Ruthenium trisbipyridine as a candidate for gas-phase spectroscopic studies in a Fourier transform mass spectrometer

Jill R. Scott^{a,*}, Jason E. Ham^b, Bill Durham^b and Paul L. Tremblay^a

^a *Idaho National Engineering and Environmental Laboratory (INEEL), Idaho Falls, ID 83415, USA*

^b *Department of Chemistry & Biochemistry, University of Arkansas, Fayetteville, AR 72701, USA*

Abstract. Metal polypyridines are excellent candidates for gas-phase optical experiments where their intrinsic properties can be studied without complications due to the presence of solvent. The fluorescence lifetimes of $[\text{Ru}(\text{bpy})_3]^{1+}$ trapped in an optical detection cell within a Fourier transform mass spectrometer were obtained using matrix-assisted laser desorption/ionization to generate the ions with either 2,5-dihydroxybenzoic acid (DHB) or sinapinic acid (SA) as matrix. All transients acquired, whether using DHB or SA for ion generation, were best described as approximately exponential decays. The rate constant for transients derived using DHB as matrix was $4 \times 10^7 \text{ s}^{-1}$, while the rate constant using SA was $1 \times 10^7 \text{ s}^{-1}$. Some suggestions of multiple exponential decay were evident although limited by the quality of the signals. Photodissociation experiments revealed that $[\text{Ru}(\text{bpy})_3]^{1+}$ generated using DHB can decompose to $[\text{Ru}(\text{bpy})_2]^{1+}$, whereas ions generated using SA showed no decomposition. Comparison of the mass spectra with the fluorescence lifetimes illustrates the promise of incorporating optical detection with trapped ion mass spectrometry techniques.

1. Introduction

Metal–polypyridine complexes have long been employed to study fundamentals of energy and electron transfer reactions in solution. For example, they have been used to investigate pathways [1], reorganizational energy [2], and electronic coupling in metallo protein systems [3]. In condensed-phase studies, ruthenium (II) trisbipyridine is one of the most exploited metal polypyridines because of properties such as structural rigidity and stability in multiple solvents [4], a relatively high quantum efficiency [5], an excited-state lifetime that does not change significantly with pressure [6] and electronic properties that vary linearly with magnetic fields [7,8]. In view of these properties, ruthenium trisbipyridine was chosen for optical studies in the gas-phase environment of a Fourier transform mass spectrometer (FTMS).

For many years, physicists have exploited the advantages of Penning traps to study the optical properties of atomic ions in the gas-phase [9]. For example, Drullinger et al. [10] observed the first laser-induced fluorescence (LIF) spectra of Mg^+ ion in 1980. They obtained a high resolution fluorescence spectrum of $<100 \text{ Mg}^+$ ions with an overall detection efficiency of 3×10^{-3} . LIF spectroscopy has since been extended to small molecular ions such as N_2^+ [11], CO^+ [12], and CO_2^{1+} [13]. Marshall and co-workers [14] reported LIF spectra for C_6H_6^+ trapped in an FTMS. In 2001, we [15] first reported

*Corresponding author: Jill R. Scott, INEEL, 2525 N. Fremont Ave., MS 2208, Idaho Falls, ID 83415, USA. E-mail: scotjr@inel.gov.

emission lifetimes for $[\text{Ru}(\text{bpy})_3]^{1+}$. Fluorescent lifetime experiments offer the advantage that the light from all wavelengths emitted contributes to the overall signal. Recently, Cage et al. [16] reported the lifetimes for $\text{C}_6\text{F}_5\text{H}^+$ and $\text{C}_6\text{F}_3\text{H}_3^+$ in an FTMS with results that compare favorably with those previously reported for these species in the gas-phase [17].

In this paper we report the emission lifetime studies of $[\text{Ru}(\text{bpy})_3]^{1+}$ using a modified version of our original optical detection system for an FTMS [15]. In light of our recent work [18] that indicated the stability of $[\text{Ru}(\text{bpy})_3]^{1+}$ generated by matrix-assisted laser desorption/ionization (MALDI) varies according to the matrix used, we compare the results from experiments using DHB or SA as matrix.

