd studies on a matrix-isolated sample.[29]

UV photolysis of matrix-isolated $[Fe(CO)_4]$ leads to the generation of $[Fe(CO)_3]$. Analysis has shown that the tricarbonyl has C_{3v} symmetry is consistent with MO predictions. Again a triplet ground state is suggested.[22]

The molecular geometry and *d*-orbital splitting schemes for $[Fe(CO)_4]$ and $[Fe(CO)_3]$ are shown in Fig. 1.

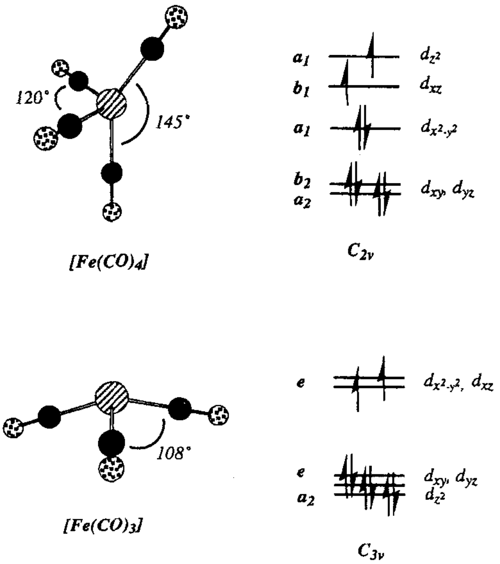


FIGURE 1 The molecular geometry and *d*-orbital splitting schemes for $[Fe(CO)_4]$ and $[Fe(CO)_3]$.

Interesting reaction chemistry is observed between matrix-isolated $[Fe(CO)_4]$ and the matrix itself.[24] If, subsequent to the formation of $[Fe(CO)_4]$, the matrix is irradiated with IR light, a reaction occurs yielding $[Fe(CO)_4L]$ where $L = N_2$, CH_4 or Xe. This process is reversed by irradiation with visible light.

$$[Fe(CO)_4] \underset{vis}{\overset{IR}{\rightleftharpoons}} Fe(CO)_4L \; \{L = N_2,\ CH_4,\ Xe\}$$

The role of the IR irradiation source is thought to be to provide thermal energy by non-radiative decay of excited states of the metal carbonyl,[30] and consequently these reactions are better termed as thermal rather than photochemical.

Matrix isolation coupled with IR laser-induced photochemistry has revealed that the carbonyl ligands of matrix-isolated isotopically labelled $[Fe(CO)_4]$ could be permuted at frequencies corresponding to an absorption of one particular isopotomer of $Fe(^{12}C^{16}O)_{4-n}(^{13}C^{18}O)_n]$ (Fig. 2).[24,25] The results show that the permutational mode of these interconversions is not that expected for the normal Berry pseudorotation, this being the first such example. Initially inexplicable, this rotation has now been rationalised on the basis of the Jahn-Teller effect.[31]

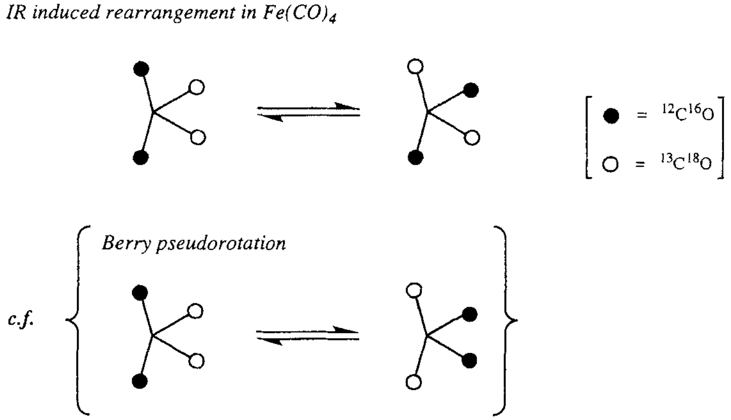


FIGURE 2 The IR induced non-Berry pseudorotation in $[Fe(CO)_4]$.

The photochemistry in matrices often may not mirror that in other chemical environments. Indeed, the matrix cage can effectively block some pathways in photochemical reactions, as is the case for $Mn_2(CO)_{10}$.[32] Photolysis of $Mn_2(CO)_{10}$ in solution can lead to either M–M bond cleavage or CO loss yielding [$\cdot Mn(CO)_5$] radicals and [$Mn_2(CO)_9$], respectively.[33,34] Photolysis of matrix-isolated $Mn_2(CO)_{10}$ yields [$Mn_2(CO)_9$] but provides no evidence for the formation of [$\cdot Mn(CO)_5$] radicals.[35] It is possible that the radicals, once formed, recombine without escaping from the matrix cage. Of interest is that [$\cdot Mn(CO)_5$] radicals can be formed in low temperature matrices by UV photolysis of $HMn(CO)_5$.[36] The combination of ^{13}C isotope enrichment and IR spectroscopy shows that [$\cdot Mn(CO)_5$] has a square pyramidal, C_{4v}, structure with an approximate axial-equatorial bond angle of ~96° (Fig. 4a), this being similar to the axial-equatorial bond angle of the "$Mn(CO)_5$" moiety in $Mn_2(CO)_{10}$.

