

# STEP-SCAN FOURIER TRANSFORM INFRARED ABSORPTION DIFFERENCE TIME-RESOLVED SPECTROSCOPY STUDIES OF EXCITED STATE DECAY KINETICS AND ELECTRONIC STRUCTURE OF LOW-SPIN $d^6$ TRANSITION METAL POLYPYRIDINE COMPLEXES WITH 10 NANOSECOND TIME RESOLUTION

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Step-scan Fourier transform absorption difference time-resolved spectroscopy ( $S^2$ FTIR  $\Delta A$  TRS) has been used to collect mid-IR time-resolved infrared spectra of the transient electronic excited states of polypyridine transition metal complexes with 10 ns time resolution. The time-resolved data can be used for kinetic analysis or to generate “snapshots” of the lowest lying excited state. Shifts of vibrational bands in the excited state relative to the ground state can be used to infer significant details of the electronic structure of the excited state. The multiplex advantage of the FTIR technique allows a wide variety of vibrational bands to be analyzed for this purpose. In the example illustrated, the shift of the ester  $\nu(\text{CO})$  band in  $\{\text{Ru}(\text{bpy})[4,4'-(\text{COOEt})_2\text{bpy}]_2\}^{2+}$  compared to those in related complexes has been used to address the question of electron delocalization in the excited state.

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## INTRODUCTION

Time-resolved vibrational spectroscopy has found wide application in the study of biological and chemical excited states and transient intermediates because of the detailed structural information available in the vibrational spectrum [1–6]. Time-resolved vibrational techniques can be loosely grouped into three categories: techniques involving upconversion of the vibrational information into the UV/visible region [1–2] (including Raman and vibronic spectroscopy, as well as various non-linear processes), infrared emission spectroscopy [3], and direct absorption difference methods with IR detection [4–6].

In the study of the transient photoexcited states of inorganic and organometallic compounds, time-resolved resonance Raman (TR<sup>3</sup>) has been extensively and effectively exploited [2]. However, due to the need to access non-resonance-enhanced modes and to avoid photochemical degradation problems associated with the TR<sup>3</sup> technique, there has been a growing interest in direct absorption difference methods. The techniques used for these studies have included tunable, frequency-shifted laser methods, tunable gas phase and solid state infrared lasers, dispersive spectrometry and interferometry (FTIR). The laser methods are generally superior in sensitivity and in time and spectral resolution, and both laser and dispersive approaches have some advantages when only single wavelength or narrow bandwidth measurements are required [4]. Pump/probe laser methods with time resolution of less than 300 fs are widely applied [4c], and dispersive measurements with 10 ns resolution have also been reported [7]. However, when broad spectral bandwidth is desired in time-resolved absorption difference infrared measurements, the spectral multiplexing of FTIR is an important advantage. Among the several approaches to time-resolved FTIR measurements, the use of the step-scan mode currently appears to be the most flexible, particularly (with the present state-of-the-art in mid-IR detectors) for time resolution down to ca. 10 ns [5, 6, 8–10].

In the step-scan mode of FTIR the retardation of the interferometer is changed incrementally, and data are collected while the retardation is held constant. The resulting interferogram is a function of path difference, but not of time (in contrast to the intrinsic time dependence of the interferogram obtained with a conventional constant velocity, continuous-scan, interferometer). In other words, the spectral multiplexing is removed from the temporal domain; there are effectively no Fourier frequencies. In the step-scan FTIR absorption difference time-resolved spectroscopy ( $S^2$  FTIR  $\Delta A$  TRS) experiment, a perturbation is applied to the sample at each retardation point, and the resulting change in the interferogram intensity is monitored as a function of time, either by use of a gated integrator or transient digitizer. The perturbation is repeated and data are coadded to achieve the desired signal-to-noise ratio (S/N) before moving to the next point. (If the response is not perfectly reversible, a flow cell or equivalent sampling may be necessary.) By AC coupling the detector, only the change in the interferogram is recorded, and as a result, the dynamic range of the experiment is maximized.

The resulting data are then sorted by time to produce a series of time-resolved interferograms, which are then transformed and converted into a stack of time-resolved absorption difference spectra. The limit of time resolution is determined by the length of the perturbation pulse, the rise time of the detector/preamplifier, and the resolution of the digitizer (or width of the gate). Current state-of-the-art performance is approximately 10 ns. The technique itself puts no restrictions on time resolution or on repetition rate. The data collection time for a specified S/N, free spectral range, and spectral resolution is determined by the magnitude of  $\Delta A$  and the available IR photon flux.

