Applications of the OTTLE Cells in the Reading Spectro-Electrochemical Laboratory and by Our Customers Elsewhere (Selected Examples)

The Room-Temperature OTTLE Cell is completely airtight. It requires a small sample volume and offers a rapid and reliable performance, easy handling and cleaning. This cell has been widely used in UV-Vis-NIR, IR, luminescence and Raman spectroelectrochemistry. Special applications include combination with fibre optics (UV-Vis absorption, time-resolved luminescence and streak camera), microscopes (resonance Raman and epifluorescence microscopy) and telescopic IR beam path reduction (FIR absorption). The cell has also been modified for vibrational circular dichroism (VCD) and laser spectroscopy (including 2D-IR) requiring no light scattering. It can be employed conveniently in studies of extremely air- and moisture-sensitive samples in a glove box.

UV-Vis-NIR and IR Spectroelectrochemistry

(a) Redox Behaviour of Transition Metal Complexes

(b) **Electrocatalytic Reduction of CO₂**

A pioneering application of the IR OTTLE technique in the in situ investigation of electrocatalytic reduction of carbon dioxide using the complex [Re(CO)₃(bpy)Cl] as a catalyst precursor was published by František Hartl (University of Reading, UK) and Michael W. George (University of Nottingham) in 1996. The electrocatalytic mechanism was shown to involve one- and two-electron pathways based on [Re(bpy)(CO)₃]^+ and [Re(bpy)(CO)₃]^-, respectively.

The IR spectral changes in the ν(CO) region accompanying the reduction of Re(bpy)(CO)₃Cl (1) in CO₂-saturated THF solution within the RT OTTLE cell are shown in the Figure above. The one-electron reduction of [Re(bpy)(CO)₃Cl] (1) initially produces [Re(bpy)(CO)₃Cl]^− (2) and reactive [Re(bpy)(CO)₃]^− which induces slow reduction of CO₂ to CO. As the CO₂ reduction progresses, [Re(bpy)(CO)₃Cl]^− (2) is converted into [Re(bpy)(CO)₃(O₂CH)]^− (10). This behaviour is evidenced by the shoulder marked X on the low-frequency side of the absorption due to the HCO₃⁻ side product, assigned to the ν₃(COO) band of the coordinated formate in 10. The much more efficient two-electron path operates in acetonitrile (*Organometallics*, 1996, 15, 3374).

(c) **Excited States of Transition Metal Complexes**

As documented by Antonín Vlček, Jr. (Queen Mary University of London, UK) and František Hartl (University of Reading, UK) in a series of articles, both charge-transfer and highly π-delocalized excited states of α-diimine metal complexes can conveniently be characterized by transient UV-Vis-NIR and IR spectroscopies in combination with UV-Vis-NIR and IR spectroelectrochemistry, using the RT OTTLE cell.

(d) Redox Intermediates


A dinuclear complex [Cp*Mo(NO)(S_{2}C_{2}Z_{2})]_{2} (Z = COOMe) was prepared and characterized by Masatsugu Kajitani (Sophia University, Japan). The electrochemical reduction of the dimer indices a shift of the N-O stretching frequency from 1653 to 1506 cm^{-1} and the ester C=O stretching absorptions at 1701 and 1732 cm^{-1} are replaced by a single band at 1711 cm^{-1}. The first observation reflects the higher electron density at the NO group of the reduced form and the latter one indicates the formation of a monomeric dithiolene complex, [Cp*Mo(NO)(S_{2}C_{2}Z_{2})]. Interestingly, this complex exhibits significant reversibility of structural interchange between the monomer and dimer upon redox cycling (J. Organomet.
APPLICATIONS OF OTTLE CELLS

Chem., 2006, 691, 3274). In this study, the RT OTTLE cell was kindly lends by our customer, Masa-aki Haga (Chuo University, Tokyo, Japan).

(e) Electronic Properties of Mixed-Valence Complexes

Heinrich Lang and co-workers (Technische Universität Chemnitz, Germany) utilize UV-Vis-NIR spectroelectrochemistry within the RT OTTLE cells to analyze the electron-transfer properties of redox-active thiophene- and fulvalenediyl-bridged homo- and heterodi- and multi-metallic complexes. In particular, the selected Figures show the structure of supercrowded 2,3,4,5-tetraferroacenylthiophene and several UV-Vis-NIR absorption bands appearing between 280 and 3000 nm when the ferrocenyl terminals in the complex are oxidized in a slow and stepwise fashion. This observation reveals that the positive charges are localized on the Fc⁺ terminals in the mixed-valent partially oxidized intermediates. No intervalence charge transfer bands of significant intensity could be detected. (Organometallics, 2010, 29, 4900; J. Organomet. Chem., 2009, 694, 655; J. Organomet. Chem., 2009, 694, 3542).