Solution:

$$Mn_2(CO)_{10} \xrightarrow{h\nu} [\bullet Mn(CO)_5] \text{ and } [Mn_2(CO)_9]$$

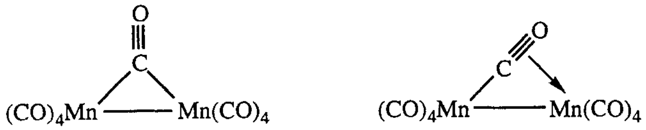
Matrix:

$$Mn_2(CO)_{10} \xrightarrow{h\nu} [Mn_2(CO)_9]$$

$$HMn(CO)_5 \xrightarrow{h\nu} [\bullet Mn(CO)_5]$$

(C) Use of Polarised Light

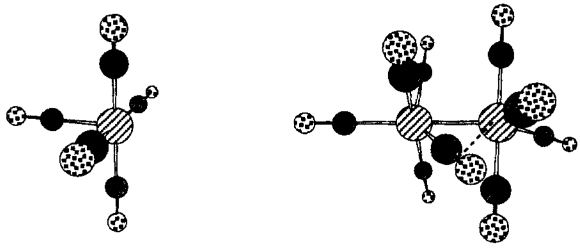
Photochemistry and spectroscopy with polarised light[37,38] have proven extremely valuable in the structural characterisation of dinuclear metal carbonyls trapped in low temperature matrices. This is exemplified clearly by the results of studies on [$Mn_2(CO)_9$].[39] The technique relies on the fact that irradiation using plane polarised light interacts preferentially with those molecules which are oriented in the matrix with their photoactive transition-moment vector parallel to the oscillating dipole moment of the light. Molecules as bulky as dinuclear metal carbonyls have insufficient thermal energy to rotate within the matrix cage at the temperature of the system (10–20 K). Consequently, this technique leads to the generation of partially oriented, dichroic samples of both parent and photoproducts in the matrix. Conventional matrix-isolation experiments have shown that [$Mn_2(CO)_9$] contains a bridging carbonyl group, as evidenced by an IR absorption at 1764 cm^{-1}.[34] The structure can thus be rationalised as containing either a ketonic bridging (μ_2-CO) or a semi-bridging (μ_2-η^1:η^2-CO) carbonyl group (Fig. 3).[36]



Ketonic bridging carbonyl group *Semi-bridging carbonyl group*

FIGURE 3 Ketonic bridging (μ_2-CO) and semi-bridging (μ_2-η^1:η^2-CO) carbonyl groups.

Irradiation of $Mn_2(CO)_{10}$ with plane-polarised UV light leads to the formation of a partially dichroic sample of the decacarbonyl starting material and $[Mn_2(CO)_9]$. Spectra from this sample show that the terminal CO peaks are substantially dichroic whereas the 1764 cm^{-1} band is not. This implies that the group corresponding to the 1764 cm^{-1} band must either be fluxional or else unable to support dichroism in some other way, such as by having an associated transition dipole oriented approximately 45° from the photoactive transition dipole of $Mn_2(CO)_{10}$. This latter explanation is the most feasible, this being consistent with a semi-bridging carbonyl group (Fig. 4b). This conclusion is in agreement with data for crystallographically characterised dinuclear manganese compounds containing semi-bridging carbonyl groups, these showing an Mn-Mn-CO bond angle on the order of 45° and exhibiting a very low CO stretching frequency in the IR spectrum.[40]



a) [•Mn(CO)$_5$] *b) [Mn$_2$(μ_2-η^1:η^2-CO)(CO)$_8$]*

FIGURE 4 The proposed structures for (a) $[\cdot Mn(CO)_5]$ and (b) $[Mn_2(CO)_9]$.

(D) Limitations

Although often proving valuable, matrix isolation has many limitations even for metal carbonyls as illustrated already in the case of the study of Mn-Mn bond scission in $Mn_2(CO)_{10}$. Matrix isolation can not be used easily for the study of charged species,[41] and little kinetic data can be obtained because of the restricted temperature range and limited diffusion. It is necessary to use a large excess of matrix so that the reactive metal carbonyl species are well separated, this having the disadvantage that, in some matrices, large regions of the IR spectrum are blotted out by the matrix itself. This is the case in the study of the interaction of $[Fe(CO)_4]$ with methane in methane matrices, and, as a consequence, no IR absorptions of the coordinated alkane can be detected.[24] A complicating feature in many vibrational studies of matrix-isolated species is that some of the IR bands are split, sometimes into as many as four components.[42] The origin of this "matrix splitting" is not known, but each component probably represents an $[M(CO)_n]$ molecule trapped in a slightly different environment within the matrix.

