PERSPECTIVE

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Using picosecond and nanosecond time-resolved infrared spectroscopy for the investigation of excited states and reaction intermediates of inorganic systems†

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Time-resolved infrared (TRIR) spectroscopy, a combination of UV flash photolysis and fast infrared detection, is a powerful technique for probing excited states and detecting reaction intermediates. In this Perspective we highlight the application of TRIR to excited states by probing the nature of the lowest excited states of *fac*-$[Re(CO)_3(dppz\text{-}Cl_2)(R)]^{n+}$ (R = Cl^- (n = 0), py (n = 1) and 4-Me_2N-py (n = 1); dppz-Cl_2 = 11,12-dichlorodipyrido-[3,2-*a*:2′,3′-*c*]phenazine) in CH_3CN. The characterisation of $[Cr(\eta^6\text{-}C_6H_6)(CO)_2Xe]$ and $[Re(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_6)]$ in supercritical Xe and liquid ethane solution exemplifies how this technique can be applied to detect new organometallic species.

Introduction

The development of flash photolysis by Norrish and Porter over 50 years ago[1] revolutionised the study of chemical reaction dynamics, allowing the characterisation of reactive intermediates and transient species on timescales inaccessible to conventional spectroscopy. Initially the technique was restricted to measuring transient absorption changes in the visible and ultraviolet spectral regions. However, although UV/VIS bands provide excellent kinetic information they are often broad and featureless and provide little structural information. In contrast, transient vibrational spectroscopy offers an excellent structural probe of short-lived species. Time-resolved infrared[2] (TRIR) and time-resolved resonance Raman[3] (TR^3) spectroscopy have a long history. This Perspective focuses on the application of TRIR to study the excited states of coordination compounds, detect intermediates and probe reaction mechanisms.

Early TRIR spectrometers were based on a sophisticated IR rapid-scan technique.[4] However, the design of such a spectrometer proved to be impractical for widespread applications and the breakthrough in the application of TRIR spectroscopy to the study of reaction mechanisms and transient intermediates came when Siebert and co-workers combined UV flash photolysis with a dispersive IR grating spectrometer and fast IR detector.[5] Grevels and co-workers used a similar approach to detect the intermediates produced following the UV photolysis of a number of transition metal carbonyl complexes in alkane solution, with a time resolution of *ca.* 5 μs.[6,7] Several different laboratories independently built IR laser-based TRIR spectrometers[8,9] to follow transition metal carbonyl photochemistry both in the gas phase and in solution. Many of the early TRIR experiments on organometallic compounds (metal carbonyls) involved the detection of reaction intermediates *via* ν(CO) IR bands in the region, 2200–1600 cm^{-1}. Both CO and IR diode lasers[10] have since been used to obtain TRIR spectra in a point-by-point fashion. In these experiments, the transmission at one particular IR frequency is monitored following UV/VIS excitation and the measurement then repeated across the desired spectral region. TRIR spectra are built-up by plotting the change in IR intensity against frequency at any given time delay following excitation. The main disadvantage of using IR lasers for TRIR measurements is that coverage of a wide spectral range using the point-by-point approach is an arduous task.

Time-resolved step-scan FTIR (s^2-FTIR) spectroscopy[11] offers a very attractive alternative to IR laser-based TRIR approaches since this technique covers the entire mid-IR region, allowing simultaneous measurement at all wavenumbers whilst maintaining the high throughput and multiplex advantages of FTIR. The s^2-FTIR technique involves the moveable mirror of the interferometer being displaced in a step-wise manner.

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Mike George

Prof. Mike George received his PhD from the University of Nottingham (1990) under the supervision of Professor Martyn Poliakoff FRS. He remained at Nottingham for a further 18 months as a Postdoctoral Fellow funded jointly by the BP Venture Research Fund and the Paul Instrument Fund of the Royal Society. During this time he began a very fruitful collaboration with Professor Jim J. Turner FRS in the area of using fast infrared spectroscopy to monitor electron transfer in inorganic excited states. Fast infrared spectroscopy has continued to be a central feature of Dr George's research. He was awarded a Royal Society/STA of Japan Postdoctoral Fellowship to probe organic excited states with Professor Hiro-o Hamaguchi at the Kanagawa Academy of Science and Technology (KAST) Japan. He returned to Nottingham as an Experimental Officer (1993) and was promoted to Research Officer (1996), Lectureship in Inorganic Chemistry (1998), Reader in Inorganic Chemistry (2001) and Professor of Chemistry (2003). His research interests combine photochemistry, fast infrared spectroscopy and instrument development spanning inorganic reaction mechanisms, organometallic alkane and noble gas complexes and, more recently, biological molecules. He has recently led the development of PIRATE, a national facility for picosecond infrared spectroscopy at the Rutherford Appleton laboratory. He was awarded the 2002–2003 Sir Edward Frankland Fellowship of the Royal Society of Chemistry.

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At each mirror position, the time-dependent change in IR intensity is measured following excitation, producing a series of time-dependent interferograms. Fourier transformation of these interferograms yields the spectral intensity changes at different time delays, which can easily be converted to the corresponding absorption spectra. Kinetic traces can be obtained by plotting the change in absorbance at any frequency or any band area as a function of time.

The point-by-point TRIR and s^2-FTIR techniques described above are both limited to a time-resolution of *ca.* 10 ns. However, many photochemical and photophysical events take place on the sub-nanosecond timescale. Ultrafast spectroscopy is a variant of the pump–probe technique; however time resolution is achieved by spatially delaying the probe pulse with respect to the pump pulse. The use of picosecond IR laser pulses in spectroscopic applications is well established. Early experiments in the 1970s used the IR pulses as a source of excitation in order to determine the vibrational relaxation dynamics of molecules in solution.[12] The ultrafast TRIR technique, which continues to develop due to constant improvements in laser and detector technology, has recently been reviewed.[2] Current state-of-the-art spectrometers are based mainly on the generation of tuneable subpicosecond mid-IR pulses using a solid state Ti : sapphire (Ti : S) laser-based system at high repetition rate (1 kHz). Improvements in infrared detector technology have also facilitated the advancement of ultrafast TRIR and typically, high bandwidth (*ca.* 100–200 cm^{-1} full-width at half maximum (FWHM)) IR probe pulses are dispersed across linear IR array detectors (composed of 32 or 64 elements)[13,14] or linear tracks of a 256 × 256 element IR focal plane array detector.[15] This method has the advantage that a large spectral region can be probed in one experiment without the need to tune the probe laser.

In this Perspective we do not intend to provide an exhaustive review of the application of TRIR to inorganic systems but rather to highlight its use for probing excited states and characterising highly reactive organometallic complexes.

Experimental

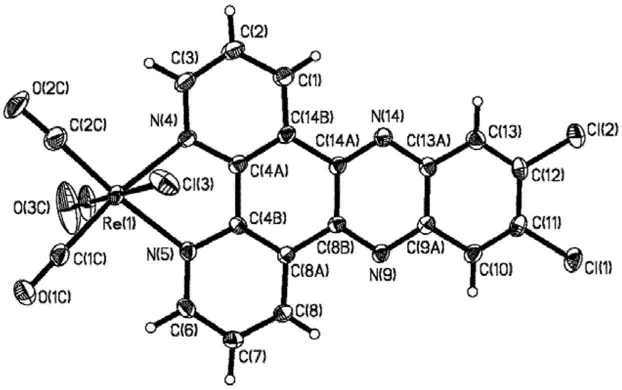
CH_3CN (Aldrich) was freshly distilled over CaH_2 under an atmosphere of dinitrogen. Anhydrous DMF, 1,10-phenanthroline-5,6-dione, pyridine, 4-(dimethylamino)pyridine, $AgPF_6$ (all Aldrich), [ReCl(CO)$_5$] (Alfa Aesar), 1,2-diamino-4,5-dichlorobenzene (Fluorochem), [Re(η^5-C_5H_5)(CO)$_3$] (**5**) (Strem), xenon (BOC, Research Grade), argon (BOC, Pureshield), CO (Air Products, Premier Grade) and C_2H_6 (BOC, 99%) were used as received. Silica (Fluorochem, 60 A, 35–70 µm) was used for column chromatography. *fac*-[ReCl(CO)$_3$(phen-5,6-dione)] was synthesised according to a literature procedure,[16] and *fac*-[Re(CO)$_3$(dppz-Cl$_2$)(py)](PF$_6$) (**1**), *fac*-[Re(CO)$_3$(dppz-Cl$_2$)(4-Me$_2$N-py)](PF$_6$) (**2**) and *fac*-[ReCl(CO)$_3$(dppz-Cl$_2$)] (**3**) were prepared by adaptation of the methods reported for similar complexes.[16] [Cr(η^6-C_6H_6)(CO)$_3$] (**4**) was purified by column chromatography (hexane/CH_2Cl_2 1 : 1 v/v). The purity of all complexes was confirmed by ^{1}H-NMR and FTIR spectroscopy.