2. Experimental

2.1. Materials

$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (bpy = bipyridine) was prepared according to standard procedures [19]. $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ was prepared from the PF_6^- salt by anion exchange using Dowex-1 (Chloride form) exchange resin (Sigma, St. Louis, MO). Acetonitrile (HPLC grade) was purchased from Aldrich Chemical (Milwaukee, WI). Matrices 3,5-dimethoxy-4-hydroxycinnamic, commonly known as sinapinic acid (SA), and 2,5-dihydroxybenzoic acid (DHB) were purchased from Aldrich Chemical (Milwaukee, WI).

2.2. Sample preparation

$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ was dissolved in acetonitrile. Either sinapinic acid or 2,5-dihydroxybenzoic acid was added to produce a molar ratio of 1000:1 (matrix:analyte). A saturated solution of the matrix was prepared and aerosprayed onto 316 SS probe tips (19 mm diam.) as a base coat using the modified aerospray apparatus described in the literature [18]. The MALDI sample was then aerosprayed on top of the base coat.

2.3. FTMS instrumentation

The FTMS is a laboratory-built design, which has been described previously [20–22]. Briefly, the system incorporates a 7 T Oxford (Oxford, England) superconducting magnet, vacuum system, and Odyssey control and data acquisition system (Finnigan FT/MS, Bremen, Germany). Traditionally, the Finnigan electronics only provide trapping potentials of ± 10 V. To increase the applied voltages, a high voltage direct current amplifier was added to apply $13.5\times$ the voltage specified in the Odyssey software to the trap plates. A Nd:YAG laser (Continuum, Santa Clara, CA) with a 6 ns pulsewidth operating at 355 nm equipped with an external laser scanning mechanism is used for both laser desorption and optical excitation of the ions [20]. Laser fluence was 4×10^5 W for both sample desorption using a 10 μm diameter spot and optical excitation using a beam width of 1.2 cm. The base pressure of the FTMS was 7×10^{-9} Torr. The system was externally calibrated using sodium-attached polyethylene glycol 1000.

2.4. ICR and optical cells

The current FTMS cell design is composed of two regions as illustrated in Fig. 1. The first region consists of a cubic ion cyclotron resonance (ICR) cell equipped with trap plates composed of 95%

Fig. 1. Schematic of combined ICR and optical detection cells showing setup during (A) desorption and isolation events and (B) fluorescence lifetime measurement. Trap plates are labeled as 1–5.

transmissive electroformed wire mesh, which has been described in the literature [20]. Ions are desorbed from the sample by a focused laser pulse and then trapped using the ICR cell. Ions of interest can then be isolated in the ICR cell. Subsequently, the desired ions are transferred into the second region for optical detection. The focusing lens is then moved out of the way by a rod mechanism, which is actuated by a TTL pulse. The trapped ions are then excited with a broad laser beam through a 1-inch quartz window. The light emitted from the ions exits a second quartz window and is then transferred to the photomultiplier tube (PMT) via the optical detection system. The two separate vacuum housing windows are necessary to avoid the light scattering within the quartz window caused by the laser beam passing through, which would interfere with detection of the fluorescent light from the ions.

2.5. Optical detection

The light collection system consists of an ellipsoidal mirror coupled via a 1/4-inch vacuum UV window to a liquid light guide (Model 77637, Oriel, Stratford, CT) as illustrated in Fig. 1. The light guide passes the light through a 480 nm low pass filter into a gated photomultiplier tube (PMT Model R928, Hamamatsu, Bridgewater, NJ) using a model S502R power supply (Products for Research, Danvers, MA) and a model 9650A delay generator (EG&G Princeton Applied Research, Oak Ridge, TN). The collection efficiency with the light guide alone is limited by the angle subtended by the ion cloud (~ 0.25 inches, 6.35 mm diam.) at the cloud to fiber distance of 118 mm or $\sim 9^\circ$ (solid angle) of the 4π (720°) available. The ellipsoidal reflector captures an additional 494° , which is 70% of the light available as compared to 1.25% if only the light guide was used. This represents an improvement by a factor of 55. The losses through the air-quartz interfaces [7] for the rest of the light gathering elements result in a direct loss of 28%, leaving the system with an improvement of $15\times$ over that of the light guide alone. The PMT has a gain of $\sim 10^7$ and a quantum efficiency of $\sim 10\%$, giving an overall detection efficiency