LOW TEMPERATURE SOLUTIONS AND LIQUID NOBLE GASES

By investigating the reaction chemistry of reactive intermediates in low temperature solutions, it is often possible to augment matrix-isolation experiments. At low temperature, reactions are more slowed down rather than, in a matrix, stopped, and there are not the problems associated with performing chemistry in rigid systems. Liquefied noble gases have found great application in this area, especially since they do not have any infrared absorptions, so long-path-length cells may be employed.[43] This allows weak absorptions of the transient intermediates to be detected. In addition, in these fluid media, kinetic measurements can be made and thus, at least in principle, estimates of bond energies can be made. By engineering high-pressure IR cells, it is possible to perform reactions in liquid noble gases at higher temperatures, even up to room temperature.[44]

In addition to coordinatively unsaturated compounds, low temperature noble gas solutions have been used to stabilise saturated complexes containing ligands which are either very labile or else exhibit unusual coordination modes. This is exemplified by the case of $H_2M(CO)_5$[M = Cr, Mo, W] which has been shown to contain a sideways bonded molecular dihydrogen group (Fig. 5).[45,46] The long path lengths possible allow for the detection of the weak $\nu_{H\text{-}H}$ band. Di-nitrogen complexes such as $Cr(CO)_{6-n}(N_2)_n$ [n = 1–5] have also been investigated in liquid xenon solutions.[47]

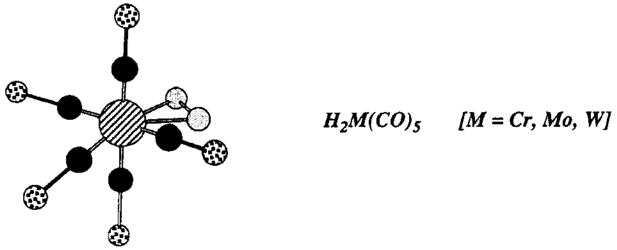


FIGURE 5 The proposed structure of $H_2M(CO)_5$ [M = Cr, Mo, W].

FLASH PHOTOLYSIS AND TIME-RESOLVED SPECTROSCOPY

(A) Outline

If a short-lived species is generated rapidly in a static system, it is possible to monitor the species some time after its generation but before its decay or subsequent reaction. Requisite in this method is a fast spectroscopic technique. In general, the reactive intermediates are produced by irradiation of the starting materials with a short duration pulse from a UV source; *flash photolysis*. The concentration of a reactive intermediate is monitored by means of a second light source producing a longer, less intense, flash of light at a wavelength which is absorbed by the species under investigation. The basic principles of flash photolysis have not changed much since the original experiments by Norrish and Porter[48] and then Pimentel,[49] but the duration of the flash and the speed and apparatus for detection have changed greatly.[50] UV-vis flash photolysis has been crucial for kinetic measurements,[51] but the limitation when applied to organometallic systems is that there is little or no variation between the UV-vis spectra of different intermediates.

A typical apparatus for flash photolysis is shown in Fig. 6. A variant on the classical flash photolysis experiments is *time-resolved infrared spectroscopy*(TRIR). Again the reactive species are generated by a flash from a UV source. The intermediates are then investigated using a tunable infrared source at one particular wavelength, the IR detector retuned and the experiment repeated. By repeating the experiment numerous times, data are accumulated at frequencies across the carbonyl spectral region; this approach is called the *point-by-point* method.

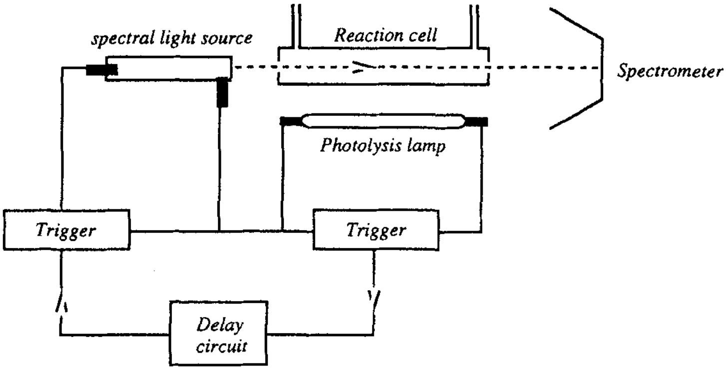


FIGURE 6 A typical apparatus for flash-photolysis.

(B) Timescales

Experiments on the millisecond (ms; 10^{-3} s) and microsecond (μs; 10^{-6} s) timescale provide information about the rates of bimolecular reaction of photogenerated fragments and excited states. Nanosecond experiments (ns; 10^{-9} s) are able to probe the fluorescent emission from singlets as well as intersystem crossing while picosecond studies (ps; 10^{-12} s) yield kinetic data about geminate recombination, solvent interactions, energy exchange, vibrational relaxation and some isomerisations and rearrangements. Femtosecond chemistry (fs; 10^{-15}s) is concerned with the very act of the molecular motion that brings about chemistry. As such, femtosecond experiments allow controlled photodissociations of reactant molecules to be studied in a whole new way.[52]

(C) Use of Lasers

Most modern TRIR experiments use lasers as both the photolysis and detection sources. The special properties of laser radiation of importance to photochemists include the high monochromicity, the possibility of very short pulses, the high peak power resulting from short pulses and the high intensity resulting from small beam area. The typical frequencies used for photolysis of organometallics are 351, 248 and 193 nm, both leading to rich photochemistry and also corresponding to the output from XeF, KrF and ArF excimer lasers, respectively.