fac-[ReCl(CO)$_3$(dppz-Cl$_2$)] (3)

A solution of *fac*-[ReCl(CO)$_3$(phen-5,6-dione)][16] (250 mg, 0.48 mmol) in EtOH (30 ml) was heated to reflux. A solution of 1,2-diamino-4,5-dichlorobenzene (110 mg, 0.62 mmol) in EtOH (5 ml) was then added dropwise and the reaction mixture was allowed to reflux for an additional 2 h. After cooling to 0 °C, the precipitate was filtered with suction, washed with Et_2O (20 ml) and dried under vacuum to afford **3** as a dark yellow solid (270 mg, 86%), (Found: C, 39.04; H, 1.65; N, 8.04%. $C_{21}H_8Cl_3N_4O_3Re$ requires C, 38.40; H, 1.23; N, 8.53%); $\tilde{\upsilon}_{max}$/cm^{-1} (CO) 2024, 1923, 1901 (CH_2Cl_2); δ_H(300 MHz; $CDCl_3$) 8.03 (2 H, dd, 5.1 Hz, 8.1 Hz, *H*-2 and *H*-7), 8.59 (2 H, s, *H*-10 and *H*-13), 9.48 (2 H, dd, 1.5 Hz, 5.1 Hz, *H*-1 and *H*-8) and 9.80 (2 H, dd, 1.5 Hz, 8.1 Hz, *H*-3 and *H*-6). The molecular structure of **3**, determined by X-ray crystallography of a crystal of **3**·0.5 THF, is shown below (atomic displacement ellipsoids are drawn at the 50% probability level). ‡

CCDC reference number 212244.

See http://www.rsc.org/suppdata/dt/b3/b306303h/ for crystallographic data in CIF or other electronic format.



fac-[Re(CO)$_3$(dppz-Cl$_2$)(4-Me$_2$N-py)](PF$_6$) (2)

A solution of complex **3** (90 mg, 0.14 mmol) in DMF (20 ml) was purged with argon for 15 min and then heated to 50 °C. $AgPF_6$ (106 mg, 0.42 mmol) was added to the reaction mixture followed, after 10 min, by a solution of 4-(dimethylamino)-pyridine (342 mg, 2.80 mmol) in DMF (3 ml). The reaction mixture was heated to 80 °C for a further 6 h under argon in the dark. The resulting solution was allowed to cool for 30 min to 0 °C and then the very fine AgCl precipitate was filtered off through a glass sinter. The filtrate was evaporated to dryness under vacuum to yield a yellow–brown solid. The solid was purified by column chromatography on silica, eluting with CH_3CN/CH_2Cl_2 (1 : 5 v/v), to yield **2** as a fine bright yellow solid (83 mg, 67%), (Found: C, 37.62; H, 2.03; N, 9.23%. $C_{28}H_{18}Cl_2F_6N_6O_3PRe$ requires C, 37.85; H, 2.04; N, 9.46%); $\tilde{\upsilon}_{max}$/cm^{-1} (CO) 2033, 1929 (CH_2Cl_2); δ_H(300 MHz; DMSO-d$_6$) 2.82 (6 H, s, (C*H*$_3$)$_2$), 6.39 (2 H, d, 6.3 Hz, *H*-3 and *H*-5 of py), 7.80 (2 H, d, 6.3 Hz, *H*-2 and *H*-6 of py), 8.40 (2 H, dd, 6.3 Hz, 7.2 Hz, *H*-2 and *H*-7 of dppz), 8.45 (2 H, s, *H*-10 and *H*-13 of dppz) and 9.80 (4 H, m, *H*-1, *H*-3, *H*-6 and *H*-8 of dppz); *m*/*z* (ES) 743 (M^+).

fac-[Re(CO)$_3$(dppz-Cl$_2$)(py)](PF$_6$) (1)

Complex **1** was synthesised using the same method as for complex **2**, with a yield of 64%; $\tilde{\upsilon}_{max}$/cm^{-1} (CO) 2043, 1939 (CH_2Cl_2); δ_H(300 MHz; DMSO-d$_6$) 7.38 (2 H, dd, 4.8 Hz, 7.8 Hz, *H*-3 and *H*-5 of py), 7.90 (1 H, t, 7.8 Hz, *H*-4 of py), 8.41 (2 H, dd, 1.3 Hz, 8.4 Hz, *H*-2 and *H*-7 of dppz), 8.54 (2 H, d, 4.8 Hz, *H*-2 and *H*-6 of py), 8.74 (2 H, s, *H*-10 and *H*-13 of dppz), 9.76 (2 H, dd, 1.3 Hz, 8.4 Hz, *H*-1 and *H*-8 of dppz) and 9.83 (2 H, dd, 1.3 Hz, 5.4 Hz, *H*-3 and *H*-6 of dppz); *m*/*z* (ES) 700 (M^+).

The current Nottingham diode laser TRIR spectrometer uses a pulsed Nd:YAG laser (Spectra Physics GCR-12S; 266, 355 or 532 nm; *ca.* 7 ns pulse width) to initiate the photochemical process and a Mütek cw IR diode laser (MDS 1100) and monochromator (MDS 1200), to monitor the transient IR signals by means of a fast photovoltaic MCT infrared detector (Kolmar

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‡ $C_{23}H_{12}Cl_3N_4O_{3.5}Re$, M = 692.92, monoclinic, a = 19.958(2), b = 18.054(2), c = 13.530(2) Å, β = 116.562(2)°, V = 4360.5(15) Å^3, T = 150(2) K, space group $C2/c$ (no. 15), Z = 8, μ(Mo-Kα) = 5.98 mm^{-1}, 13248 reflections measured, 4906 unique (R_{int} = 0.024) which were used in all calculations. The final $wR(F^2)$ = 0.0722 (all data), $R_1(F)$ = 0.0261 (4176 observed reflections, where $I > 2\sigma(I)$).

Technologies, KMPV11-0.5-J1/BC) and digital storage oscilloscope. By tuning the IR diode laser/monochromator across the spectral region of interest, a series of IR kinetic traces are obtained, which can be combined and used to generate a point-by-point TRIR spectrum at any desired time interval after the laser flash.

Time-resolved step-scan FTIR (s^2-FTIR) experiments were conducted using a combination of a Nicolet Magna 860 Interferometer and a Nd:YAG laser (Spectra Physics GCR-12S). Synchronisation of the laser with data collection was achieved using a pulse generator (Stanford DG535). The interferometer was equipped with both an internal 100 kHz 16-bit digitiser and an external 100 MHz 12-bit digitiser (GAGE 8012A). In these experiments a 1 mm photovoltaic MCT detector was used with a 20 MHz preamplifier. This detector has AC and DC outputs, which are digitised simultaneously to ensure proper phase matching. The AC signal was amplified by an external preamplifier (Stanford SR 560) to use the full dynamic range of the digitiser. Single sided interferograms were obtained using one laser pulse at each mirror position. An external optical bench (Nicolet-TOM®) was used for locating the sample cell and MCT detector, allowing easy manipulation of the UV laser beam through the cell. All s^2-FTIR spectra reported in this Perspective were recorded at 8 cm^{-1} resolution with 8 scans of the interferometer.

The picosecond TRIR experiments were carried out on the PIRATE apparatus at the Central Laser Facility of the CCLRC Rutherford Appleton Laboratory. This apparatus has been described in detail previously.[14] Part of the output from a 1 kHz, 800 nm, 150 fs, 2 mJ Ti-Sapphire oscillator/regenerative amplifier (Spectra Physics Tsunami/Spitfire) was used to pump a white light continuum seeded β-BaB_2O_4 (BBO) optical parametric amplifier (OPA). The signal and idler produced by this OPA were difference frequency mixed in a type I $AgGaS_2$ crystal to generate tuneable mid-infrared pulses (*ca.* 150 cm^{-1} FWHM, 1 μJ), which were split to give probe and reference pulses. Second harmonic generation of the residual 800 nm light provided 400 nm pump pulses. Both the pump and probe pulses were focused to a diameter of 200–300 μm in the sample. Changes in infrared absorption at various pump–probe time delays were recorded by normalising the outputs from a pair of 64-element MCT infrared linear array detectors on a shot-by-shot basis.

