

A time-resolved infrared vibrational spectroscopic study of the photo-dynamics of crystalline materials

K L Ronayne, M Towrie, A W Parker

Central Laser Facility, CCLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxon., OX11 0QX, UK

K F Bowes

Department of Chemistry, University of Cambridge, Lensfield Rd, Cambridge, CB2 1EW, UK

P R Raithby

Department of Chemistry, University of Bath, Claverton Down, Bath, Avon, BA2 7AY, UK

Main contact email address: k.l.ronayne@rl.ac.uk

Introduction

Solid materials in crystalline and amorphous states are currently finding applications in molecular photonic devices such as LEDs and displays. Development and optimisation of these devices requires detailed knowledge of the electronically excited states of the materials in the solid state. Vibrational spectroscopic techniques such as TR³ and TRIR have been extensively used to probe photophysical and photochemical properties of excited states in the solution phase. However, they have only rarely been applied to solids due to experimental factors mainly relating to photo-degradation and the relatively low sensitivity of the instruments employed. In this light we have recently developed methods to employ ps-TRIR to investigate the excited state and chemical intermediates within the solid state.

The application of time-resolved infra-red spectroscopic techniques to studying the excited state dynamics of metal carbonyl species has been comprehensively demonstrated over the last decades¹. However, in the main, these studies have been limited to the behaviour of these complexes in solution phase and have not attempted to examine the photophysical properties of the complex after undergoing excitation in the solid. TRIR techniques have been used to examine the electron injection process of TiO₂ films into ruthenium polypyridyl complexes using a carboxyl labelled diimine ligand to produce a spectroscopic signature².

In this work, we compare the behaviour of three different types of system in the solution phase and in the solid state. Initial studies focussed on [Re(CO)₃bpyCl] as the MLCT state has been widely studied in solution phase and in glass matrices. Several iridium acac (acetylacetonate) based complexes, see Figure 1 which are of interest for display screen technology³ were examined as were a series of ESIPT (excited state intramolecular proton transfer) systems with illustrative data shown in a separate contribution⁴.

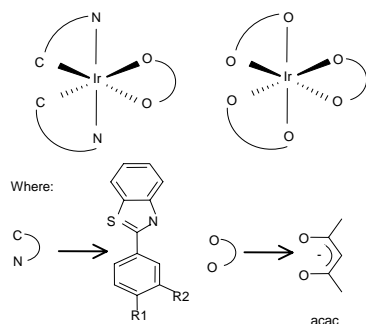


Figure 1. Structural representations of the iridium complexes.

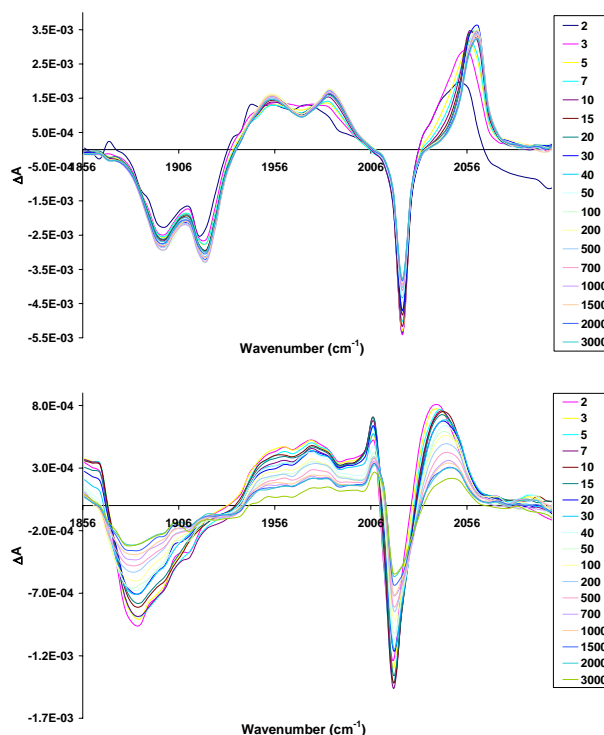


Figure 2. TRIR spectra of [Re(CO)₃bpyCl] in a) dichloromethane and b) thin film. All delays are in ps.

Experimental

Solution samples of [Re(CO)₃bpyCl] in dichloromethane, the iridium complexes in dichloroethane and ESIPT complexes in chloroform were approximately 10⁻⁴ M. Solid state samples were prepared by spin coating a saturated solution of the complex in dichloromethane onto a CaF₂ plate at 1600 rpm for 20 s. The PIRATE apparatus which has been extensively described elsewhere^{5,6} was used to interrogate the photophysical decay of the samples over the ps to μs regime.

Results and Discussion

Figure 2a shows the spectra recorded for [Re(CO)₃bpyCl] (where bpy = 2,2'-bipyridine) in solution which indicate the population of an initially vibrationally hot ³MLCT state with a lifetime of ~1 μs in accordance with previously published studies on this complex⁷. In the thin film, Figure 2b, the ground state carbonyl stretching bands are slightly downshifted relative to the solution phase spectrum and the low frequency a'' and a'(2) vibrations are no longer resolvable. The presence of transient bands at 2042, 1974 and 1961 cm⁻¹ indicate population of the ³MLCT although these are also slightly red-shifted with respect to the characteristic triplet bands of the excited state in solution. The lifetime of the state is also significantly reduced, to ~650 ps and the appearance of additional transient features at 2007 cm⁻¹ and 1860 cm⁻¹ are indicative of population of a

second excited state which has been assigned as $^3\pi-\pi^*$ in origin. In solution, the $^3\pi-\pi^*$ state is not accessible. However, in the thin film the change in local environment appears to lower the energy resulting in population of this state. This is probably due to crystal lattice effects which hinder the degree of Re \rightarrow bpy charge transfer. The degree of population of the two triplet states was found to be strongly pump power dependent with the $^3\pi-\pi^*$ becoming more populated at higher laser fluence. Investigations into the packing of the [Re(CO)₃bpyCl] crystal lattice are underway to further rationalize this hypothesis.