Photolysis experiments on the nanosecond timescale or slower generally rely on pulsed lasers as the UV irradiation source. Experiments on the picosecond timescale and shorter begin to require rather different approaches. The exciting flash has to be obtained from Q-switched or mode-locked lasers. In a normal laser, stimulated emission starts once the active medium has achieved a large enough population inversion for oscillation to be maintained. In a Q-switched laser, stimulated emission is prevented, by moving a reflector or by inserting an absorbent medium in the laser cavity, until population inversion has reached a peak level far greater than it would ordinarily attain. When the cavity performance, Q, is subsequently restored, all the energy accumulated in the inversion can then be released as a large pulse of very short duration, often on the nanosecond timescale. Pulses of shorter duration can be obtained by mode-locking. This involves forcing the laser modes of oscillation, which are usually irregular, to oscillate with similar amplitudes and/or with their phases locked so that they interfere with each other. Then, constructive interference occurs as a series of sharp peaks separated by regions of destructive interference. The power of the laser is then obtained in bursts with a duration on the picosecond timescale. Pulses lasting a few femtoseconds can be obtained by refinements in this techniques.

For IR detection, early experiments used either a CO laser[53] or glowbar[54] as the probe light source. However, these have inherent disadvantages. Since the CO laser, by necessity, operates on transitions that can be absorbed by internally excited CO, it is possible for these absorptions to obscure those from the photogenerated unsaturated metal carbonyls. In addition, in order to obtain the greatest versatility in tuning and to extend the high-frequency tuning range to approximately 2150 cm^{-1}, the CO laser has to be liquid nitrogen cooled. With a glowbar a continuous spectrum can be constructed, but this is concomitant with a far poorer signal to noise ratio than with a CO laser. Recent trends are towards the use of a diode laser as a probe light source.[5] This combines the advantages of both the CO laser and glowbar. Since it is continuously tunable, the frequency of operation can be chosen such that it does not overlap the discrete sets of frequencies that correspond to free CO in excited vibrational or rotational states. In addition, a diode laser can be tuned to far higher frequency than a CO laser, this greatly facilitating studies. IR detectors have a time resolution limit of about 100 ns. Consequently, in order to obtain spectra in the picosecond and sub-picosecond range the apparatus must be modified.[55] This is done either by using laser mixing techniques to monitor IR changes in the UV-vis region where much faster detectors are available or by measuring the changes in IR bandwidths with temperature.[56]

An typical apparatus for laser TRIR experiments is shown diagramatically in Fig. 7.

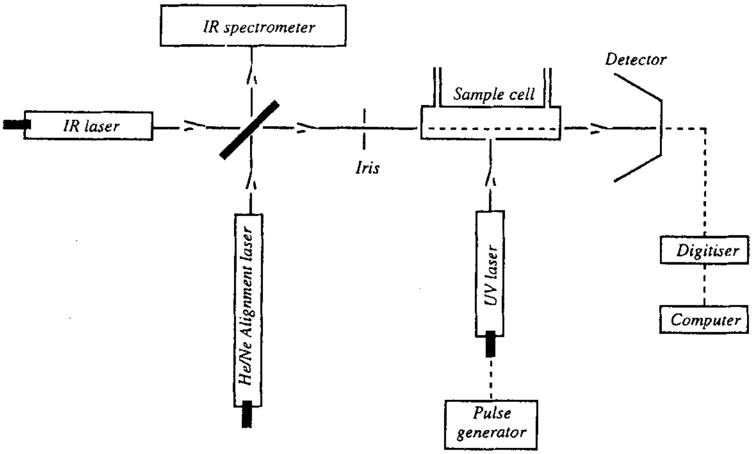


FIGURE 7 A typical apparatus for laser TRIR experiments.

(D) Solution versus Gas Phase Studies

Flash photolysis and TRIR experiments have been performed in both solution and in the gas phase. Investigations in the gas phase have the advantage over solution studies in that the "naked" unsaturated species can be studied without the influence of solvent.[57] In addition, putative measurements of association rate constants can be effected by the finite loss of the associated solvent molecules. Gas phase studies allow for real-time kinetic information to be obtained on coordinatively unsaturated compounds and also offer a far richer photochemistry than in the solution phase.[58] Solution TRIR has proven useful for studying the interaction of transient intermediates with otherwise considered inert solvents such as in the case of photolysis of $Cr(CO)_6$ with cyclohexane to generate $[Cr(CO)_5(cyclohexane)]$.[59] In addition, bimolecular reactions occur much slower in solution as opposed to the gas phase. In solution, reactions can not occur faster than the diffusion limit of around $\sim 10^9$-10^{10} dm^3mol^{-1}.[60] By comparison, the fastest rate of reaction for neutral species in the gas phase is around 10^{11} dm^3mol^{-1}.[50] It is therefore often necessary to use nanosecond and sub-nanosecond spectroscopy to study primary photoproducts generated in the gas phase.

(E) Applications

The photochemistry of $Mn_2(CO)_{10}$ has been investigated using both UV-vis flash photolysis and TRIR.

