Photo- and redox activation of homo-and heteronuclear transition metal clusters: experiment and theory
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Chapter 2

Research Methods and Instrumentation
2.1 Introduction

The research described in this Thesis deals with the syntheses, characterization and photo- and electrochemical properties of transition metal carbonyl clusters. In order to gain thorough understanding of the processes induced by photo- or redox activation of these complex systems, it is of utmost importance to learn about the electronic and molecular structures of the different intermediates along the reaction pathways and to study their kinetics. Sophisticated spectroscopic techniques in combination with theoretical support have been applied to obtain this detailed information. In this Chapter the most important, 'non-conventional' methods (both experimental and theoretical) used in this Thesis will be discussed. The aim is to give short outlines rather than comprehensive reviews for which the reader is referred to the literature. First, time-resolved spectroscopic methods are described that were used to investigate the character of the excited state, the formation of the primary photoproducts and the dynamics of photoinduced chemical reactions. Secondly, attention is focused on the (spectro)electrochemical techniques applied in the study of the cluster redox processes. The employed quantum chemical calculation methods are described at the end of this chapter. The 'conventional' spectroscopic techniques (UV-vis, (rapid scan) FTIR and X-ray diffraction) are described in detail in the particular experimental chapters.

2.2 Time-resolved spectroscopic techniques

Characterization of long-lived intermediates and final photoproduct(s) can be accomplished by steady-state spectroscopic techniques like UV-vis absorption, Fourier Transform IR (FTIR), (resonance) Raman (rR), EPR and NMR spectroscopies. Beside this part, a thorough description of the mechanism of photochemical reactions requires knowledge of the primary photochemical steps. Traditionally, the nature of the primary photoproducts was investigated by stabilizing them at low temperatures or in solid inert matrices. However, the excited state processes occurring directly after the absorption of a photon require a different approach, as they remain too fast even at low temperatures. Excitation itself takes place within a few femtoseconds ($10^{-15}$ s), while internal conversion and reorganisation of the surrounding (dipole) solvent molecules is completed within picoseconds ($10^{-12}$ s). In coordination compounds, allowed or avoided crossings between close-lying excited states of different (spin) character, which often determine the course of the photochemical process, generally occur on pico- to nanosecond time scales ($10^{-12}$ - $10^{-9}$ s). The study of these processes requires the use of (ultra)fast time-resolved spectroscopic techniques. Whereas nowadays nanosecond time-resolved experiments are more or less routine, a study of the excited state processes on the pico- and femtosecond time scales has
only become possible with the development of lasers, generating high-energy pulses of femtosecond duration.

**Time-resolved absorption spectroscopy**

Time-resolved absorption spectroscopy provides a powerful tool for obtaining valuable information about the nature and dynamics of excited states and short-lived photochemical intermediates. It relies on recording electronic absorption spectra of transient species (excited molecules or photoproducts) at selected time delays after the excitation pulse. The transient absorption signal can either be recorded over an extended wavelength range (full spectrum) or at a single wavelength. In the former approach the excitation pulse is followed by a white light pulse that is used for monitoring. In nanosecond transient absorption white-light pulses are typically generated by a pulsed Xe lamp; in (sub)picosecond transient absorption this is achieved via non-linear optical processes, for example by focusing a laser pulse into a water-containing cuvette or sapphire crystal. The white light that is transmitted by the sample, can be recorded by a spectrographic detection system, such as an optical multichannel analyser (OMA) or streak camera. Transient absorption spectra are generally obtained as difference spectra, showing the time-resolved absorbance changes relative to the ground state absorption.

By recording the transient absorption signal at a single wavelength at different time delays after the excitation pulse, kinetic traces can be constructed that allow accurate analysis of the dynamics of excited states and primary photoproducts. Kinetic traces in the nanosecond time domain are usually obtained by replacing the spectrographic detection system with a monochromator-photomultiplier combination, in order to select the desired wavelength from the complete spectrum. In picosecond transient absorption spectroscopy, single-wavelength measurements require the use of a second laser line. In this case, the desired time resolution, *i.e.* the variable time delays between the excitation (pump) and monitoring (probe) laser pulses, is obtained by passing one of the two lines over a so-called delay line.