In all TRIR experiments using conventional solvents, dry, degassed solutions were saturated with argon and flowed through a home-built flow system incorporating an IR cell (Harrick Scientific Corp.) and a re-circulating pump (Micropump) or Teflon peristaltic pump (Cole Palmer). High-pressure solutions were prepared in a high-pressure cell that has been described previously for conventional spectroscopic monitoring.[17] The cell was used with CaF_2 windows and a pressure transducer (RDP Electronics) and the solution was flowed through a high-pressure flow system using a magnetically coupled re-circulating gear pump (Texas Process Equipment/Micropump).

Applications of TRIR

1 Probing excited states with TRIR

The photophysics and photochemistry of mixed-ligand transition metal complexes is an area of intense interest. Transition metal α-diimine complexes usually offer a rich manifold of excited states, the relative energies of which can be tuned by donor/acceptor substituents and environmental properties. This has led[18] to the extensive application of such coordination compounds for solar energy conversion and storage, photocatalysis, as building blocks for light harvesting devices, as light emitting diodes (LEDs) with high efficiency and also as molecular probes for electron/energy transfer.

An understanding of the structure of excited states and the relationship between these structural features and their properties is a prerequisite to a more complete understanding of photochemistry. Since the first experiment by Woodruff *et al.*,[19] elucidating the localised nature of the MLCT state of excited $[Ru(bpy^{\bullet-})(bpy)_2]^{2+}$, TR^3 has been widely used for the determination of the structural features of the excited states of coordination compounds. However there are limitations to the use of TR^3. For example, only totally symmetric vibrations are resonantly enhanced and only those vibrations that are coupled to the excited state formed will appear in the TR^3 spectrum.

TRIR can provide complementary information to TR^3 since the selection rules for IR spectroscopy are different. Significantly there is also no requirement for the resonance enhancement of the vibrations in the TRIR spectrum. TRIR is particularly useful for the elucidation of the nature of the lowest excited states of metal carbonyls and cyanides due to the high oscillator strengths of ν(CO) and ν(CN) vibrations and the sensitivity of their position and bandwidth to the electron density distribution in the molecule.[20,21] The majority of TRIR studies on the excited state nature of inorganic chromophores have focussed on d^6 and d^8 metal complexes, *e.g.* Re(I), Ru(II), Os(II) and Pt(II), possessing MLCT,[20,22] mixed MLCT/halogen-to-ligand CT (XLCT),[23] σ–π*,[24] and π–π*[22,25] excited states. Vlcek and co-workers have used[26] ps-TRIR to monitor the excited states and photochemistry of $[Cr(2,2'\text{-bipy})(CO)_4]$, $[MnBr(CO)_3(^iPr\text{-DAB})]$ (^iPr-DAB = *N*,*N*′-bis-isopropyl-1,4-diaza-1,3-butadiene), $[Re(MQ^+)(CO)_3(dmb)]^{2+}$ (MQ^+ = *N*-methyl-4,4′-bipyridinium; dmb = 4,4′-dimethyl-2,2′-bipyridine), $[W(CO)_4(en)]$ and $[W(CO)_4(N,N'\text{-bis-alkyl-1,4-diaza-1,3-butadiene})]$. Palmer and co-workers have recently reported the MLCT excited state of the d^{10} Cu(I) complexes, $[Cu(dmp)_2]^+$, $[Cu(dmp)(PPh_3)_2]^+$ and $[Cu(dbp)(dmp)]^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline and dbp = 2,9-di-*tert*-butyl-1,10-phenanthroline).[27] Excitation of a metal complex to produce a MLCT excited state results in a reduction of electron density at the metal centre and, in the case of metal carbonyl complexes, a shift of the ν(CO) bands to higher energy by *ca.* 50–60 cm^{-1} relative to the ground state absorptions. For complexes with intra-ligand (IL) π–π* lowest excited states, both the HOMO and LUMO are localised on the diimine ligand and the ν(CO) bands shift only slightly on production of the excited state.[20,22] The TRIR method has also been used to probe the mixing of excited states. For example, the lowest excited state of $[Ru(X)(CO)_2(Me)(^iPr\text{-DAB})]$ (X = Cl, Br or I) was described as a mixture of MLCT and XLCT. As the halogen was changed from Cl ⟶ I, the positive ν(CO) shift upon formation of the excited state decreased in the order Cl > Br > I, thus indicating the increase of XLCT character in the lowest excited state.[23] A rare example of a ligand field (LF) excited state is presented in the TRIR study of $[W(CO)_5(py)]$ in a glass matrix at 77 K.[28] Brozik and co-workers have recently exploited the use of 77 K glasses to obtain the IR spectrum of the LMCT excited state of $[Ti(\eta^5\text{-}C_5H_5)_2(NCS)_2]$.[29] Peripheral IR reporter groups such as carboxylic acids and esters on substituted diimine ligands have also been utilised to indirectly probe charge transfer processes using both ns- and ps-TRIR.[30] TRIR studies in the fingerprint region have also probed[31] the structural features of the excited states of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$.

1.1 Elucidating the lowest excited state of *fac*-$[Re(CO)_3(dppz\text{-}Cl_2)(R)]^{n+}$ (R = Cl^- (*n* = 0), py (*n* = 1) and (4-dimethylamino)pyridine (*n* = 1); dppz-Cl_2 = 11,12-dichlorodipyrido[3,2-a:2′,3′-c]phenazine). Transition metal complexes have been widely used as probes for DNA and the study of DNA mediated electron transfer and DNA damage.[32] Intercalating ligands such as dppz provide a convenient method for binding the metal complex into the DNA double helix. A large number of complexes of Ru(II), Os(II) and Re(I) containing dppz ligands and its derivatives have been extensively studied by the combination of time-resolved and steady state spectroscopic techniques. However the photophysical properties of such probes still remain somewhat ambiguous. This is partly due to the dppz ligand being a fusion of two moieties, phen and phenazine (phz), each containing localised π* acceptor orbitals.[33] The close proximity in energy of these orbitals has been confirmed by a number of electrochemical, spectroelectrochemical and photophysical methods.[33–36] In principle this leads to four possible low lying triplet states for metal dppz complexes, involving a ππ* IL or MLCT transition to either the phen- or phz-based LUMO orbital. The possibility of altering the energy of both the phen and phz orbitals by various substituents and environmental properties such as solvent polarity or the ability to form hydrogen bonds adds to the complexity of the electronic structure.[35–37] It is clear that a structural assignment of the excited states involved is important since this is key in understanding the mechanism of the action of metal complexes as DNA probes.

$[M^{II}(\alpha\text{-diimine})_2(dppz)]^{2+}$ (M^{II} = Ru(II) or Os(II); α-diimine = 2,2′-bipy or phen) complexes provide an example of the importance of the ordering of excited states of different orbital origin. These exhibit a ‘light-switch’ effect, showing intense ^{3}MLCT emission in non-aqueous solvents but no emission in aqueous solution. In the presence of DNA in aqueous solution the emission is restored, thus providing a probe for DNA.[38] The ‘light-switch’ effect originates from an interplay between the close lying phen and phz localised MLCT states, but even with complexes as well studied as $[Ru^{II}(2,2'\text{-bipy})_2(dppz)]^{2+}$ there is ambiguity in the assignment of the lowest excited state in different environments and DNA.[35,39] Therefore, there is a need to obtain direct structural information on the nature of the orbitals involved in such processes. Resonance Raman and TR^3 spectroscopy have been used to probe transition metal dppz complexes in various environments[40,41] and also their interactions with DNA.[36,42]

The sensitivity of the *ν*(CO) vibrations of metal carbonyl complexes to the electron density on the metal centre allows for the differentiation between MLCT and IL ππ* excited states, as well as phen and phz localised MLCT states, since the formation of these states leads to substantially different electron density distribution in the molecule. We have recently demonstrated,[43] using TRIR, transient absorption and TR^3 that upon photoexcitation of *fac*-$[Re(CO)_3(dppz)(py)]^+$ a relaxed ^{3}IL ππ*(dppz) state, which exists on the ns timescale, is formed within 30 ps from a precursor state. This emissive excited state is then equilibrated on the ns timescale with a close-lying ^{3}MLCT excited state which was assigned by TRIR as a dπ(Re)⟶π*(phz) state. In this section we report a TRIR investigation into the photophysics of *fac*-$[Re(CO)_3(dppz\text{-}Cl_2)(R)]^{n+}$, (R = Cl^- (*n* = 0), py (*n* = 1) and (4-dimethylamino)pyridine (*n* = 1)) in CH_3CN solution at room temperature in order to demonstrate the effect of ligand substitution on the excited state nature of transition metal complexes.