Initial UV-vis flash-photolysis studies, performed on the millisecond timescale, suggested that the only photoprocess in $Mn_2(CO)_{10}$ in the solution phase is metal-metal bond homolysis and that any dinuclear complexes characterised were not formed as primary photoproducts.[61] However, work on the nanosecond timescale in cyclohexane solution shows the formation of the two photoproducts generated in the matrix-isolation experiments, namely $[\cdot Mn(CO)_5]$ and $[Mn_2(CO)_9]$.[62] The generation of these intermediates has also been shown by picosecond flash-photolysis experiments.[63] The absorption band attributable to $[\cdot Mn(CO)_5]$ disappears within 30 μs of excitation whereas that due to $[Mn_2(CO)_9]$ does not decay within this time period. The increased stability of $[Mn_2(CO)_9]$ as opposed to $[\cdot Mn(CO)_5]$. has already been explained in terms of a semi-bridging carbonyl group, this being a four electron donor, giving $[Mn_2(CO)_9]$ a stable electron count of 36 as compared to an unstable count of 17 in $[\cdot Mn(CO)_5]$. This being the case, recombination of $[Mn_2(CO)_9]$ with CO involves an addition reaction rather than a simple association. This is in accord with the observation that this recombination is not accelerated in perfluoro solvents as opposed to hydrocarbons, implying that there is no easily assessable site for solvent interaction with $[Mn_2(CO)_9]$.[64]

In tetrachloromethane or trichloromethane solutions, the transient absorption intensity due to $[\cdot Mn(CO)_5]$ decreases according to first order kinetics, showing that the reaction of [$\cdot Mn(CO)_5$] with the chlorocarbon solvents is faster than [$\cdot Mn(CO)_5$] recombination. The decay of [$Mn_2(CO)_9$] also follows first order kinetics, this being interpreted in terms of the reaction of [$Mn_2(CO)_9$] with the chlorocarbon radical $\cdot CCl_3$ formed in the reaction of the solvent with [$\cdot Mn(CO)_5$].

As emphasised previously, although flash photolysis with UV-visible detection leads to interesting results, the structural information gathered is minimal. Intermediates can be identified from their reaction kinetics and, sometimes, with the help of UV-visible data from matrix-isolation experiments.

TRIR spectroscopy has been used to assist in the characterisation of the primary photoproducts and other intermediates formed on photolysis of $Mn_2(CO)_{10}$ in the solution phase. TRIR shows the formation of the two primary photoproducts, [$\cdot Mn(CO)_5$] and [$Mn_2(CO)_9$], on photolysis of $Mn_2(CO)_{10}$. Analysis of the IR spectra of the photoproducts shows that, in solution, [$\cdot Mn(CO)_5$] has C_{4v} symmetry and that [$Mn_2(CO)_9$] is unsymmetrical, containing a semi-bridging (μ_2-η^1:η^2-CO) carbonyl group. This is in agreement with the structural characterisation of these intermediates in low-temperature matrices.

Gas phase TRIR has been used in the study of a number of organometallic transients.[50] In the gas phase there is the possibility for multiple CO dissociation from metal carbonyls after the absorption of a single UV photon. The degree of fragmentation can be varied by changing the photolysis wavelength. Gas phase TRIR has both allowed for the structural characterisation of highly reactive transient intermediates and also enabled kinetic parameters for the reaction of photofragments to be measured. Experiments on $Fe(CO)_5$ have lead to the generation and detection of [$Fe(CO)_{5-x}$] [x = 1–4] species, the degree of fragmentation increasing with greater photon energy.

$$Fe(CO)_5 \xrightarrow{h\nu\ (351\ nm)} [Fe(CO)_4] + [Fe(CO)_3]$$

$$Fe(CO)_5 \xrightarrow{h\nu\ (248\ nm)} [Fe(CO)_4] + [Fe(CO)_3] + [Fe(CO)_2]$$

$$Fe(CO)_5 \xrightarrow{h\nu\ (193\ nm)} [Fe(CO)_4]+[Fe(CO)_3]+[Fe(CO)_2]+[Fe(CO)]$$

These studies have shown that the C_{2v} geometry and triplet ground state for [$Fe(CO)_4$] are not unique to matrix-isolation conditions. The kinetics of recombination of the coordinatively unsaturated fragments with CO has been investigated and this has shown that the ground states of [$Fe(CO)_3$] and [$Fe(CO)_2$] are also triplets.

The observation that the coordinatively unsaturated iron carbonyl fragments have the same structure both in the gas phase and in low temperature matricies unifies these techniques for characterising highly reactive organometallic fragments.[65] Indeed, in general, though bands that are observed often contain less detail, IR spectra of fragments in the gas phase are compatible with the structure of these fragments determined by matrix-isolation experiments.[66] A notable exception to this rule is $Mn_2(CO)_{10}$.[67]

Both [$\cdot Mn(CO)_5$] and [$Mn_2(CO)_9$] are primary photoproducts of the UV photolysis of gas phase $Mn_2(CO)_{10}$, this mirroring the case in low temperature matrices and in solution.[64] However, the vibrational stretching frequency for the bridging carbonyl group is considerably lower in the gas phase than in condensed phases. This is unexpected since, generally, CO absorptions in the gas phase shift to higher frequency than in condensed media.[68] This implies that the semi-bridging carbonyl group is readily deformed, the structure and/or potential energy surface being highly sensitive to the matrix environment.