In this Thesis, transient absorption spectra and kinetic traces were recorded on the pico- and nanosecond time scale. The experimental details of the employed set-ups are described below.

**Experimental set-ups**

Picosecond transient absorption (ps TA) measurements were performed using the set-up installed at the University of Amsterdam (see Figure 1). The laser system is based on a Spectra Physics Hurricane Ti-sapphire regenerative amplifier system. The optical bench assembly of the Hurricane includes a seeding pump laser (Mai Tai), a pulse stretcher, a Ti-
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sapphire regenerative amplifier, a Q-switched pump laser (Evolution) and a pulse compressor. The output power of the laser is typically 1 mJ pulse\(^{-1}\) (130 fs FWHM) at a repetition rate of 1 kHz. Two different pump-probe set-ups were employed: (i) a full-spectrum set-up based on an optical parametric amplifier (Spectra-Physics OPA 800) as a pump, where the residual fundamental light (150 μJ pulse\(^{-1}\)) from the pump OPA was used for generation of white light that was detected with a CCD spectrograph; (ii) a single-wavelength kinetics set-up based on two OPA’s, one of them being used as a pump and the other one as a probe, and an amplified Si photodiode for detection. For both set-ups the pump OPA was used to generate excitation pulses at 350 nm (fourth harmonic of the 1400 nm OPA signal beam), 430 nm (fourth harmonic of the 1500 nm OPA signal beam) or 505 nm (fourth harmonic of the 2020 nm OPA idler beam). The output power was typically 5 μJ pulse\(^{-1}\). The white-light generation was accomplished by focusing the fundamental (800 nm) into a H₂O flow-through cell (10 mm; Hellma). For the single wavelength measurements, the polarization of the probe light was controlled by a Berek Polarization Compensator (New Focus). The probe light was passed over the delay line (Physik Instrumente, M-531DD) that provides an experimental time window of 1.8 ns with a maximal resolution of 0.6 fs step\(^{-1}\). The energy of the probe pulses was approximately 5x10\(^{-3}\) μJ pulse\(^{-1}\) at the sample. The angle between the pump and probe beam was typically 7-10°. The circular cuvette \((d = 1.8 \text{ cm}, 1 \text{ mm}, \text{ Hellma})\) with a sample solution was placed in a home-made rotating ball bearing (1000 rpm) to avoid local heating and sample decomposition by the laser beams. The sample solutions were prepared with an optical density of \textit{ca.} 0.8 at the excitation wavelength. For the white light/CCD set-up, the probe beam was coupled into a 400 μm optical fiber after passing through the sample, and detected by a CCD spectrometer (Ocean Optics, PC2000). The chopper (Rofin Ltd., \(f = 10\)-20 Hz), placed in the excitation beam, provided \(I\) and \(I_0\), depending on the status of the chopper (open or closed). The excited state spectra were obtained by \(\Delta A = \log(I / I_0)\). Typically two thousand excitation pulses were averaged to obtain the transient at a particular time delay. Due to the lenses a chirp of \textit{ca.} 1 ps is observed between 460-650 nm. For the single-wavelength kinetic measurements, an amplified Si photodiode (New-Port, 818 UV/4832-C) was used for detection. The output of the Si photodiode was conducted to an AD-converter (National Instruments, PCI 4451, 205 kS s\(^{-1}\)), which enabled the measurement of the intensity of each separate pulse. Again, the chopper \((f = 50 \text{ Hz})\) placed in the excitation beam provided \(I\) and \(I_0\) and \(\Delta A\), respectively. Typically, 500 excitation pulses were averaged to obtain the transient at a particular time. The absorbance spectra of the solutions were measured before and after the experiments. In all cases less then 10% photodecomposition was observed.
Nanosecond transient absorption (ns TA) spectra were obtained by irradiating the samples with 2 ns pulses (FWHM) of a continuously tunable (420-710 nm) Coherent Infinity XPO laser. The output power of the laser was typically less than 5 mJ pulse\(^{-1}\) at a repetition rate of 10 Hz. Samples in a 1 cm quartz cuvette had ca. 0.8 optical density at the excitation wavelength. The probe light from a low-pressure, high-power EG&G FX-504 Xe lamp passed through the sample cell and was dispersed by an Acton Spectra-Pro-150 spectrograph, equipped with 150 g/mm or 600 g/mm grating and a tunable slit (1-500 μm), resulting in 6 or 1.2 nm maximum resolution, respectively. The data collection system consisted of a gated intensified CCD detector (Princeton Instruments ICCD-576EMG/RB), a programmable pulse generator (PG-200), and an EG&G Princeton Applied Research Model 9650 digital delay generator. With this OMA-4 setup (see Figure 2), \(I\) and \(I_0\) values are measured simultaneously, using a double kernel 200 μm optical fiber.