of $\sim 7\%$. The signal from the PMT was connected through a fast amplifier (Model SR445, Stanford Research Systems, Sunnyvale, CA) to a digital oscilloscope (Model 7200A, LeCroy, Chestnut Ridge, NY) interfaced to a PC through a GPIB communications card (National Instruments, Austin, TX). For each transient, 2000 data points over $2\ \mu\text{s}$ were collected. The timing of the optical detection utilized a variable beam splitter to send part of laser beam to a photodiode (Model ET-2016, Electro-Optics Technology, Traverse City, MI). The interface and data analysis software was provided by the Durham research group, which has been successfully used for solution laser flash photolysis experiments [23].

The limits of detection for the optical system are dependent on the minimum signal that can be detected. For a conservative estimate, a detectable signal is defined as having a signal-to-noise ratio (S/N) of ~ 3 . Multiple experiments have shown that a signal of 10 mV is the smallest signal discernable above the noise with the current apparatus. An exponential transient with a maximum amplitude of 10 mV and a lifetime of 400 ns measured with an oscilloscope with a 50 ohm input impedance corresponds to a total charge from all electrons detected at the PMT anode of $8 \times 10^{-11}\ \text{C}$ or 5×10^8 electrons. Using the R928 photomultiplier with a gain of 1×10^7 and a quantum efficiency of 0.1, the minimum detection limit is 500 photons. The total number of photons detected for each optical transient was determined by integrating the area under the curve using the trapezoidal rule in Origin 6.0 (Microcal, Northampton, MA).

2.6. FTMS sequence of events and parameters

During laser desorption, the sample (Fig. 1) was located 0.5 cm from trap plate #1 and the focusing lens was along the z-axis. The sample was then moved approximately 0.5 m from trap plate #1 and the lens removed from the optical path for the remainder of the experiment. Initially, the trap plates were at zero potential, then trap plates #2 and #3 were raised to +6 V, 0.5 s after the desorption event. Ions not of interest were radially swept from the cell using SWIFT [24] excitation at a radius of 2.3 cm for complete ejection. The ions present in the cell were initially interrogated using low resolution FTMS parameters. A chirp excitation over the range of 50 to 800 kHz was applied for the pre-optical detection to ensure that all unwanted ions had been ejected. After a delay of 0.6 ms, the ions were detected in direct mode using 64 K data points. Data were then baseline corrected, Hamming apodized, zero filled, and Fourier transformed to produce the mass spectra. A crude, but conservative approximation using the signal-to-noise ratio and estimated limit of detection for an FTMS [25], suggests that the number of ions initially in the cell was on the order of 10^5 .

The ions were then transferred into the optical cell by raising the potential on trap plate #1 (Fig. 1) to +130 V while the potential on trap plate #5 was raised to +70 V. Trap plates #4 and #5 were then raised to +120 V to provide the deep potential well centered a focus of the ellipsoidal reflector. It is estimated that there is a loss of $\sim 50\%$ of the ions during the transfer resulting in $\sim 10^4$ ions in the optical cell during detection. Potentials of +27 V and -27 V were applied to trap plates #1 and #2, respectively, during the optical detection event to prevent any stray ions in the vacuum chamber from entering the optical cell. The ion cloud was then excited by a broad laser beam (1.2 cm diam.) operating at a rate of 10 Hz. Unless specified otherwise, 9 emission transients were acquired and averaged using the digital oscilloscope software. After optical detection, the ions were then transferred back to the ICR cell by applying voltages of +135 V and +70 V on trap plates #5 and #1, respectively, while all other trap plates were at a potential of 0 V. This transfer phase also resulted in a loss of $\sim 50\%$ of the ions. For the final FTMS detection, a potential of +1 V was applied to both trap plates #2 and #3 while all other trap plates were set to a potential of 0 V. A chirp excitation over the range of 50 to 800 kHz with a $360\ \text{Hz}/\mu\text{s}$