FEMTOCHEMISTRY

Advances in laser technology now allow for the study of metal carbonyls in solution and in the gas phase on the femtosecond (fs) timescale.[69] In a typical experiment, an fs laser is used to excite a molecule to a dissociative state. The products are then detected either by time-of-flight mass spectroscopy (TOF ms) with fs resolution or by firing a second fs laser at a series of intervals after the dissociating pulse, the frequency of the second pulse being set at an absorption of one of the free fragmentation products.[70] In both detection methods, the relative abundance of the dissociation products are measured.

Using TOF-MS with fs resolution the elementary photodissociation dynamics of $Mn_2(CO)_{10}$ have been investigated.[71] Both Mn-CO and Mn-Mn bond cleavage occur on the fs timescale, the former being faster than the latter. This disparity has been accounted for on simple kinematic grounds, the reduced mass in the Mn-CO cleavage being approximately four times smaller than that of the Mn-Mn process. The [$\cdot Mn(CO)_5$] builds up and lives for at least 100 fs. On the other hand, the signal due to nascent $[Mn_2(CO)_9]$ decays in approximately 160 fs, this decay being related to the molecular rearrangement of the nascent $[Mn_2(CO)_9]$ to adopt the semi-bridged geometry.

The ultra-fast dynamics of the dissociations of $M(CO)_6$ [M = Cr, Mo, W] in alkane[72] and methanol[73] solutions have also been studied using fs spectroscopy. UV photolysis leads to an efficient CO loss in $M(CO)_6$ to yield $[M(CO)_5]$ in less than 240 fs. In the hydrocarbon solutions, signals due to $[M(CO)_5]$ decay within 300 fs, this being attributed to regeneration of $M(CO)_6$ within only one or two collisions with the surrounding solvent cage. Although the percentage of the pentacarbonyl species that undergoes this fast geminate recombination can not be determined quantitatively because it occurs too fast for detection using the apparatus (240 fs),[74] this regeneration of $M(CO)_6$ would be expected to contribute to the non-unit photosubstitution quantum yields observed for these compounds.[75] In methanol, complexation of $[M(CO)_5]$ with a solvent molecule is observed on a several picosecond timescale, the product $M(CO)_5(MeOH)$ relaxing both electronically and vibrationally over a slower period of around 50 ps. Again, these studies show that the "naked" $[M(CO)_5]$ is formed within 300 fs.

In all these cases, as well as clarifying the results from matrix-isolation and from solution and gas phase TRIR experiments, fs studies allow for a deeper understanding of the photodynamics of bond cleavage.

THE STUDY OF EXCITED STATES IN ORGANOMETALLIC COMPOUNDS

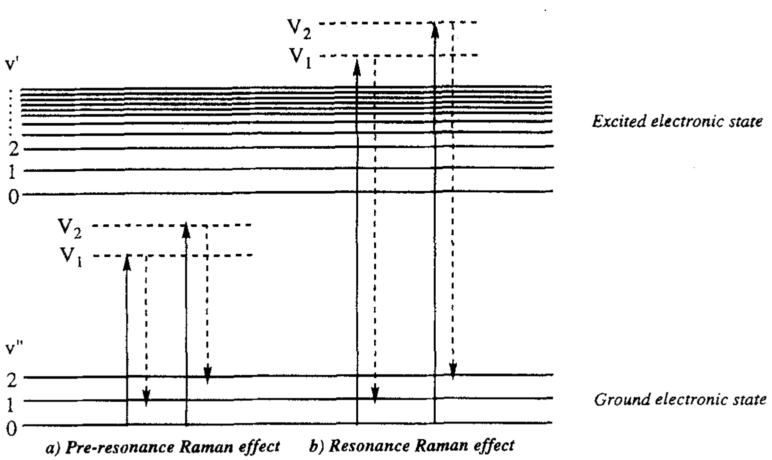
(A) Outline

A molecule in its first excited state is a very different entity from that in the ground state. It possesses additional energy and often has a different structure, at least with respect to small changes in bond lengths and angles. It has different electronic and vibrational spectra and a novel chemistry. By studying the excited state(s) of organometallic compounds, their photochemistry can be more fully understood.[76] Since quantum chemistry is not able to calculate the excited state geometries of large molecules like organometallics, alternative techniques are required.[77] Recent studies have shown that it is possible to probe the excited states of molecules using fast spectroscopy, in particular time-resolved Raman and IR techniques.