The Creutz-Taube mixed-valence complexes containing the dppz and dioxolene/dithiolate ligands have been prepared and characterized by the research group of Michael Ward (University of Sheffield, UK). Using UV-Vis and IR spectroelectrochemistry, electronic structures of these complexes have also been resolved, suggesting that the electronic delocalization in these complexes is modulated by the coordinated thiacrown, dithiolate, and dioxolene ligands. One-electron reduction of the dinuclear complex \([\{\text{Ru}^{II}(\text{[n]aneS}_4)\}(\text{bpta})]\) (see below) results in a collapse of low-energy MLCT bands and growth of a higher-energy band centred at

![Diagram](image-url)
APPLICATIONS OF OTTLE CELLS


In collaboration with Frantisek Hartl (University of Reading, UK), Gerard van Koten (Utrecht University, The Netherlands) has also investigated electronic communication in diverse mixed-valence oligonuclear metal complexes through diverse bridging cyclometalated, pincer and photochromic ligands. For example, UV-Vis-NIR spectroelectrochemical measurements were employed to characterize the different redox states of the dinuclear Ru complex featuring the bridging bis(NCN) pincer ligand (see Figure above). The one-electron oxidized mixed-valence complex (class II-III) exhibits a very intense band centred at 747 nm. (*Chem. Eur. J.*, 2010, 16, 14322; *Inorg. Chem.*, 2009, 48, 1711; *Inorg. Chem.*, 2009, 48, 5685; *Inorg. Chem.*, 2007, 46, 11133; *Eur. J. Inorg. Chem.*, 2007, 29, 2111)

(f) **Electron Transfer in Transition Metal Clusters**

Recently, Piero Leoni (Università di Pisa, Italy) has demonstrated light-induced platinum-cluster-to-iron charge transfer in ferrocenylethynyl substituted multinuclear platinum derivatives by using IR and UV-Vis-NIR spectroelectrochemistry.
APPLICATIONS OF OTTL CELLS

As shown in the Figures above, the absorption in the UV-Vis region does change upon stepwise two-electron oxidation of the cluster; however, a broad band in the NIR region appears progressively, suggesting consecutive metal-to-metal charge transfers (MMCT) from the Pt$_6$ cluster to the peripheral ferrocenium subunits. *(Inorg. Chem., 2010, 49, 3714; Inorg. Chem., 2009, 48, 10126).*

**Carlo Nervi** (Dipartimento di Chimica IFM, Università di Torino, Italy) reports the use of IR spectroelectrochemistry in combination with theoretical calculations in a study of the electronic structures and redox properties of dodecahedral transition metal clusters featuring the cyclooctatetraene ligand. Selected Figures show the spectral changes of [Co$_4$(CO)$_6$(C$_8$H$_8$)$_2$] in the region of carbonyl stretching during the one-electron reduction, which leads partial decomposition of the bis(cyclooctatetraene) system, as marked with stars. *(Chem. Eur. J., 2009, 15, 3130; Organometallics, 2005, 24, 1284; Dalton Trans., 2002, 3705).*

**Piero Zanello** (Università di Siena, Italy) and co-workers have studied electron transfer and bonding properties in mixed-valence transition metal clusters. Concerning the IR spectroelectrochemical investigation of [{Fe$_4$Cu$_3$C(O)$_{12}$($\mu$-pz)$_2$}]$^{2-}$ displayed in Figure below, the one-electron cathodic process causes the original bands in the terminal $\nu$CO region at 2002 cm$^{-1}$ and 1975 cm$^{-1}$ to halve in magnitude in favour of the new bands rising at 1952 and 1926 cm$^{-1}$. This observation is in agreement with the theoretical calculations, confirming that the two electrons simultaneously enter a single Fe$_4$C unit and these two units are not electronically communicating. *(Dalton Trans., 2011, 40, 5464; Dalton Trans., 2010, 39, 5286; Eur. J. Inorg. Chem., 2010, 30, 4831; Organometallics, 2009, 28, 2707; Inorg. Chem., 2007, 46, 10659).*

**Paul Low** (Durham University, UK) and **František Hartl** (University of Reading) investigated the electronic interaction between a remote substituent and the organometallic end-caps in mixed metal clusters. IR spectral changes in the C≡C and C≡O...