The UV/VIS absorption spectra of *fac*-$[Re(CO)_3(dppz\text{-}Cl_2)(py)]^+$ (**1**) and *fac*-$[Re(CO)_3(dppz\text{-}Cl_2)(4\text{-}Me_2N\text{-}py)]^+$ (**2**) are dominated by intense transitions centred around 360–380 nm, which are characteristic of IL ππ* transitions of the dppz ligand.[41] These spectra also exhibit a tailing of the IL ππ* band into the visible region. However, this effect is more pronounced for complex **2**. This indicates an extra spectral feature superimposed onto the IL ππ* transitions. This broad featureless band of low intensity could correspond to a close-lying ^{1}MLCT state, the low intensity being due to the lack of overlap between the metal dπ and dppz π* orbitals.[44] Therefore, as discussed by Schanze and co-workers for similar complexes,[16] irradiation of **1** and **2** in the near-UV is likely to cause the simultaneous population of both ^{1}MLCT and ^{1}IL ππ* excited states. *fac*-$[ReCl(CO)_3(dppz\text{-}Cl_2)]$ (**3**) has previously been shown not to emit at room temperature.[41] However, 400 nm excitation of **1** and **2** results in luminescence. The emission spectrum of **1** shows clearly resolved vibrational structure indicative of the IL ππ* nature of the emitting state. However, the emission lifetime is surprisingly short (7 (±1) ns), suggesting that the photophysics of **1** might be more complex. The emission band of **2**, centred at 570 nm is broad and featureless with a lifetime of 1.5 (±1) ns.§ Both UV/VIS absorption and emission spectra suggest that there is MLCT character in the lowest emitting excited state of **2**. However, the emission data do not allow an unambiguous determination of the orbital origin of the lowest excited states of **1** and **2**. Also emission measurements offer no conclusive information on the phen or phz localisation of the LUMOs for the complexes under study.

Figs. 1, 2 and 3 show the ps-TRIR results obtained following 400 nm excitation of **1**, **2** and **3** respectively. The ground state FTIR spectrum of **1** in CH_3CN possesses two bands in the *ν*(CO) stretching region at 2037 and 1934 cm^{-1} [Fig. 1(a)]. The ps-TRIR spectra obtained at a series of time delays between 2 and 2000 ps following excitation of this solution are shown in Fig. 1(b). Several conclusions can be drawn from these data. The spectrum obtained after 2 ps shows that the parent absorptions have been bleached and two new broad absorption bands centred at *ca.* 2029 and 1917 cm^{-1} are formed. The shift of the excited state bands to lower energy of the parent absorptions is consistent with the formation of a ππ*(dppz) IL excited state similar to the results obtained on the ps-timescale for *fac*-$[Re(CO)_3(dppz)(py)]^+$.[43] Thus ps-TRIR supports the assignment of the emissive excited state as IL ππ* (dppz). As Δ*t* is increased from 2 to 50 ps, the transient bands narrow and shift to slightly higher wavenumber (2032 and 1928 cm^{-1}). In principle, this shift may correspond to several processes, namely vibrational cooling, a transition between different IL excited states *e.g.* IL ππ* (phen) and IL ππ* (phz), or conversion of the initially formed singlet state into a triplet. However, the latter is unlikely since in metal complexes the conversion of a singlet to a triplet state is expected to proceed on a much faster timescale. For example, the ^{1}MLCT to ^{3}MLCT conversion for

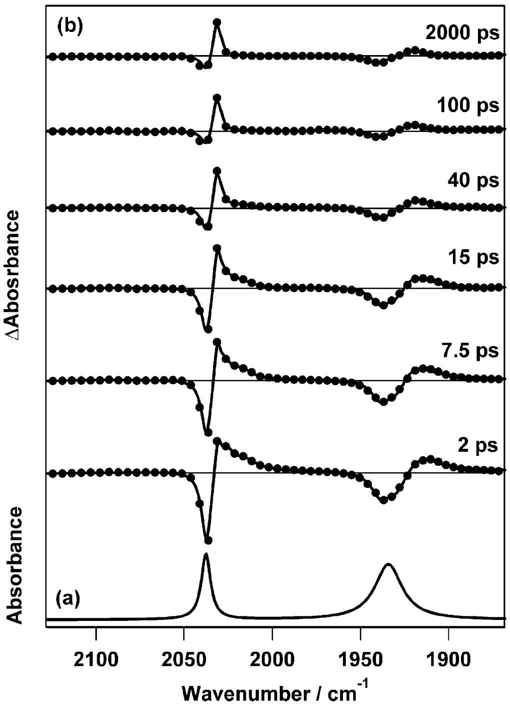

Fig. 1 (a) FTIR spectrum of *fac*-$[Re(CO)_3(dppz\text{-}Cl_2)(py)](PF_6)$ (**1**) in CH_3CN at room temperature. (b) Series of TRIR spectra obtained between 2 and 2000 ps after 400 nm excitation of this solution.

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§ Note that the large error reported is due to the short lifetime being close to the instrument response time.

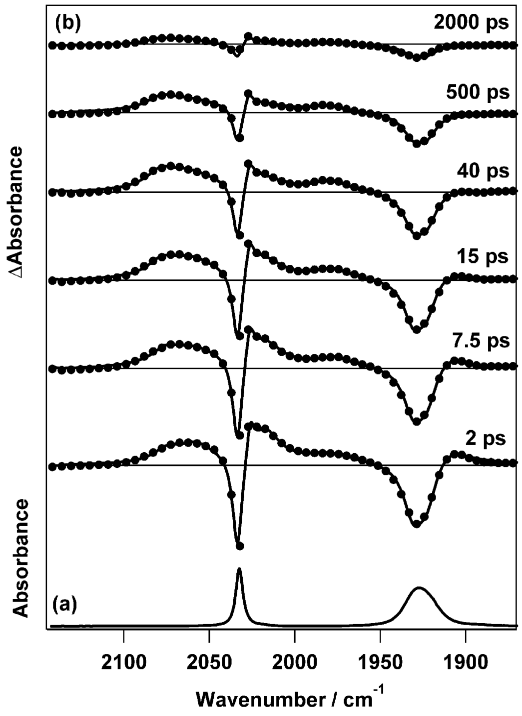

Fig. 2 (a) FTIR spectrum of *fac*-[Re(CO)$_3$(dppz-Cl$_2$)(4-Me$_2$N-py)]-(PF$_6$) (**2**) in CH$_3$CN at room temperature. (b) Series of TRIR spectra obtained between 2 and 2000 ps after 400 nm excitation of this solution.

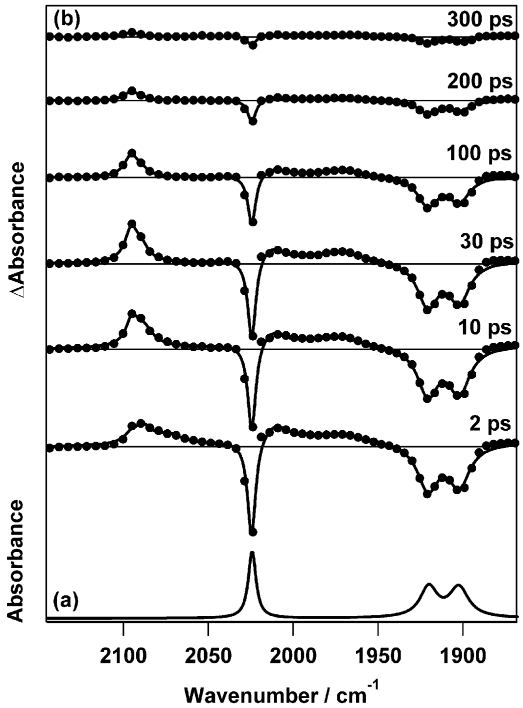

Fig. 3 (a) FTIR spectrum of *fac*-[ReCl(CO)$_3$(dppz-Cl$_2$)] (**3**) in CH$_3$CN at room temperature. (b) Series of TRIR spectra obtained between 2 and 300 ps after 400 nm excitation of this solution.

[Ru(bpy)$_3$]$^{2+}$ is completed within 40 fs.[45] The narrowing and blue shifting of the ν(CO) bands over the first 50 ps following excitation is consistent with vibrational cooling processes, which have been well-documented for transition metal carbonyls.[46,47] However, as discussed in a recent publication,[43] the band shift is also consistent with an IL $\pi\pi^*$ (phen) to IL $\pi\pi^*$ (phz) interconversion and both of these processes could occur on a similar timescale, with both contributing to the observed spectral changes. TRIR kinetic traces (not shown) were produced to estimate the rate of narrowing and shifting of the transient ν(CO) bands using multi-Lorentzian curve fitting of the ps-TRIR spectra at different time delays. The observed rate was found to have an exponential form, giving an estimated time constant of *ca.* 20 ps for the possible vibrational cooling process and/or interconversion of the IL $\pi\pi^*$ (phen) to IL $\pi\pi^*$ (phz) state.