(B) Raman and TRIR Spectroscopy in Excited-State Chemistry

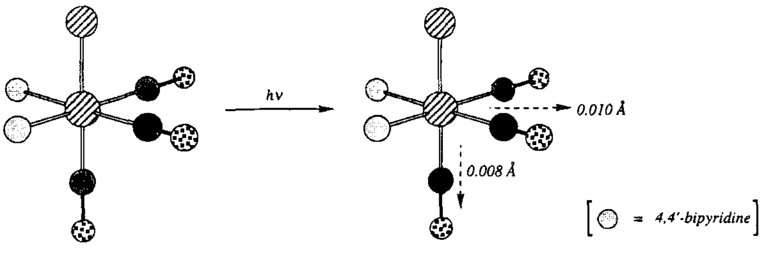
So far in this article, emphasis has been placed on UV-vis and IR spectroscopy and its applications to the characterisation of transient intermediates. In principle, *Raman spectroscopy* should also provide valuable information for study of transient intermediates.[78] However, for organometallic compounds and in particular metal carbonyls, due to the high degree of photolability, Raman spectroscopy can often lead to further photoreactions of both parent compounds and the photofragments under study. In addition, analysis of the Raman spectrum for large molecules is not a trivial task.[79] The development of *resonance* and *pre-resonance* Raman techniques has aided study.[80] Pre-resonance Raman spectroscopy involves the study of transitions which occur between the ground electronic state and virtual states that are near, but below, the first electronic state (Fig. 8a). Resonance Raman spectroscopy involves the study of transitions from the ground electronic state to virtual states lying within a continuum of states above the excited electronic state (Fig. 8b). By using the so-called *time-dependent* model,[81] Raman spectroscopy has been applied to organometallics with some degree of success.[82] In simple terms, the time-dependent model shows that the intensity of a peak in a resonance Raman spectrum provides detailed information about the displacement of the excited-state potential energy surface along the normal mode giving rise to that peak. Raman spectroscopy coupled with electronic spectroscopy can then be used to study molecular distortions in excited electronic states.

The first report of the application of TRIR to the excited states of organometallic complexes involved $ClRe(CO)_3(4,4'\text{-bipyridine})_2$.[83] This species was chosen because the lowest MLCT state is known to be stable and long lived (~1 μs).[84] In addition, on charge transfer from Re to bipy, the metal centre is oxidised. This effects ν_{CO}, a significant shift to higher frequency being observed in TRIR experiments on the nanosecond timescale.[85] Energy-factored force-field calculations have shown that it is possible, at least in this case, to relate force constants and/or frequencies to bond length changes, the results showing that the $M\text{-}CO_{ax}$ bond length increases by 0.008 Å and the $M\text{-}CO_{eq}$ bond length by 0.010 Å (Fig. 9).[86]



a) Pre-resonance Raman effect ***b) Resonance Raman effect***

FIGURE 8 (a) The pre-resonance Raman effect; (b) the resonance Raman effect.



$ClRe(CO)_3(4,4'\text{-bipyridine})_2$

FIGURE 9 The structure and excited-state perturbations of $ClRe(CO)_3(4,4'\text{-bipyridine})_2$.

The structure of $W(CO)_5$(pyridine) in the ground state and the lowest LF excited state has been probed using both pre-resonance Raman and TRIR spectroscopy. However, in this case, the results from Raman and TRIR experiments contradict each other.

The lowest LF excited state of $W(CO)_5$(pyridine) has been assigned to the $^1A_1 \rightarrow {}^3E$ (d_{xz}, $d_{yz} \rightarrow d_{z^2}$) transition (Fig. 10a).[87] This population of d_{z^2} orbital would be expected to weaken σ-bonding primarily in the z direction. The ground-state pre-resonance Raman spectrum of

W(CO)$_5$(pyridine) has been recorded and, using the time-dependent formalism, molecular distortions in the first excited state determined. The greatest distortion occurs along the W-N bond and the W-C bond *trans* to the pyridine ligand, these both being elongated. Slight elongation of the *cis* M-C bonds is also observed. This agrees with predictions from simplified extended Hückel molecular orbital (EHMO) calculations, the lowest energy excited state wavefunction being dominated by a large character.[88] The small but non-zero distortions along the xy plane can be attributed to mixing of states, some $d_{z^2} - d_{y^2}$ orbital character being involved in the first excited state.

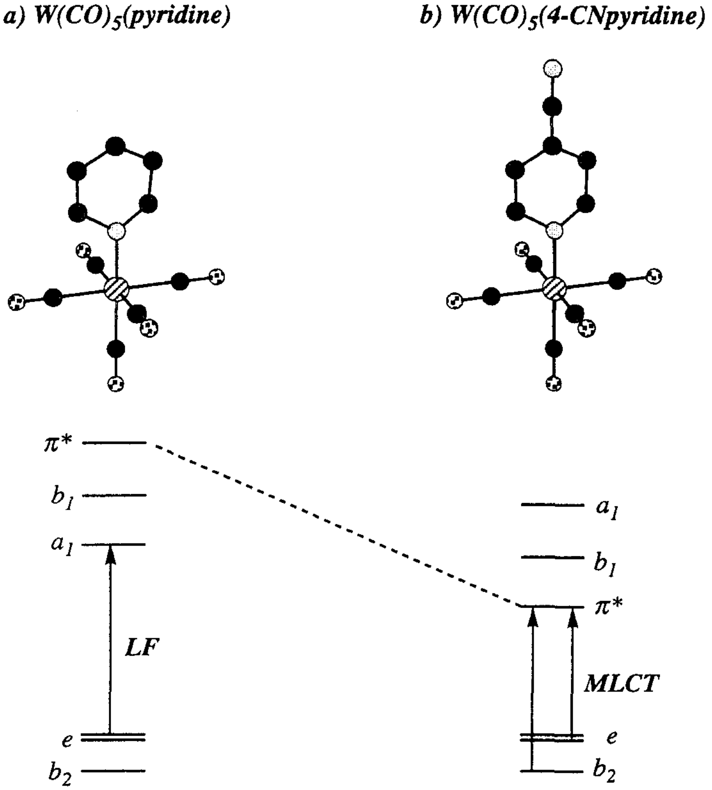

a) W(CO)$_5$(pyridine)
b) W(CO)$_5$(4-CNpyridine)

FIGURE 10 The structures and energy-level schemes for (a) W(CO)$_5$(pyridine) and (b) W(CO)$_5$(4-CNpyridine).