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**APPLICATIONS OF OTTLE CELLS**

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(g) *Organometallic Compounds with Carbon-Rich Chains*


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**Rainer Winter** (Universität Konstanz, Germany) also investigates in details intervalence charge transfer and electron delocalization in mixed-valence oligonuclear complexes through the vinybenzoate, vinylypyridine, vinyl, styryl, (ethynyl)(vinyl)phenylene, vinylpyrenyl, heteroaryl bridges and ligands linked by multiple hydrogen bonds. As shown below, oxidation of the dinuclear Ru complex induced numerous IR spectral changes, in particular the

Barry Lever (York University, Ontario, Canada) presented a hexadecaalkoxyphthalocyanine ligand in transition metal complexes based on Co, Mn, Ni, Fe, Ta, Ti and V have been prepared and studied by Tebello Nyokong (Rhodes University, South Africa). Spectroelectrochemistry offers excellent opportunities to identify and understand the redox processes in these complexes. Upon one-electron reduction at –0.5 V, the UV-Vis spectrum of a cobalt phthalocyanine (see the structure below) shows a shift of the Q-band from 693 to 708 nm and a new absorbance appears centred at 480 nm, which is associated with the reduction of the metal centre (Co\(^{II}\) to Co\(^{I}\)). Co\(^{I}\) exhibits low binding affinity to the axial ligand, and the secondary reactions may be reflected in lacking isosbestic points. (Polyhedron, 2011, 30, 2132; Polyhedron, 2011, 30, 508; Synth. Met., 2011, 161, 241; Inorg. Chem. Commun., 2011, 14, 330; Inorg. Chim. Acta, 2010, 363, 3662; Inorg. Chim. Acta, 2010, 363, 3229; Polyhedron, 2010, 29, 2352; Polyhedron, 2010, 29, 1257; Polyhedron, 2009, 28, 2831)
APPLICATIONS OF OTTL CELLS

of Mg, Mn and Ru). In these studies, spectroelectro-chemistry was used to characterize the products of the metallophthalocyanine oxidation or reduction. The first reduction process of the sample complex below results in a shift of the Q-band around 810 nm to a higher energy region, revealing a metal centre based redox process (Mn$^{III}$ to Mn$^{II}$) (Inorg. Chim. Acta, 2006, 359, 2690; J. Porphyr. Phthalocyanines, 2005, 9, 626).

Anthony Harriman (Molecular Photonics Laboratory, Newcastle University, UK) studied charge delocalization in metalloporphyrins and clarified the intermolecular electron transfer in Dawson-type polyoxometalates (POM) covalently linked to porphyrin residues by UV-Vis and IR spectroelectrochemistry. Two-electron reduction of the POM results in a pronounced effect on absorption spectrum of ZnP-PA and leads to formation of the ZnP radical anion. The red-shift of both Soret and Q bands may have its origin in replacement of the weakly coordinated DMF molecule with a stronger coordinating ligand (J. Org. Chem., 2010, 75, 2018; J. Phys. Chem. C, 2009, 113, 5834).

(i) Characterization of Redox-Active Chain Molecules

Victor Hernandez (Universidad de Malaga, Spain) has studied, recently also in close collaboration with our laboratory, π-dimerization of oxidized π-conjugated oligothiophenoacenes by in situ UV-Vis-NIR spectroelectrochemistry. As evidenced by spectroelectrochemical measurements, neutral TMS-T5-TMS (Figure b) showing the π-π* transition at 369 nm converts to oxidized species characterised by new bands at 492, 603 and 805 nm (Figure c). Specifically, the bands at about 500 and 800 nm are assigned to the corresponding radical cation and the band at about 600 nm to the corresponding dimer dication. (Chem. Eur. J., 2010, 16, 5481; Chem. Eur. J., 2009, 15, 12346)
Applications of OTTLE Cells

(j) Supramolecular Chemistry

Fred Brouwer (University of Amsterdam, The Netherlands) and Frantisek Hartl (University of Reading, UK) used IR spectroelectrochemistry to demonstrate a redox triggered molecular motion in a bistable rotaxane supramolecule, where the macrocycle is hydrogen-bonded to the neutral succinamide, but it can move toward the naphthalimide site when the former is reduced.