The TRIR spectrum obtained 2 ps following excitation of **2** (Fig. 2) shows that the parent bands at 2033 and 1927 cm^{-1} are bleached and new transient ν(CO) bands are formed. Together with the transient ν(CO) bands at lower wavenumber than the parent (2026 and 1913 cm^{-1}), indicative of an IL $\pi\pi^*$ state, there are also bands shifted to higher frequency (*ca.* 2072, 2020 and 1980 cm^{-1}). The shift to higher wavenumber in the ν(CO) bands of **2** on going from the ground to excited state is consistent with formation of a MLCT excited state. Furthermore the magnitude of the shift is consistent with the formation of a dπ(Re) $\longrightarrow$ π^*(phen) MLCT excited state since the shifts for **2** are of the same magnitude as observed upon excitation of [ReCl(CO)$_3$(phen)].[20] Both the MLCT and IL $\pi\pi^*$ transient bands narrow and shift to higher frequency within 70 ps (τ = 20 ps),¶ consistent with vibrational cooling of the newly formed species, and then decay together with a lifetime of 1.0 (± 0.2) ns, Fig. 4. However, we cannot rule out the possibility that interconversion between IL $\pi\pi^*$ states is also occurring within the first 20–30 ps. The similar rates of decay of the ^{3}MLCT (phen) and IL $\pi\pi^*$ excited states implies that there is an equilibrium between these states for **2** on the timescale between 2 ps and 2.5 ns, although we still cannot discount the possibility that the two excited states might have similar lifetimes and are not in equilibrium. Emission is observed from the MLCT state, suggesting that this state is slightly lower in energy.

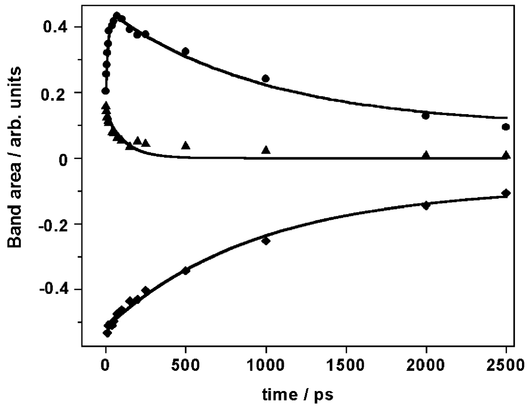

Fig. 4 TRIR kinetic traces obtained from the Lorentzian curve-fitted band areas of the high frequency ν(CO) transient and low frequency bleach in the ps-TRIR spectra of **2** (◆, area of bleach), (▲, area of vibrationally "hot" transient component), (●, area of vibrationally "cool" transient component). The "hot" component decays exponentially with a lifetime (τ = 20 ps) that is identical to the growth of the "cool" component. This timescale is assigned to the vibrational relaxation lifetime of the "hot" MLCT state. Subsequently the transient decays back to the ground state with a lifetime of 1.0 (±0.2) ns.

Complex **3** is not luminescent in CH$_3$CN solution at room temperature. In addition, a previous resonance Raman investigation into the nature of the lowest excited state of this complex did not provide a clear assignment.[41] This complex has C_s symmetry and as such exhibits three ν(CO) bands in CH$_3$CN solution at 2024, 1920 and 1902 cm^{-1}. The TRIR spectrum obtained 2 ps after excitation shows depletion of the three parent bands and production of three new ν(CO) bands shifted to higher wavenumber, which is consistent with the production of an MLCT excited state, Fig. 3. These bands first narrow and

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¶ The high frequency ν(CO) transient was modelled as the sum of two Lorentzian components.

shift to higher wavenumber (2094, 2017 and 1978 cm^{-1}) due to vibrational relaxation ($\tau \sim 20$ ps) and then decay back to the ground state with a lifetime of 150 (± 20) ps, Fig. 5. The short lifetime of the excited state is consistent with the absence of emission in fluid solution at room temperature. The MLCT bands observed for **3** are shifted to much higher wavenumber compared to those of **2**. This shift is similar to the shift observed in the ns-TRIR spectrum of *fac*-[Re(CO)$_3$(dppz)(py)]$^+$, which was interpreted[43] in terms of the charge in the excited state being localised on an orbital which is further from the Re centre *e.g.* the phz-localised MO. This should cause a further reduction in backbonding to the CO ligands compared to a phen-based MLCT state and therefore a greater shift of the ν(CO) excited state bands. We therefore assign the transient bands observed in the ps-TRIR spectrum of **3** to a dπ(Re)⟶π*(phz) ^{3}MLCT excited state species.

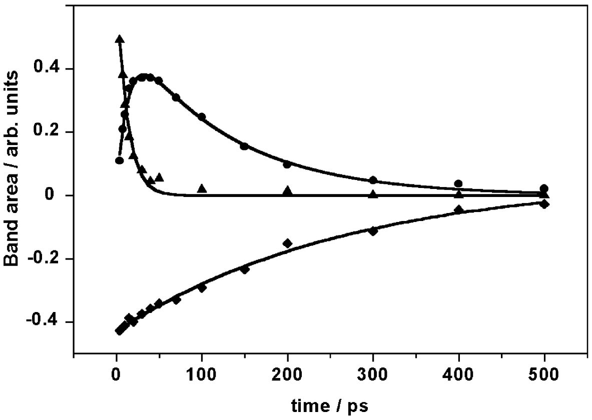

Fig. 5 TRIR kinetic traces obtained from the Lorentzian curve-fitted band areas of the high frequency ν(CO) transient and bleach in the ps-TRIR spectra of **3** (◆, area of bleach), (▲, area of vibrationally "hot" transient component), (●, area of vibrationally "cool" transient component). The "hot" component decays exponentially with a lifetime ($\tau = 20$ ps) that is identical to the growth of the "cool" component. This timescale is assigned to the vibrational relaxation lifetime of the "hot" MLCT state. Subsequently the transient decays back to the ground sate with a lifetime of 150 (±20) ps.

The present study shows that modification of ligand R in *fac*-[Re(CO)$_3$(dppz-Cl$_2$)(R)]$^{n+}$ leads to substantial changes in the photophysics of the complexes. In CH$_3$CN solution at room temperature, changing from the neutral *fac*-[Re(CO)$_3$(dppz-Cl$_2$)(R)] (R = Cl$^-$), which possesses a phz-based MLCT state, to R = py or 4-Me$_2$N-py leads to charged complexes with low-lying IL ππ*(dppz) states. The introduction of a donor substituent on the pyridine moiety results in an equilibrium between the MLCT (phen) and IL ππ*(dppz) excited states for **2**. The proximity of the various excited states also offers the possibility of tuning the nature of the lowest excited state with changes in the environment polarity or hydrogen bonding.[43] The complexes studied in this Perspective all contain IR reporters with high oscillator strengths. However, it should be noted that organic CO groups have been effectively used[30] to probe the electron distribution in excited states and improvements in the sensitivity of the TRIR technique have allowed structural fingerprints to be obtained for complexes lacking strong IR absorbing bands.[31]

2 Probing reaction mechanisms and detecting intermediates with TRIR

TRIR spectroscopy has been used to probe reactions under a wide range of conditions including the gas phase,[48] conventional solution,[2,49] supercritical fluids,[50] zeolites[51] and TiO$_2$.[52] A key step in elucidating reaction mechanisms is to characterise the structure and monitor the reactivity of the intermediates.