TRIR data for the ligand-field excited state of $W(CO)_5$(pyridine) have been recorded and, coupled with energy-factored force-field calculations, show that the ν_{CO} vibrational frequencies and the corresponding C-O force constants all decrease on promotion into the lowest excited state.[89] Consequently, the C-O bond lengths increase, implying that the W-C bond lengths all *decrease* on excitation rather than, on the basis of the pre-resonance Raman data, *increase.* These IR data have been critically assessed and EHMO calculations on the model compound $W(CO)_5(NH_3)$ performed.[88] These calculations indicate that, although the LUMO d_{z^2} is antibonding with respect to W-N, it is bonding with respect to W-C. In addition, the LUMO is antibonding with respect to C-O. by far the greatest effect being observed for the C-O_{eq} bonds. Clearly, population of the d_{z^2} orbital will lead to the distortion changes predicted on the basis of the excited state IR data.

TRIR has also been used to study $W(CO)_5$(4-CNpyridine)[90] in which there is proposed to be a delicate balance between MLCT and LF photochemistry (Fig. 10b) on the basis of quantum yield measurements.[91] Unlike the case of $W(CO)_5$(pyridine) where the lowest transition is of LF character, in $W(CO)_5$(4-CNpyridine) the MLCT transition is lowest. TRIR can not only monitor the formation of the MLCT excited state after irradiation but also can be used to study the decay of this species both back to the ground state and to $[W(CO)_5]$. As the yield of $[W(CO)_5]$ can be monitored directly, the equilibrium between MLCT and LF states can be investigated. Results show an energy difference of ~4000 cm^{-1} between the lowest MLCT and LF states. In addition, TRIR experiments have shown that if $W(CO)_5$(4-CNpyridine) photolysed using a wavelength of excitation corresponding to the energy gap between the ground state and the first ligand-field excited state, $[W(CO)_5]$ is, as expected, formed instantaneously rather than after generation of an MLCT excited state.

There have been numerous other investigations into the excited state character and structure of organometallic complexes containing heterocyclic ligands,[4] in particular those containing a-diimine ligands,[92] but it is beyond the scope of this article to discuss these in detail. Suffice it to say that with the development of absorption, resonance Raman and TRIR techniques, detailed information is now being obtained about the character of the lowest excited state of these and other complexes.[93]

CONCLUSIONS AND A LOOK TO THE FUTURE

In this Comment, only a small part of the interesting chemistry displayed by unstable organometallic intermediates has been discussed. It is clear that the best and most unambiguous studies of transient species involve combinations of experimental techniques.

Matrix isolation in many ways is ideal for the study of metal carbonyl species since conventional spectroscopic techniques can be brought to bear in determining the identity of photogenerated intermediates and also in gaining structural information. However, matrix-isolation studies have the drawbacks that they give little or no kinetic information, and also there is no guarantee that the structure adopted in the matrix environment is the same as that in the solution or gas phase. The study of photoreactions in low-temperature solutions such as noble gases has gone some way to bridging the gap between matrix and room temperature studies. By performing reactions in liquid noble gases it is possible not only to study photogenerated intermediates but also examine the structure of unstable coordinatively saturated species. This has been applied successfully to complexes containing highly labile ligands such as H_2, N_2 and C_2H_4.

The applications of time-resolved infrared spectroscopy are now well grounded in the study of coordinatively unsaturated organometallic intermediates. It is thus possible to measure the infrared spectra of transient intermediates in solution or in the gas phase. These experiments compliment matrix-isolation studies, giving further structural information but also providing kinetic data and often offering a more varied photochemistry.

The developments in TRIR apparatus accompanied by the evolution of resonance and pre-resonance Raman techniques have made the study of the excited states of organometallics possible. It is often the case that TRIR and Raman studies compliment each other in providing structural information, however, caution must be exercised as exhibited in the case of $W(CO)_5$(pyridine) where the two techniques yield contradictory information.

With the use of all these experimental techniques and others, the future study of the photochemistry of organometallics promises to be exciting. Of course, as these experiments probe the mechanism of reactions in greater detail, a whole set of new questions will be raised. Developments in laser chemistry open avenues for study of organometallic photoprocesses, the investigation of single and multiple photon photodissociations being but one example. With advances in supersonic molecular beam technology, rotationally resolved IR spectroscopy in the gas phase will become a reliable method to study structure and dynamics. In addition, there is the possibility to study the vibrational and translational energy distributions of photofragments formed under these collision-free conditions.

Concomitant with this progress, theoretical studies on molecules in the ground and first excited states will prove invaluable and, together with modeling of the dynamics of photodissociation, will assist greatly the study of the photoprocesses in organometallics. Even if the development o quantitative models for the dynamics of reactions are still some way off, qualitative approache will serve as a useful, unifying framework for investigating photoreactions.

We now look forward to advances in experimental technique and in the understanding of the fundamental processes intimately involved in photochemistry.

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