The conformational switching upon the one-electron reduction of the binding site can be monitored by the hydrogen-bond-dependent shifts of the amide $\nu$(CO) and $\nu$(NH) frequencies. These red shifts are due to the hydrogen bonding between the NH groups of the macrocycle and the carbonyls of the radical anion suggesting the translational movement of the macrocycle for the succinamide to the naphthalimide radical anion (Chem. Eur. J., 2008, 14, 1935).

Margarita Venturi (Universita di Bologna, Italy) investigated a series of redox-active rotaxanes and catenanes. UV-Vis-NIR OTTLE measurements show that the ring components of these supramolecules undergo reversible shuttling driven by the electrochemical reaction of the thread molecules. The first one-electron reduction of the catenane below is assigned to the 4,4′-bipyridinium dication (MV)-localized process and the second one is bielectronic and ascribed to the simultaneous reduction of the MV and PMI (pyromellitic diimide) linkers. (J. Am. Chem. Soc., 2010, 132, 1110; J. Am. Chem. Soc., 2007, 129, 12159; PNAS, 2006, 103, 1178).
APPLICATIONS OF OTTLE CELLS

(k) Electrochromism

Klaudia Wagner (University of Wollongong, Australia) has reported colour changes accompanying oxidative transformation of electroactive nitrospiropyran incorporated into a polymer backbone, polyterthiophene, into strongly coloured isomeric merocyanine forms. Parent spiropyran can be regenerated photochemically. The irreversible oxidative opening of the spiropyran ring (not bound to the polymer chain) within the OTTLE cell was monitored by UV-Vis-NIR spectroscopy (see below). In this unique multichromophoric and multiswitchable system the planar merocyanine form causes a smoother polymer film. (J. Am. Chem. Soc. 2011, 133, 5453).

(l) Biochemistry and Biocatalysis

A square planar complex [Pt(pyrimol)Cl] with the tridentate ligand 4-methyl-2-N-(2-pyridylmethylene)aminophenolate (pyrimol, see below) cleaves oxidatively supercoiled double-stranded DNA in a non-specific manner without any external oxidant added. UV-Vis spectroelectrochemistry is particularly useful in this case to monitor the 1e$^-$ oxidation of the neutral complex, revealing formation of the phenoxy radical derived from pyrimol, which absorbs between 400 and 600 nm. Based on this assignment Jan Reedijk (Leiden University, The Netherlands) and Frantisek Hartl (University of Reading, UK) have argued that the formation of the phenoxy radical is responsible for the DNA cleavage. This observation may be useful for the development of novel antitumor drugs (Dalton Trans., 2009, 38, 10846).

A related square-planar compound [Cu(pyrimol)Cl] was described by the same authors as a biomimetic model of the enzyme galactose oxidase (GOase). This copper(II) compound is capable of stoichiometric aerobic oxidation of activated primary alcohols in acetonitrile/water to the corresponding aldehydes. Evidence for the dominant Cu$^{II}$–L$^-$ chromophore (L$^-$ = phenoxy radical) in the oxidized catalyst was obtained from spectroelectrochemistry in the visible spectral region that revealed electronic absorption having a mixed $\pi$$\rightarrow$$\pi^*$ character. (Inorg. Chim. Acta, 2011, 374, 406.)
Applications of OTTLE Cells

Special Applications

(m) Thin-Layer Coulometry

Lubomír Pospíšil (UOCHB, Prague) and Magdalena Hromadová (J. Heyrovsky Institute of Physical Chemistry, Czech Republic) have reported electron transfer in extended viologen-type wires and further investigated their chemical stability after multiple one-electron reduction by UV-Vis spectroelectrochemical monitoring (Phys. Chem. Chem. Phys., 2011, 13, 11422). Importantly, the apparent number of consumed electrons was determined first time by combining thin-layer coulometry with UV-Vis spectroelectrochemistry. The rapid coulometry in a small volume is a reliable and highly convenient method with many envisaged future applications. In the Figure below, the reduction of methyl viologen in the OTTLE cell results in a linear decay of the absorbance at 265 nm with increasing consumed charge Q. In particular, the intercept value of 0.88 mC corresponds to the exhaustion of the reduced viologen in the optical path. Further, this value can be assigned to the concentration of methyl viologen in the thin solution layer, giving the charge consumption of 0.484 Cmol⁻¹L⁻¹ that can be used as a standard value to determine the number of electrons consumed by the new compound (see below). (Anal. Chim. Acta, 2011, 697, 23)

(n) Vibrational Circular Dichroism

Vibrational Circular Dichroism (VCD), the infrared circular dichroism associated with vibrational transitions of chiral molecules, is a relatively new and potentially very useful technique for investigating molecular configuration and conformation in solution, in particular, for the molecules ranging from helical chiral polymers, helical peptides to transition metal complexes and metalloproteins.