Many of the early TRIR experiments focused on studying metal carbonyl intermediates and probing reaction mechanisms in solution for compounds such as [M(CO)$_6$] (M = Cr, Mo or W),[53,54] [M(CO)$_5$] (M = Fe or Os),[55] [Fe(η^5-C$_5$H$_5$)(CO)$_2$]$_2$,[9] [Mn$_2$(CO)$_{10}$],[7] [Os$_2$(CO)$_8$(μ-η^1,η^1-H$_2$CCH$_2$)][56] and [Ru$_3$(CO)$_{12}$].[57] The photochemical substitution of complexes such as [M(CO)$_6$] continues to be the subject of intense interest.[58] TRIR has also been used to probe photocatalytic reactions,[54,59] bioinorganic systems[60] and other biological processes such as protein folding.[61]

2.1 Organometallic noble gas complexes

The recent isolation[62] of the first stable transition metal-noble gas complex, [AuXe$_4$]$^{2+}$[Sb$_2$F$_{11}$]$^-_2$ by Seidel and Seppelt was a key development in the past 30 years of research worldwide. The discovery in 1972[63] that [Cr(CO)$_5$] could form a complex with CH$_4$ prompted Poliakoff and Turner to use matrix isolation and infrared spectroscopy[64] to characterise [Fe(CO)$_4$Xe] in low temperature matrices. Perutz and Turner later reported a detailed matrix isolation study[65] of noble gas coordination to transition metal centres by following the UV/VIS photochemistry of [M(CO)$_6$] in noble gas, methane and other matrices at 4 and 20 K. Since this study many experimental and theoretical investigations have demonstrated that noble gases coordinate to unsaturated transition metal centers *via* σ-donation.[66] Although matrix isolation spectroscopy has proved to be an invaluable technique for the isolation and characterisation of transition metal noble gas complexes, it does have some limitations. For example, it is impossible to accurately predict the reactivity of these species in solution at room temperature solely from matrix isolation data.

In an effort to characterise transition metal noble gas complexes under more conventional conditions, several techniques have been employed since the early matrix isolation experiments. For example, cryogenic liquefied noble gases are a useful alternative to solid noble gas matrices. By operating at only moderate pressures, the liquid ranges of the noble gases become relatively large (*e.g.* 160–248 K for Xe at 22 atm). Furthermore, the solubility of organometallic complexes in these liquefied gases is generally comparable to that in common organic solvents. This permits the characterisation of noble gas complexes in solution over a range of temperatures and therefore the calculation of activation parameters for their subsequent reactions. Following the observation of [Cr(CO)$_5$Xe] in liquefied noble gas solution[67] several other noble gas complexes have been characterised using TRIR spectroscopy in these cryogenic solvents.[66] TRIR experiments have also been performed in the gas phase, permitting the room temperature observation of [M(CO)$_5$(L)] (L = Kr and Xe; M = Cr, Mo (Xe only) and W).[68] However, although a great deal of information can be obtained from gas phase measurements, regarding the relative room temperature stabilities and reactivities of various organometallic noble gas fragments, the conditions are still far removed from the room temperature condensed phase.

Using a combination of TRIR spectroscopy and supercritical fluids we have been able to obtain the IR spectra of short-lived transition metal noble gas complexes in *solution* at *room temperature*. Supercritical fluids are a hybrid of gases and liquids and are excellent solvents for many organometallic complexes.[69] [W(CO)$_5$Ar], [M(CO)$_5$Kr] and [M(CO)$_5$Xe] (M = Cr, Mo or W) were characterised and their reactivity towards CO measured at ambient temperature in supercritical Ar (scAr), scKr and scXe respectively.[50] These experiments revealed that for each complex, [M(CO)$_5$Kr] or [M(CO)$_5$Xe] the order of reactivity towards CO is Cr ≈ Mo > W. For each metal, the reactivity of [M(CO)$_5$(L)] complexes follows the order Kr > Xe. Organometallic alkane complexes are similar to noble gas complexes in that their bonding mainly involves σ donation to the metal centre.[70] Currently, [Re(η^5-C$_5$H$_5$)(CO)$_2$(alkane)] is the

Table 1 Comparison of the IR ν(CO) band positions of various [Cr(η^6-C_6H_6)$(CO)_2$(L)] complexes characterised under different conditions

Complex	Conditions	ν_{CO}/cm^{-1}	Ref.
[Cr(η^6-C_6H_6)$(CO)_3$]	scXe (1500 psi, 293 K)	1988, 1922	This work
[Cr(η^6-C_6H_6)$(CO)_3$]	Ar Matrix (12 K)	1990, 1923	74
[Cr(η^6-C_6H_6)$(CO)_3$]	CH_4 Matrix (12 K)	1983, 1913	74
[Cr(η^6-C_6H_6)$(CO)_3$]	N_2 Matrix (12 K)	1984, 1914	74
[Cr(η^6-C_6H_6)$(CO)_3$]	*n*-Heptane (293 K)	1983, 1915	75
[Cr(η^6-C_6H_6)$(CO)_2$Xe]	scXe (1500 psi, 293 K)	1937, 1886	This work
[Cr(η^6-C_6H_6)$(CO)_2$Ar]	Ar Matrix (12 K)	1938, 1885	74
[Cr(η^6-C_6H_6)$(CO)_2$(CH_4)]	CH_4 Matrix (12 K)	1925, 1870	74
[Cr(η^6-C_6H_6)$(CO)_2$(N_2)]	N_2 Matrix (12 K)	1940, 1896	74
[Cr(η^6-C_6H_6)$(CO)_2$(*n*-heptane)]	*n*-Heptane (293 K)	1927, 1877	75

least reactive of the reported organometallic alkane complexes[71] and the only alkane complex to be characterised so far in solution by NMR spectroscopy.[72] [Re(η^5-C_5H_5)$(CO)_2$Xe] and [Re(η^5-C_5H_5)$(CO)_2$Kr] are also significantly less reactive towards CO than the corresponding [W$(CO)_5$Xe] and [W$(CO)_5$-Kr] complexes.[73] Furthermore, experiments conducted in scKr doped with Xe showed that the formation of the Re–Xe complex was slow enough to be followed in real time, presumably as a result of a significant Re–Kr interaction in scKr.

2.1.1 Formation and reactivity of [Cr(η^6-C_6H_6)$(CO)_2$Xe].

Fig. 6(a) shows the FTIR spectrum of [Cr(η^6-C_6H_6)$(CO)_3$] (**4**) in scXe (1500 psi) in the presence of CO (30 psi). A series of step-scan FTIR spectra obtained following 355 nm laser excitation of this solution at room temperature are shown in Fig. 6(b). It is clear that the parent ν(CO) absorptions are bleached and two transient ν(CO) bands are produced at 1937 and 1886 cm^{-1}. These two bands decay at the same rate and can readily be assigned to [Cr(η^6-C_6H_6)$(CO)_2$Xe] by comparison with previous matrix isolation[74] and TRIR experiments[75] (see Table 1). [Cr(η^6-C_6H_6)$(CO)_2$Xe] decays to reform **4** in the presence of CO. Fig. 7(a) shows the TRIR decay traces of [Cr(η^6-C_6H_6)$(CO)_2$-Xe] obtained under a range of different CO concentrations. In the presence of CO [Cr(η^6-C_6H_6)$(CO)_2$Xe] decays *via* pseudo first order kinetics (k_{obs}) and the rate of decay depends linearly upon CO concentration (see Fig. 7(b)) affording the second order rate constant (k_{CO}) for the reaction of [Cr(η^6-C_6H_6)$(CO)_2$Xe] with CO in scXe ($k_{CO} = 1.6\ (\pm 0.2) \times 10^7$ M^{-1} s^{-1}). The rate of reaction of [Cr(η^6-C_6H_6)$(CO)_2$Xe] with CO, obtained in the current experiment, can be compared with the reactivities of other Xe complexes towards CO in scXe. The reactivity of [Cr(η^6-C_6H_6)$(CO)_2$Xe] fits into the already established trend of reactivities for Group 5, 6, and 7 Xe carbonyl complexes, in which the reactivity decreases down and across the groups from left to right. [Cr(η^6-C_6H_6)$(CO)_2$Xe] is one of the most reactive transition metal Xe complexes[76] that has been characterised in a supercritical fluid at room temperature, having a slightly greater reactivity than that of the more simple [Cr$(CO)_5$Xe] complex.[50] We have probed the reactivity of [Cr(η^6-C_6H_6)-$(CO)_2$Xe] further by examining the activation parameters for the reaction of [Cr(η^6-C_6H_6)$(CO)_2$Xe] with CO in scXe. The $\Delta H^\ddagger$ value obtained ($\Delta H^\ddagger$ = 17 (±2) kJ mol^{-1}) is much lower than those measured for other transition metal Xe complexes in scXe, such as [M(η^5-C_5R_5)$(CO)_2$Xe] (M = Mn or Re; R = H, Me or Et (Mn only))[77] and [W$(CO)_5$Xe],[50] which is consistent with the higher reactivity of [Cr(η^6-C_6H_6)$(CO)_2$Xe]. The value of $\Delta S^\ddagger$ that we have obtained (−51 (±5) J K^{-1} mol^{-1}) suggests an associative mechanism for the reaction of [Cr(η^6-C_6H_6)-$(CO)_2$Xe] with CO in scXe. ||