## EXPERIMENTAL

The transient data reported here were measured on a step-scan modified Bruker IFS88 spectrometer with a standard globar source and dry air purge. The samples were dissolved in  $\text{CH}_3\text{CN}$  to give an absorbance between 0.2 and 0.6 in a  $250\ \mu\text{m}$  pathlength for the vibrational bands analyzed. Samples were deoxygenated by sparging

with argon for 20 minutes and were loaded into a CaF<sub>2</sub>-windowed cell by syringe under argon.

The samples were excited by use of the third harmonic (355 nm, 10 ns, 10 Hz, 3 mJ/pulse) from a Q-switched Quanta-Ray DCR-1 Nd:YAG laser. The laser excitation and data acquisition were synchronized with a Stanford Research Model DG535 pulse generator. An AC/DC-coupled photovoltaic Kolmar Technologies mercury cadmium telluride (MCT) detector with a 50 MHz preamplifier and an effective rise time of  $\sim 20$  ns was used to sample the transmitted infrared signal. The AC signal was sent through a Stanford Research Model SR445 preamplifier ( $\times 250$ ) before being directed to a 486 personal computer equipped with 100 MHz PAD82 transient digitizer. The DC signal was sent directly to the digitizer to be used for phase correction of the AC signal. The data were processed using the standard Bruker Opus software.

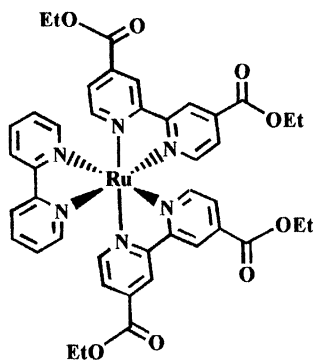
The spectral window observed was limited to 1150 to 2250 cm<sup>-1</sup> by the CaF<sub>2</sub> cell windows and a germanium low-pass filter placed over the detector window. The interferogram response before and after each laser flash was digitized at 10 ns intervals, and in a typical experiment, data from 100–200 laser flashes were averaged at each point. Data collection time was ca. 30 min. The  $\Delta A$  spectra were calculated from the single beam  $\Delta I$  transforms by the relation,  $\Delta A(\nu, t) = -\log[1 + \Delta I(\nu, t)/I(\nu)]$ , where  $I(\nu)$  is the detected intensity before laser excitation and  $\Delta I(\nu, t)$  is the change in intensity at time  $t$ . For  $\Delta A$  “snapshots”, several post-excitation time slices were averaged for greater S/N. Although one 30 min. experiment usually yields adequate band shift data, further improvement in S/N for a full kinetic analysis is achieved by averaging several experiments. Spectroscopic grade CH<sub>3</sub>CN was purchased from Burdick and Jackson and was used without further purification. The low-spin metal complexes were synthesized by literature methods and, in the case of the example presented, purified as the PF<sub>6</sub><sup>-</sup> salt.

## RESULTS AND DISCUSSION

By use of the techniques described above, the transient excited state spectra of numerous low-spin d<sup>6</sup> transition metal polypyridine

complexes of interest in catalytic and photovoltaic conversion reactions have been measured with 10 ns time resolution [8–10]. For most of these complexes, the data reveal the lowest, and longest lived excited state, which may be either a  $d\pi-p\pi^*$  metal-to-ligand charge transfer (MLCT) state or a ligand-localized  $p\pi-p\pi^*$  state. However, in cases where states of both types are close in energy, both may be observed [11]. The differences in vibrational band energies between the ground and excited states can provide valuable information on the nature of the excitation process, the identity of the lowest excited state, and its electronic structure.

While excited state kinetic data are often easily obtained for these compounds from electronic emission spectra, in the case of complex excited state processes, the time-resolved infrared provides more detailed and specific data. The multiplex advantage of FTIR and the flexibility of the step-scan mode allow simultaneous monitoring of vibrations of classical “reporter” ligands such as CO and  $CN^-$ , as well as the vibrations of other functional groups in these complexes. For purposes of illustration, data from a complex currently under study are presented here.



(1)

Figure 1 shows part of a 10 ns stack plot of time-resolved  $\Delta A$  spectra for  $\{Ru(bpy)[4,4'-(COOEt)_2bpy]_2\}^{2+}$  (1) (bpy = 2,2'-bipyridine). The initial time slices are pre-excitation, while the later spectra