Herein, Sérgio Domingos, Sander Woutersen and Wybren Jan. Buma (University of Amsterdam, The Netherlands) and Frantisek Hartl (University of Reading, UK) reported the first VCD measurements on an electrochemically generated radical anion species (Chem. Commun., 2012, 48, 353).
APPLICATIONS OF OTTLE CELLS

Customized OTTLE cell for VCD measurements

Spectroelectrochemistry of the chiral molecules (R)-1 and (S)-1 was carried out within a customized infrared optically transparent thin-layer electrochemical (IR OTTLE) cell. The primary modification of the cell involved the polyethylene electrode spacer, into which the three electrodes are melt-sealed. A small cut was made in the centre of the Pt mini-grid, resulting in a cylindrical protrusion in the centre of the working electrode. Further, a 1 mm thick PTFE spacer with a circular aperture of 4 mm sits on top of this construction, giving an increased optical path length. Compared to the neutral forms of (R)-1 and (S)-1, the radical anions show a red shift of the mirror image features $R_2$, $R_3$ and $R_4$ and a strong increase in the signal intensities of the VCD spectra. The latter observation is attributed to a strong vibronically induced mixing of low-lying electronic excited states with the ground state in the electrochemically generated radical anion species.

(o) Redox Controlled Time-Resolved Luminescence

Luisa De Cola (Universität Münster, Germany) and Frantisek Hartl (University of Reading) employed the RT OTTLE cell for measurements of emission spectra and emission lifetimes during electrochemical quenching experiments with a diruthenium complex featuring a bridging bis(dipyridylphenazine) ligand.
APPLICATIONS OF OTTLE CELLS

In these experiments, the emission spectra were recorded using optical fibres connected to an Nd-YAG laser and a streak camera. As shown below, the parent complex (in acetonitrile) exhibits an intense luminescence at 650 nm with a lifetime of 130 ns. This phosphorescence becomes completely quenched upon the two-electron reduction. This observation is due to efficient electron transfer from the electrochemically reduced bridging ligand to the excited metal centre. Protonation of the reduced ligand may recover and modify the emission. (Eur. J. Inorg. Chem., 2002, 24, 335).

(p) Coupling OTTLE with Epifluorescence Microscopy

Fabien Miomandre and Pierre Audebert (Ecole Normale Supérieure de Cachan, France) and František Hartl (University of Reading) reported the first example of RT OTTLE spectroelectrochemical cell coupled to epifluorescence microscopy in the total internal reflectance mode and the application in the study of electrochemically modulated fluorescence of an organic dye (p-chloromethoxytetrazine) in solution. In this approach, the OTTLE cell was placed on the microscope stage and connected to a potentiostat. The laser beam was focused on a thin solution layer above the Pt mini grid working electrode. The thin-layer cell allows generating fully reversible fluorescence based on the reversible redox switch of the dye and offers the advantage of an exhaustive redox conversion that avoids any residual fluorescence in the dark state. The lifetime of the fluorescence was shown to decrease progressively with the conversion of the neutral dye to the corresponding radical anion due to the electron transfer quenching of the emissive excited state. (Electrochem. Commun., 2011, 13, 574)

(q) Resonance Raman Spectroelectrochemistry

Barry Lever (York University, Ontario, Canada) and František Hartl (University of Reading, UK) published a resonance Raman spectroelectrochemical study of the [(bpy)2Ru(µ-Q-Q)Ru(bpy)2]4+ (Q = quinonediimine, bpy = 2,2’-bipyridine) complex and its one-, two- and four-electron reduced products. The spectroelectrochemical investigation of the redox series was carried
APPLICATIONS OF OTTLE CELLS

out by using a Raman spectrometer in a back-scattering mode. The OTTLE cell was placed in the beam path and the laser beam was carefully focused in the thin solution layer at the surface of the minigrid working electrode. The set up is shown in the following Figure.