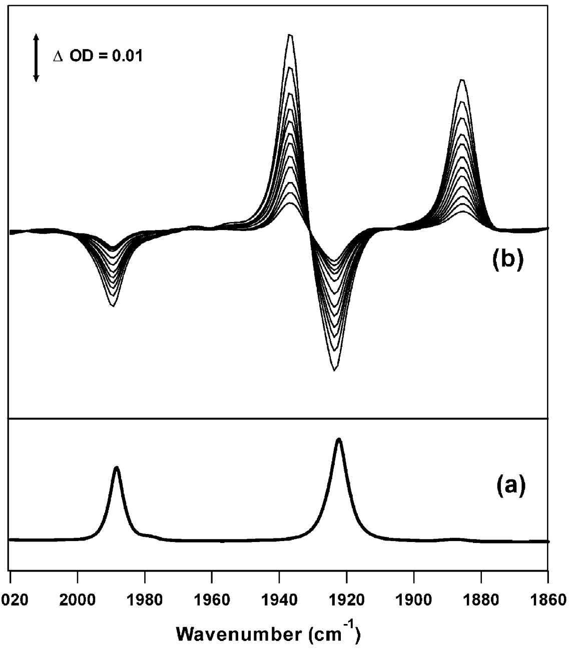

Fig. 6 (a) FTIR spectrum of [Cr(η^6-C_6H_6)$(CO)_3$] (**4**) in scXe (298 K, 1500 psi) in the presence of CO (30 psi). (b) s^2-FTIR overlay spectra of this solution obtained between 1.0 and 2.1 µs after 355 nm UV excitation at intervals of 0.1 µs.

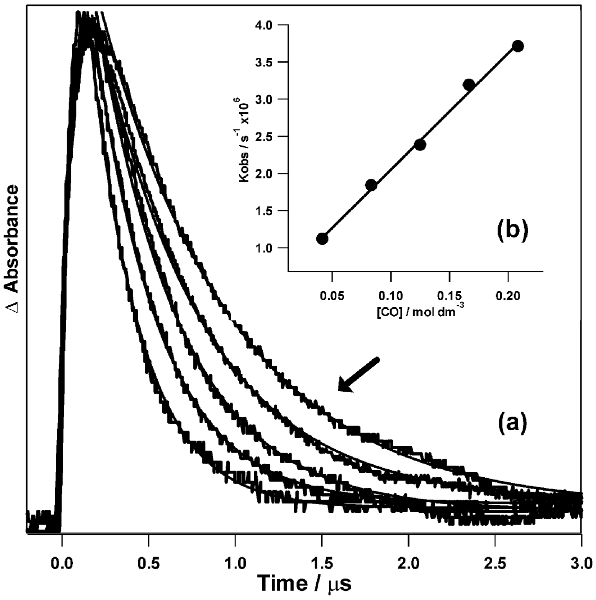

Fig. 7 (a) Point-by-point TRIR kinetic traces obtained following 355 nm excitation of **4** in scXe (1500 psi) at room temperature in the presence of increasing CO pressures. Arrow indicates direction of increasing CO pressure. (b) Graph of observed decay rate, k_{obs} (obtained from exponential fits to the data in (a)) *versus* CO concentration. The linear slope yields the second-order rate constant (k_{CO}) for the reaction of [Cr(η^6-C_6H_6)$(CO)_2$Xe] with CO (k_{CO} = 1.6 (±0.2) × 10^7 dm^3 mol^{-1} s^{-1}).

|| It should be noted that extreme caution should be exercised when interpreting the significance of $\Delta S^\ddagger$ values since large errors can be introduced when extrapolating the data to the intercept of the Eyring plot.

Table 2 IR ν(CO) band positions of [Re(η^5-C_5H_5)(CO)$_2$(L)] (L = CO, alkane or noble gas) complexes under different conditions

Complex	Conditions	ν(CO)/cm^{-1}	Ref.
[Re(η^5-C_5H_5)(CO)$_3$]	Nujol (77 K)	2029, 1934	95
[Re(η^5-C_5H_5)(CO)$_3$]	*n*-Heptane (298 K)	2031, 1940	73
[Re(η^5-C_5H_5)(CO)$_3$]	Cyclopentane (298 K)	2031, 1940	71
[Re(η^5-C_5H_5)(CO)$_3$]	*liq*C_2H_6 (298 K)	2036, 1947	This work
[Re(η^5-C_5H_5)(CO)$_3$]	scC_2H_6 (308 K)	2037, 1948	This work
[Re(η^5-C_5H_5)(CO)$_3$]	scXe (298 K)	2035, 1946	73
[Re(η^5-C_5H_5)(CO)$_3$]	scKr (298 K)	2038, 1952	73
[Re(η^5-C_5H_5)(CO)$_2$]	Nujol (77 K)	1947, 1879	95
[Re(η^5-C_5H_5)(CO)$_2$(*n*-C_7H_{16})]	*n*-Heptane (298 K)	1954, 1890	73
[Re(η^5-C_5H_5)(CO)$_2$(C_5H_{10})]	Cyclopentane (298 K)	1951, 1886	71
[Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)]	*liq*C_2H_6 (298 K)	1959, 1896	This work
[Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)]	scC_2H_6 (308 K)	1960, 1897	This work
[Re(η^5-C_5H_5)(CO)$_2$Xe]	scXe (298 K)	1957, 1894	73
[Re(η^5-C_5H_5)(CO)$_2$Kr]	scKr (298 K)	1965, 1903	73

2.2 Organometallic alkane complexes

Another area where TRIR has had a major impact is in the detection of intermediate species in the C–H activation of alkanes. The photochemistry of transition metal complexes that can oxidatively insert into alkane C–H bonds has been the subject of intense study[47,78] since Bergman and Graham independently reported the first direct observation for this process.[79] Infrared spectroscopy is a powerful tool for monitoring the C–H activation mechanisms of metal carbonyls since the positions of the ν(CO) bands offer a direct probe of the oxidation state of the metal centre. It is now well established that σ-bound alkane complexes are intermediates in the photochemical C–H activation of alkanes by transition metal complexes.[70,80]

It is clear that organometallic alkane complexes are of fundamental interest particularly because of their key role as intermediates in the C–H activation process and there are several recent reviews in this area.[70,81,82] Information regarding both the structure and reactivity of alkane complexes is important for a better understanding of the C–H activation process. Hence the isolation of a stable transition metal alkane complex remains an unfulfilled but realistic goal.[81] Unstable organometallic alkane complexes have been known for over 30 years.[63] Although the early matrix isolation experiments permitted the characterisation of these complexes at low temperature, they did not provide the kinetic information needed to quantify their reactivity. In alkane solution the solvation process for [Cr(CO)$_5$] occurs *within the first picosecond* following UV irradiation of [Cr(CO)$_6$].[83] The reactivity of organometallic alkane complexes decreases both *across* and *down* Groups 5, 6 and 7, with [Re(η^5-C_5H_5)(CO)$_2$(*n*-heptane)] reacting 50000 times more slowly than [V(η^5-C_5H_5)(CO)$_3$(*n*-heptane)].[84] The stability of [Re(η^5-C_5H_5)(CO)$_2$(alkane)] is significant and Ball and co-workers[72] have been able to characterise [Re(η^5-C_5H_5)(CO)$_2$(cyclopentane)] at low temperature (~180 K) using ^{1}H NMR spectroscopy. The factors controlling the reactivity of unstable organometallic alkane complexes have been the subject of several investigations.[75,77,85,86]

2.2.1 Formation and reactivity of [Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)].

We have used nanosecond s^2-FTIR and point-by-point TRIR spectroscopy to probe the formation of an organometallic ethane complex in solution at and above room temperature. Fig. 8(a) shows the FTIR spectrum of [Re(η^5-C_5H_5)(CO)$_3$] (**5**) dissolved in liquid C_2H_6 (*liq*C_2H_6) (298 K, 1550 psi) in the presence of CO (30 psi). Fig. 8(b) shows the TRIR spectrum obtained 4 μs after 266 nm excitation of this solution. The parent bands are clearly bleached and a transient with two new ν(CO) bands is produced. These new bands can be assigned to [Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)] by comparison with previous TRIR and matrix isolation studies (see Table 2). The formation of [Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)] under these conditions is reversible. The decay of [Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)] depends linearly on CO concentration,[87] Fig. 8(c). This allows the calculation of the second order rate constant (k_{CO} = 6.9 (±0.5) × 10^3 dm^3 mol^{-1} s^{-1}) for the reaction of [Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)] with CO in *liq*C_2H_6 at room temperature. The k_{CO} value obtained for the reactivity of [Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)] with CO in this experiment can be compared to the rate constants previously obtained for similar complexes in more conventional alkane solvents, Table 3. From these results it is evident that [Re(η^5-C_5H_5)(CO)$_2$(C_5H_{10})] and [Re(η^5-C_5H_5)(CO)$_2$(*n*-C_7H_{16})] are less reactive than the complex with the shorter alkane, [Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)]. This is consistent with previous gas phase studies by Rayner and co-workers,[88,89] who obtained the binding energies for a series of different alkanes to [W(CO)$_5$] using TRIR spectroscopy. They observed an increase in the alkane binding energies from ethane to longer linear alkanes like pentane and hexane. There was no evidence for an interaction between [W(CO)$_5$] and CH_4 in their experiments and they obtained[89] a tungsten–ethane binding energy of 31 (±8) kJ mol^{-1} for [W(CO)$_5$(C_2H_6)]. Theoretical calculations on a series of [W(CO)$_5$(alkane)] complexes have also predicted a trend of increasing bonding energies with increasing alkane size.[90] These investigations into metal alkane interactions suggest that