**Figure 2.** Schematic representation of the nanosecond transient absorption set-up: 1. laser, 2. Xe lamp, 3. sample, 4. spectrograph, 5. CCD camera, 6. pulser, 7. computer.
Nanosecond flash photolysis transient kinetics was measured by irradiating the sample with 7 ns (FWHM) pulses of a Spectra Physics GCR-3 Nd:YAG laser (10 Hz repetition rate) and using pulsed Xe-lamp probe light perpendicular to the laser beam. The excitation wavelength was obtained by frequency doubling (532 nm). The 450 W Xe lamp was equipped with a Müller Electronic MSP05 pulsing unit (giving pulses of 0.5 ms). A shutter, placed between the lamp and the sample, was opened for 10 ms to prevent photomultiplier fatigue. Suitable pre- and postcut-off and bandpass filters were used to minimize both the probe light and the scattered light of the laser. The sampling rate was kept at a relatively long time (intervals of 10 s) to prevent accumulation of possible photoinduced intermediates. The light was collected in an Oriel monochromator, detected by a P28 PMT (Hamamatsu), and recorded on a Tektronix TDS3052 (500 MHz) oscilloscope. The laser oscillator, Q-switch, lamp, shutter and trigger were externally controlled with a home-made digital logic circuit, which allowed for synchronous timing. The absorption transients were plotted as $\Delta A = \log(I/I_0)$ vs time, where $I_0$ is the monitoring light intensity prior to the laser pulse and $I_t$ is the observed signal at delay time $t$.

**Time-resolved infrared (TRIR) spectroscopy**

Although time-resolved UV-vis absorption spectroscopy generally provides excellent kinetic data, the structural information on excited molecules or photogenerated transients is rather limited. This problem can be addressed using time-resolved IR (TRIR) spectroscopy. This technique, which involves a combination of UV-vis flash photolysis with fast IR detection, has developed significantly over the last few years. Conventionally, TRIR spectra on the microsecond time scale were recorded using continuous wave IR sources and fast IR detectors. Advances in step-scan Fourier Transform IR, however, enabled faster data acquisition and recording of TRIR spectra on the early nanosecond time scale. Recently, TRIR measurements can also be performed on ultrafast (pico- and femtosecond) time scales, using pump-probe methods similar to those applied in ultrafast electronic absorption spectroscopy. The ultrafast IR probe pulse can either be obtained by upconversion of a continuous wave IR signal with a fast visible pulse or by difference frequency mixing of two (visible) laser pulses (this Thesis).

TRIR spectroscopy is particularly useful in studying the excited states and primary photoproducts of transition metal complexes containing strongly IR active ligands, such as carbonyls. For, the frequencies of the stretching vibrations of carbonyl ligands ($v(\text{CO})$) are very sensitive to the molecular structure of the complex and can act as direct probes of the electron density at the metal centre. In addition, the absorption molar coefficients of the IR $v(\text{CO})$ bands are typically high and the carbonyl stretching region is relatively transparent. The first application of TRIR to the excited states of transition metal carbonyl complexes
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dates back to 1989, when Glyn et al. detected the $^3$MLCT excited state of [Re(CO)$_3$Cl(4,4'-bpy)$_2$]. Upon population of the MLCT excited state, all three carbonyl stretching bands were shifted to considerable larger wavenumbers. This shift is explained by decreased metal-to-CO π-backdonation due to a lower electron density on the metal centre.