Careful analysis of the Raman spectra recorded at different excitation wavelengths allowed to attribute the visible absorption bands to particular electronic transition (see below). The presence of separate RuQ and RuSQ (SQ = semiquinone diimine) chromophores in the 1e reduced product revealed a persistent twist angle between the bridging ligand halves. In contrast, the SQ-SQ ligand is planar, thereby promoting electronic communication between the Ru(II) centres. The ultimate 4e reduced product could only be studied within the superior OTTLE cell. Slow decomposition prevents its isolation. (*Inorg. Chem.*, 1995, 34, 3887).
APPLICATIONS OF OTTLE CELLS

The OTTLE cell combined with a Raman microscope system also provides an effective way to study the electronic properties of redox active compounds, for example poly(aryl)amine based charge transfer materials such as DMTPD (N,N’-diphenyl-N,N’-bis(2,4-dimethylphenyl)(1,1’-biphenyl)-4,4’-diamine). In this case, the laser beam was focused with precision onto a pore within the Pt minigrid working electrode. Using this setup, Paul Low (Durham University, UK) and Ewen Smith (University of Strathclyde, UK) presented significant discrimination of Raman scattering from the mono- and dications due to resonance enhancement associating with the dominant absorptions at 472 nm (monocation, excited at 514.5 nm) and 742 nm (dication, excited at 632.7 nm), see below, (Phys. Chem. Chem. Phys., 2004, 6, 3257).

Keeping advantages of RT OTTLE cell, our Low-Temperature OTTLE cell is designed to be user-friendly and to facilitate operation from 298-175 K for temperature dependent mechanistic redox studies and for characterisation of thermally unstable transient redox products in the UV-Vis-NIR-IR region.

Low-temperature spectroelectrochemistry in the UV-Vis-NIR region was employed by Saerio Santi (Universita degli Studi di Padova, Italy) to study the electronic features and coupling of a series of mixed-valence complexes. In particular, for the complex...
below, the stable mixed-valence cation is obtained at -45 °C and shows a strong absorption band centred at 6650 cm$^{-1}$ and a weak shoulder around 9450 cm$^{-1}$. By Gaussian deconvolution, these bands are associated with multiple through-bridge interactions of mixed-valence Fe-Cr transition and Rh-Fe transition, respectively. (Organometallics, 2010, 29, 2046; Organometallics, 2009, 28, 3319; Organometallics, 2007, 26, 5867; Chem. Eur. J., 2007, 13, 7933; Chem. Eur. J., 2007, 13, 1955)


temperatures in UV-Vis-NIR and IR regions. As shown below, a reversible NO-centred reduction (left Figure) and a reversible metal centre based oxidation (right Figure) were observed by IR spectroelectrochemistry at -40 °C in PrCN for K[Cl₃Ir(NO)] and (Bu₄N)₂[Cl₃Ru(NO)], respectively. In these cases, a large low-energy shift of the NO stretching arises from the formation of metal-bonded NO⁺ and a high-energy shift of the NO stretching is caused by weakening the π donor ability of the metal toward NO⁺ and strengthening the σ donor component of NO⁺ towards the metal due to the oxidation of the metal centre. Moreover, under this condition, redox reactions do not result in significant decomposition of the complexes.

Frantisek Hartl (University of Reading, UK) and co-workers reported the stable redox intermediates of some transition metal complexes monitored by LT FTIR spectroelectrochemistry (Organometallics, 2007, 26, 4066; Chem. Eur. J., 2002, 8, 1741). For the trans-tetracarbonyl olefin tungsten complex below, it displays one strong νCO at 2035 cm⁻¹ with a shoulder at 2055 cm⁻¹ and a medium-intensity band at 2125 cm⁻¹ upon one-electron oxidation at room temperature. This observation corresponds to the formation of cis-isomer, which is probably due to a fast trans-cis isomerisation of the radical cation following the one-electron oxidation of the trans-complex at room temperature. While at 243 K (the following Figure), the IR spectrum significantly differ from the band pattern obtained at room temperature indicating IR spectroscopic detection of the initially formed cation trans-I⁺.

APPLICATIONS OF OTTLE CELLS

(Queen Mary University of London, UK) in collaboration with our laboratory. For example, at room temperature IR spectroelectrochemistry of [Re(bopy)(CO)3(bpy)]⁺ shows an electrode-catalyzed substitution of the bopy ligand by the solvent of PrCN. However, at low temperature of 233 K the first reduction leads that IR bands shift to 2022, 1919, 1905 and 1624 cm⁻¹. In particular, the band at 1624 cm⁻¹ is resulted from the disappearance of the parent ketone ν(C=O) stretching of the bopy ligand suggesting that the first reduction is bopy-localized.