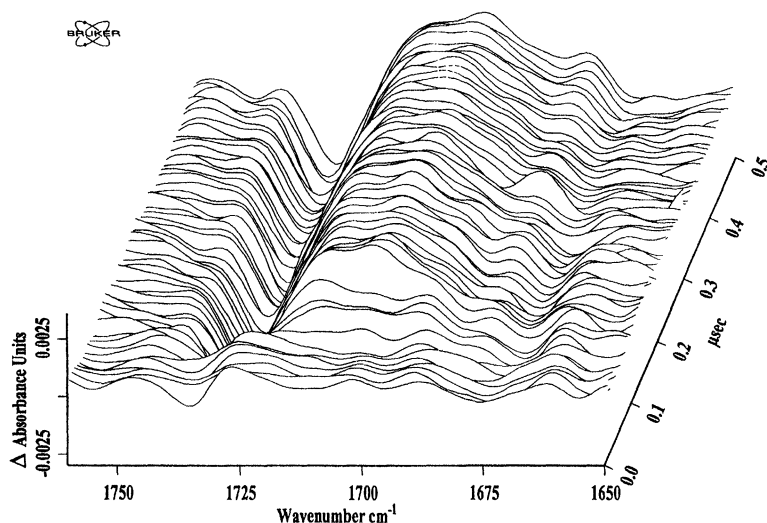


FIGURE 1 Stack plot of  $S^2$  FTIR  $\Delta A$  TR spectra of  $\{\text{Ru}(\text{bpy})[4,4'-(\text{COOEt})_2\text{bpy}]_2\}^{2+}$  in the ester  $\nu(\text{CO})$  stretching region before and after 355 nm laser excitation. The time resolution shown is 10 ns, and the data were obtained with 30 minutes of data collection.

correspond to the early stages of decay of the lowest lying excited state, a metal-to-ligand charge transfer (MLCT) state, following the laser excitation. The prominent, negative  $\Delta A$  feature is due to the bleaching of the ground state ester  $\nu(\text{CO})$  stretch, and the positive band centered  $26\text{ cm}^{-1}$  to lower energy is the corresponding band in the excited state.

Collection of 10 ns time-resolved spectra over the entire excited state lifetime provides the information necessary to determine decay kinetics and shows that the band at  $1705\text{ cm}^{-1}$  decays with the same  $t_{1/2}$  as the ground state bleach at  $1731\text{ cm}^{-1}$ . Figure 2 shows a  $\Delta A$  “snapshot” of (1) calculated by averaging several of the post-excitation time slices taken from the excited state decay spectra in Figure 1.

First, the low-energy shift of the ester  $\nu(\text{CO})$  band of the bis-diester complex (1) illustrated here is consistent with the participation of the  $\pi^*$  orbital of the ester CO in the receiving orbital of the MLCT excited state. Secondly, the  $26\text{ cm}^{-1}$  shift of the ester  $\nu(\text{CO})$  relative to its value in the ground state, and the fact that this shift is the same as observed in the analogous mono-diester complex [10], are strong indications of

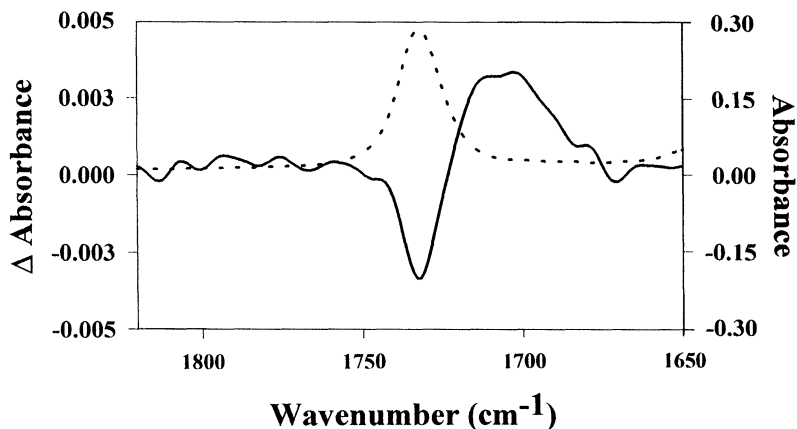


FIGURE 2 Absorption difference "snapshot" spectra (solid line) of the lowest lying excited state, a metal-to-ligand charge transfer state, in  $\{\text{Ru}(\text{bpy})[4,4'-(\text{COOEt})_2\text{bpy}]_2\}^{2+}$ . Frequency shift data for the excited state bands are determined by comparison with their ground state absorptions (dotted line).

the localization of the excited electron on only one of the ester-substituted bipyridine ligands in the *bis*-diester complex.

This use of vibrational band shifts for bands not subject to resonant enhancement (as in a  $\text{TR}^3$  experiment) to infer electronic structure in a transient excited state is an indication of the power of IR  $\Delta A$  TRS, and of  $\text{S}^2$  FTIR  $\Delta A$  TRS in particular. The additional abilities of  $\text{S}^2$  FTIR  $\Delta A$  TRS to simultaneously monitor the intensities of widely separated bands in transient states with lifetimes as short as 30 ns has also been illustrated [8–10]. With shorter pulse excitation sources and as faster mid-IR detectors and digitization electronics and brighter infrared sources become available,  $\text{S}^2$  FTIR  $\Delta A$  TRS promises to push the time resolution barrier into the sub-nanosecond range.

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