Apart from the shift induced by the change in the electronic structure, initially broadened ν(CO) bands frequently undergo blue shift and concomitant narrowing on the early picosecond time scale. These spectral changes result from vibrational relaxation processes. In a simplified picture, the relaxation processes after photoexcitation may be separated into two steps. (i) Internal Vibrational Redistribution (IVR), which dissipates the energy from an initial, non-thermal energy distribution to a fully thermalized state (usually, but not always, on the subpicosecond time scale) where all vibrational modes are excited according to a thermal Boltzmann factor. This implies that especially low-frequency vibrational modes (e.g. skeletal modes) are activated to very high quanta. At this point after the excitation, the molecule can be extremely hot. (ii) External Vibrational Redistribution (EVR), where the heat of the molecules starts to flow to the surrounding solvent shells. The rate of this second process is usually determined by the subsequent transport of heat from one solvent shell to another. Depending on the solvent and the size of the molecule, characteristic 'cooling' constants of several picoseconds are frequently encountered. Due to the coupling of the high-frequency CO-stretching vibration to the highly activated skeletal modes, the position and bandwith of ν(CO) IR bands are significantly influenced by the EVR relaxation of these low-frequency modes, taking place on the early picosecond time scale.

Experimental set-up

All time-resolved IR experiments were performed using the Picosecond Infrared Absorption and Transient Excitation (PIRATE) facility at the Rutherford Appleton Laboratory in Didcot, United Kingdom (see Figure 3). The laser system is based on a Ti-sapphire regenerative amplifier (Spectra Physics/Positive Light, Superspitfire), operating at 1 kHz repetition rate at ca. 800 nm, with an energy of 2-3 mJ pulse$^{-1}$ (150 fs FWHM). The regenerative amplifier is seeded by a 100 fs pulse from a mode-locked Ti-sapphire laser (Spectra Physics, Tsunami). Tuneable mid-IR outputs (150-200 cm$^{-1}$ FWHM, 200 fs) were generated by frequency-down conversion of the signal and idler outputs of a white-light seeded, 800 nm pumped BBO OPA in an AgGaS$_2$ crystal. Second harmonic generation of the residual fundamental light (800 nm) provided 400 nm pulses, which were either used directly for excitation of the sample or to pump a second OPA, generating 500 nm excitation pulses. The mid-IR beam generated by the first OPA was split into reference and probe beams, using a 50 % germanium beamsplitter. Below 1800 cm$^{-1}$, N$_2$-purged infrared beam paths were applied to reduce probe beam absorption by water vapour. The probe beam was focused to
about 150 μm into the sample cell, using an f = 30 gold-coated spherical mirror. The flow-through cell, consisting of two CaF₂ windows separated by 0.25-1 mm spacers, was allowed to make a rastering movement perpendicular to the probe beam in order to avoid local heating and sample decomposition by the laser beams. Two separate 64 element HgCdTe linear array detectors (MCT-13-64el (Infrared Associates Inc.) and MCT-64000 pre-amplifiers (Infrared Systems Development Corp.)) were used to detect the mid-IR reference and probe signals. The data were analysed in pump on/pump off pairs to create a rolling average using the following equation:

$$\Delta A_N = \log[1 + \frac{I_R}{I_P} \{\frac{I_{probe}}{I_{ref}}|_{pump \ on} - \{\frac{I_{probe}}{I_{ref}}|_{pump \ off}\}] + \Delta A_{N-1}(N-1)/N$$

where $I_R$ and $I_P$ are the final averages of the pump-off spectra on the reference and probe sides, respectively, and N is the total number of acquisitions. Further software discrimination removes large fluctuations, such as laser 'drop outs' or fluctuations associated with gas bubbles in the sample flow stream, on a shot-by-shot basis. TRIR spectra comprising the whole CO-stretching region (2200-1700 cm⁻¹) were constructed by precise overlap of three or four 150 cm⁻¹ windows. Calibration of the spectra was established by comparing the parent bleach positions with the peak positions of the corresponding v(CO) bands in the regular FTIR spectra.

![Diagram](image)

**Figure 3.** Schematic representation of the picosecond time-resolved IR set-up: 1. Superspiffire, 2. second harmonic generator, 3. OPA-400 nm (pump), 4. OPA-800 nm (probe), 5. mid-IR light generator, 6. delay line, 7. sample, 8. MCT detector, 9. computer.