As nujol mulls are often employed in FTIR studies of solid state samples, transient spectra of the complex in this medium were also recorded. These differed from both the solution and solid state data presented above but on closer investigation, it proved difficult to obtain reproducible data as the shape and position of the observed spectral features seemed to vary from sample to sample. This originated from saturated absorption of the IR probe within the suspended crystals.

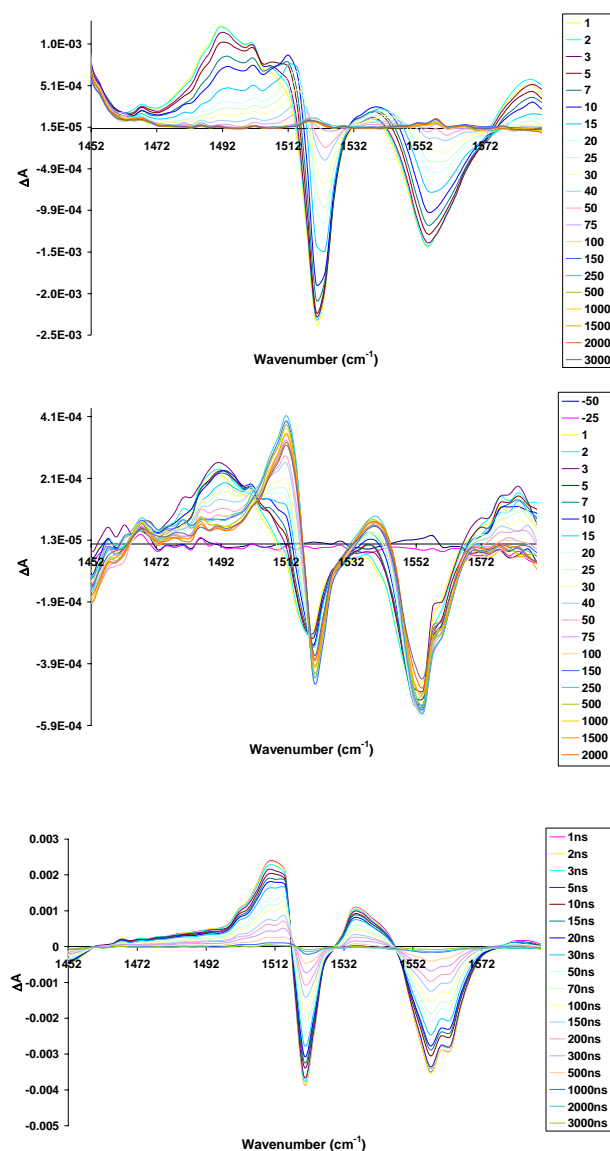


Figure 3. TRIR spectra of [Ir(acac)₃] in a) solution and thin film recorded in b) ps regime and c) ns regime.

In contrast to the behaviour of the rhenium carbonyl system, the thin film sample of the tris acac iridium complex was found to exhibit longer excited states than for the solution phase measurements, whilst in the other iridium compounds the lifetimes in solution and solid state were comparable (Figure 3).

On 400 nm excitation of the thin film of Ir(acac)₃ strong bleaching of the ground state carbonyl stretching frequencies at 1520, 1554 and 1560 cm⁻¹ is observed. This is accompanied by the appearance of transient features at both higher and lower frequencies. The broad bands at 1490 and 1583 cm⁻¹ have a relatively short lifetime \sim 40 ps with longer lived bands at 1512 and 1540 cm⁻¹ growing in over a similar timescale. At longer (ns) times, these peaks become more sharply defined, decaying over a microsecond timescale back to the ground state. It therefore appears that there are two excited states populated, a short-lived state which is largely insensitive to environment and a longer-lived one which is stabilised in the solid state. Luminescence and computational studies are underway on this complex in order to provide a good working model for this system.

Substitution of two acac ligands to a bis-benzothiazole complex results in changes in the nature of the lowest excited state of the system. Luminescence studies have shown that the lowest lying MLCT is to the benzothiazole ligand and that the acac is not directly involved in the emissive state⁸). Solid state and solution phase TRIR spectra recorded for these complexes, using acac as a reporter ligand, indicate population of a single excited state in all cases on the timescales examined. Interpretation of the data is non-trivial due to mixing of vibrational modes therefore DFT methods will be employed to aid mode assignment.

Conclusions

We have demonstrated a method for the interrogation of solid state samples by means of TRIR. As expected, the dynamics of excited state decay were found to be very different in the solid state compared with traditional solution phase measurements. The results illustrate the usefulness of TRIR as a probe for the photo-dynamic studies of in crystalline materials that would be complimented if used in conjunction with other ultrafast pump-probe techniques such as Raman, UV-Vis absorption, fluorescence and in the future X-Ray diffraction.

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