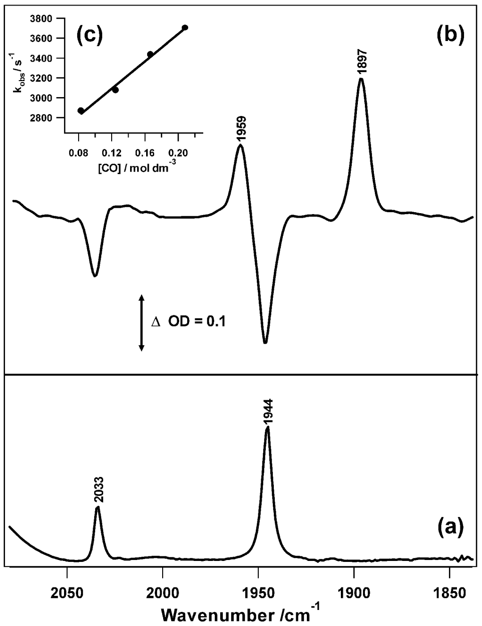

Fig. 8 (a) FTIR spectrum of [Re(η^5-C_5H_5)(CO)$_3$] in liquid C_2H_6 (298 K, 1550 psi) in the presence of CO (30 psi). (b) s^2-FTIR spectrum of this solution obtained 4 μs after 266 nm excitation. (c) Plot of observed rate constant, k_{obs} for the decay of [Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)] *versus* CO concentration, yielding the second order rate constant, k_{CO} for the reaction of [Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)] with CO in liquid C_2H_6 at room temperature.

Table 3 Second order rate constants (k_{CO}) for the reaction of [Re(η^5-C_5H_5)(CO)$_2$(alkane)] complexes with CO at room temperature

Complex	Conditions	k_{CO}/dm^3 mol^{-1} s^{-1}	Ref.
[Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)]	*liq*C_2H_6 (298 K)	6.9 (±0.5) × 10^3	This work
[Re(η^5-C_5H_5)(CO)$_2$(*n*-C_7H_{16})]	*n*-Heptane (298 K)	2.5 (±0.2) × 10^3	71
[Re(η^5-C_5H_5)(CO)$_2$(C_5H_{10})]	Cyclopentane (298 K)	1.1 (±0.2) × 10^3	71

coordination to secondary alkane C–H bonds is stronger than to primary C–H bonds. The results presented in this Perspective may be interpreted by suggesting that the k_{CO} values for the C_2H_6 and *n*-C_7H_{16} complexes differ because *n*-heptane is capable of co-ordinating through a secondary C–H bond while ethane does not possess a secondary C–H bond to co-ordinate with the metal centre. Long and co-workers have identified a different trend in reactivity to these observations.[75,86] They found that changing the length of linear alkanes from *n*-pentane through *n*-heptane to *n*-dodecane resulted in an increase in reactivity of the alkane complex. The difference in reactivity was concluded to be due to differences in activation entropy.

To probe the reactivity of the Re–ethane complex further we have determined the activation parameters for the reaction of [Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)] with CO in supercritical ethane (scC_2H_6).** TRIR experiments were carried out at a range of CO concentrations as a function of temperature. Pseudo first-order conditions were maintained for all experiments, and at each temperature the second order rate constant (k_{CO}) was obtained by a plot of k_{obs} *versus* [CO]. The activation enthalpy ($\Delta H^\ddagger$ = 43 (±2) kJ mol^{-1}) for the reaction of [Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)] with CO in scC_2H_6, obtained from an Eyring plot, can be compared with the activation enthalpies previously measured[71] for [Re(η^5-C_5H_5)(CO)$_2$(*n*-C_7H_{16})] in *n*-heptane ($\Delta H^\ddagger$ = 46 (±2) kJ mol^{-1}) and [Re(η^5-C_5H_5)(CO)$_2$(C_5H_{10})] in cyclopentane ($\Delta H^\ddagger$ = 32 (±2) kJ mol^{-1}). Interpretation of the differences between activation parameters for the reaction of alkane complexes with CO requires careful consideration,[71,77] since the reaction may proceed *via* an associative, associative interchange, dissociative interchange or dissociative mechanism, or by a combination of these pathways. $\Delta H^\ddagger$ values for metal–alkane complexes provide an indication of the metal–alkane bond strength. Photoacoustic calorimetry (PAC) is a useful method for measuring metal–alkane bond dissociation energies (BDEs) in metal carbonyl complexes. The accuracy of PAC measurements relies on a precise knowledge of the M–CO BDE. Although no Re–alkane complexes have been measured using PAC, early experiments by Yang and co-workers[91] estimated the Mn–heptane BDE in [Mn(η^5-C_5H_5)(CO)$_2$(*n*-C_7H_{16})] to be 33–38 kJ mol^{-1}. Burkey independently obtained[92] a Mn–heptane BDE of 42 kJ mol^{-1} for the same complex. PAC has also been used to determine the M–heptane BDEs in [Cr(CO)$_5$(*n*-C_7H_{16})] (BDE = 50 (±5) kJ mol^{-1})[86] and [W(CO)$_5$(*n*-C_7H_{16})] (BDE = 62.8 kJ mol^{-1}).[93] The measured values of $\Delta H^\ddagger$ for [M(η^5-C_5H_5)(CO)$_2$-(*n*-C_7H_{16})] (M = Mn and Re)[77] are not a good estimate of the M–heptane BDEs, suggesting that these complexes react with CO *via* an associative or associative interchange mechanism. The activation enthalpy determined here is a lower limit for the Re–C_2H_6 BDE. Further study is required to quantify a more precise value for this bond energy. This could possibly be achieved by the recently developed technique of high-pressure PAC.[94]

Conclusions

In this Perspective we have shown how TRIR spectroscopy can be used to probe the nature of the excited states of coordination compounds. As an example, 400 nm excitation of *fac*-[ReCl-(CO)$_3$(dppz-Cl$_2$)] (**3**) in CH_3CN solution generates a MLCT excited state involving the phz-part of the dppz ligand, which was assigned from a characteristic shift of the *ν*(CO) vibrations from the ground to excited state in the ps TRIR spectrum. However, the charged complexes, *fac*-[Re(CO)$_3$(dppz-Cl$_2$)(py)]$^+$ (**1**) and *fac*-[Re(CO)$_3$(dppz-Cl$_2$)(4-Me$_2$N-py)]$^+$ (**2**) were shown to possess low-lying IL ππ*(dppz) excited states. For **2**, the increased electron donating ability of the 4-Me$_2$N-py ligand led to the production of an equilibrium between the MLCT (phen) and IL ππ*(dppz) excited states. In addition, we successfully used both ns point-by-point TRIR and s^2-FTIR to probe the formation and reactivity of organometallic noble gas and alkane complexes in supercritical fluids and high-pressure liquid solution. The reactivitiy of [Cr(η^6-C_6H_6)(CO)$_2$Xe] in scXe and [Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)] in liquid and scC_2H_6 with CO was investigated. We found that both transient species react with CO to reform the parent tricarbonyl complexes **4** and **5**, respectively. [Cr(η^6-C_6H_6)(CO)$_2$Xe] was found to be one of the most unstable transition metal Xe complexes that has been reported and [Re(η^5-C_5H_5)(CO)$_2$(C_2H_6)] reacted approx. three to six times faster with CO than the corresponding *n*-heptane and cyclopentane complexes respectively, although the measured activation enthalpy was not significantly higher than for the cyclopentane complex. Investigations are currently underway to find new transition metal alkane and noble gas complexes, which exhibit even higher stability.

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