### 2.3 Cyclic voltammetry and spectroelectrochemistry

As photo- and electrochemical activations often involve the same frontier orbitals, the information obtained from reversible electrochemical processes can supplement that from photochemical measurements. By studying the changes in redox potentials upon
coordination of different ligands in a series of coordination compounds, electrochemistry may, for example, provide valuable information about the character of the frontier orbitals of these complexes. In addition, some photoproducts (e.g. radicals) can be conveniently generated by electrochemical methods while the correlation between the redox and optical orbitals offers the possibility to assign transient species (e.g. D'-A' states) observed in time-resolved spectra by comparison with the spectra of the independently electrochemically oxidized donor and reduced acceptor moieties.

In order to follow electrochemical processes a great variety of electrochemical techniques have been developed (e.g. cyclic voltammetry, coulometry, polarography, pulse chronoamperometry). In cyclic voltammetry, the potential is varied linearly back and forth between certain predefined potentials, while the current response is measured and plotted as a function of the applied potential to afford a current-voltage curve, known as 'cyclic voltammogram'. Cyclic voltammetric studies provide valuable information about redox potentials, diffusion constants and the number of electrons involved in the redox process. In addition, cyclic voltammetry is often used to establish the degree of (electro)chemical reversibility of a redox process, which relates to the structural changes induced by the external electron transfer reactions. The amount of information on the molecular structure of secondary products of complex redox reactions is, however, limited. This problem is addressed by the development of in situ methods combining electrochemistry with spectroscopic techniques, such as IR, UV-vis, EPR and Raman. Progress in the methodology of spectroelectrochemistry was stimulated by the development of suitable optically transparent thin-layer electrochemical (OTTLE) cells, in which the working electrode consists of a fine minigrid of thin gold or platinum wires. As the optical beam can pass directly through the electrode, the redox processes taking place in the thin solution layer surrounding the working electrode can be studied spectroscopically. With the development of low-temperature OTTLE cells, the study of many thermally instable redox products at low temperatures has become possible. Several of the above mentioned spectroelectrochemical techniques have been employed in this Thesis to study the redox processes of homo- and heteronuclear transition metal clusters.

Experimental details

Cyclic voltammograms (CV) of approximately $10^{-3}$ M parent clusters in $10^{-1}$ M Bu$_4$NPF$_6$ electrolyte solution were recorded in a gas-tight, single-compartment, three-electrode cell equipped with platinum disc working (apparent surface of 0.42 mm$^2$), coiled platinum wire auxiliary and silver wire pseudoreference electrodes. The cell was connected to a computer-controlled PAR Model 283 potentiostat. All redox potentials are reported against the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple.
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IR and UV-vis spectroelectrochemical measurements at variable temperatures were performed with previously described optically transparent thin-layer electrochemical (OTTLE) cells equipped with a Pt minigrid working electrode (32 wires/cm) and CaF$_2$/NaCl or CaF$_2$/quartz windows. The working electrode surroundings were masked carefully to avoid spectral interference with the non-electrolyzed solution. EPR spectra of the electrogenerated radicals were recorded at variable temperatures, using a modified three-electrode Allendoerfer-type spectroelectrochemical cell equipped with a single-point Ag pseudoreference electrode. The potential during these measurements was controlled by a PA4 (EKOM, Czech Republic) potentiostat. The cluster concentration in the spectroelectrochemical experiments varied from $10^{-3}$ (UV-vis, EPR) to $10^{-2}$ (IR) mol dm$^{-3}$.

2.4 Quantum chemical calculations

In combination with the experimental results, quantum chemical calculations provide a powerful tool to obtain a detailed understanding of the electronic structure of cluster compounds in the ground- and excited states and to assign their low-energy electronic transitions. While, in theory, the electronic structure of a molecule can be calculated by solving the Schrödinger equation, the latter is analytically unsolvable for multi-electron systems, due to difficulties in describing the repulsive electron-electron interactions. In order to overcome this problem, several methods have been developed, in which the electron-electron interaction is approximated in such a way that the equation can be solved, while at the same time giving reliable results. These methods can be divided into semi-empirical approaches, in which parameters are introduced and adjusted to fit various experimental quantities, and ab initio methods.

In ab initio calculations, the molecular $n$-electron wavefunction is commonly approximated by $n$ one-electron functions built from linear combinations of atomic orbitals. These wavefunctions describe the movement of each electron in the field of the nuclei and the remaining $n-1$ electrons. The mean field is not known a priori but depends on the orbitals, which are determined via an iterative process referred to as a self-consistent field (SCF) technique. A severe limitation of the SCF approach is that it assumes each electron to move independently, ignoring spatial correlation. In order to improve the mean field description different strategies have been developed to introduce electron correlation effects, which include perturbation methods (e.g. MP2) and configuration interaction (CI). In general, the number of integrals which have to be computed in ab initio methods formally scales with $N^4$, where $N$ is the number of basis functions. The dramatic increase in duration and complexity of the calculations upon increasing the number of electrons, together with the difficulty to deal with relativistic effects, make ab initio methods less suitable for transition metal clusters. Even small-sized clusters have therefore mainly been treated with the more simple semi-
empirical Extended Hückel Molecular Orbital (EHMO) method. The latter type of calculations, in which the number of integrals that have to be explicitly calculated is drastically reduced, can be useful as a first approximation to clarify the extent and character of the metal-metal bonding and to give some ideas with regard to the nature of the frontier orbitals. It should be pointed out, however, that the reliability of these methods for quantitative predictions is in general very limited.

An attractive alternative to conventional ab initio methods is offered by density functional theory (DFT). In contrast to ab initio calculations, DFT starts from the assertion that the total energy of an electronic system can be expressed as a unique functional (= the integration of a function over space) of the system's electron density. Instead of solving the Schrödinger equation, in DFT calculations it is the aim to minimize the energy functional. This functional can be separated into three terms: a kinetic energy contribution, the classical coulombic interaction of the charge distribution under study, and a remainder which comprises the electron exchange and correlation interactions. The minimization of the overall functional can be carried out by using a self-consistent field approach (vide supra). The quality of the results mainly depends on the quality of the approximation of the electron exchange and correlation term. Several approximations to treat the latter term have been suggested, whereby a popular choice is to assume that the system can be approximated locally as a weakly inhomogeneous electron gas. This approach is called the local density approximation (LDA). It is also possible to apply non-local corrections to the exchange and correlation energy by using gradient-corrected exchange correlation functionals (Generalized Gradient Approximation (GGA)). The Becke's exchange functional used in this Thesis provides a well-known example of such a functional. Another important factor concerns the choice of the basis set. The orbitals of a molecular system can be expressed as a linear combination of a finite set of one-electron atomic orbitals or basis functions, which form the basis set. There are two types of basis orbitals commonly used, Slater-type orbitals (STO's) and Gaussian-type orbitals (GTO's). Considerable research effort has been devoted to the development of better basis sets, providing a more accurate description of the molecular orbitals. Over the last two decades, time-dependent DFT (TD-DFT) methods have been developed which permit a more accurate determination of excited state energies and electronic transitions. Since the computational effort increases with the number of basis functions as roughly $N^3$, the power of (TD-)DFT lies undoubtedly in its speed. Advanced corrections like the incorporation of relativistic effects, are nowadays available with only very small compromises to the overall quality. DFT therefore allows accurate treatment of transition metal clusters where ab initio methods are not easily applicable.
Computational details

All density functional calculations were carried out with the Amsterdam Density Functional (ADF2000) programme. Vosko, Wilk and Nusair’s local exchange correlation potential was used. Gradient-corrected geometry optimizations were performed, using the Generalized Gradient Approximation (Becke’s exchange and Perdew’s correlation functionals). Relativistic effects were treated by the ZORA method. The core orbitals were frozen for Os (ls-5s, 1p-5p, 3d, 4d), Ru (ls-4s, 1p-4p, 3d) and C, N, O (ls). Triple \( \zeta \) Slater-type orbitals (STO) were used to describe the valence shells of H (ls), C and O (2s and 2p), Ru (5s and 5p) and Os (6s and 6p). A set of polarization functions was added: H (single \( \zeta \), 2p, 3d), C, N, O (single \( \zeta \), 3d, 4f), Ru (single \( \zeta \), 4f), Os (single \( \zeta \), 5f). Full geometry optimizations were performed without any symmetry constraints on models based on the available crystal structures.

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