rate was applied. After a delay of 0.6 ms, the ions were detected in direct mode using 256 K data points. Data were then baseline corrected, Hamming apodized, zero filled, and Fourier transformed to produce the mass spectra. All FTMS spectra were recorded in the positive mode. At the end of the experiment, the cell is quenched of all ions. Pressure during analysis was 5×10^{-8} Torr, which is higher than the base pressure because of the neutrals formed during the MALDI events.

3. Results

In an attempt to guarantee that enough fluorophores were present for optical detection, parameters were adjusted to collect as many ions as possible in the ICR cell (Fig. 1). After unwanted ions were radially swept from the cell, the ions left were briefly examined to ensure that only isotopes of $[\text{Ru}(\text{bpy})_3]^{1+}$ centered at $m/z \sim 570$ remained. The mass spectrum produced (Fig. 2A) has very poor m/z resolution primarily because of the space to charge effects due to the excessive number of ions present [26,27]; therefore, it is not possible to observe the isotope distribution as is possible with fewer ions present in the cell (Fig. 2B). While the ions were still trapped in the ICR cell, a baseline emission measurement was made (Fig. 3A) to assess that the optical detection cell was quiet and no signal was observed in the absence of the selected ions. The ions were then shuttled to the optical detection cell (Fig. 1) with a transfer efficiency of $\sim 50\%$.

In the optical detection cell, the ions were excited by a broad laser beam created by moving the focusing lens out of the z-axis (Fig. 1B). Light emitted from those ions centered around one focus of the ellipsoidal reflector was transmitted to the other focus, which is located within the collection cone of the liquid light guide with the assistance of the refractive index of a quartz window in the vacuum chamber (Fig. 1). The emission transients recorded for $[\text{Ru}(\text{bpy})_3]^{1+}$ generated with matrices DHB and SA vary significantly in intensity and rate of decay as illustrated in Figs 3B and 3C, respectively. The transients in Figs 3B and 3C were the best transients acquired for experiments using DHB and SA, respectively. Both transients can be best described as approximately exponential. The rate constant obtained with $[\text{Ru}(\text{bpy})_3]^{1+}$ generated using DHB (Fig. 3B) is $= 4 \times 10^7 \text{ s}^{-1}$. The same experiment performed with SA as a matrix yields a rate constant of approximately $1 \times 10^7 \text{ s}^{-1}$. Thus, the measured rate constants are slower for the SA generated $[\text{Ru}(\text{bpy})_3]^{1+}$ than for $[\text{Ru}(\text{bpy})_3]^{1+}$ generated with DHB. In addition, the S/N is better with SA than with DHB. The number of photons contributing to the emission signal in Fig. 3C is ~ 5400 compared to only ~ 1100 in Fig. 3B. It should be noted that not all experiments resulted in observable transients. Using DHB measurable transients were obtained in 1 out of every 15 attempts and with SA measurable transients were observed in 1 out of every 6 attempts.

Some suggestions were obtained during the analysis of the data that indicated that the transients may contain multiple exponential components. To check for the presence of other ions that might contribute to the emission signals, possibly generated by photodissociation products, the ions were transferred back to the ICR cell after optical detection to acquire a mass spectrum (Fig. 2B). As seen in Fig. 2B, no other ions, such as $[\text{Ru}(\text{bpy})_2]^{1+}$ at m/z 414, were observed. In addition, the higher quality mass spectrum allows the isotopic distribution to be observed because the conditions for detection were more typical for an FTMS [28]. In this spectrum, the isotopic distribution is similar to the theoretical spectrum and does not show significant signs of H loss, which have been previously observed [18]. However, loss of H was observed in some experiments with both DHB and SA. There was also evidence of $[\text{Ru}(\text{bpy})_2]^{1+}$ produced after optical excitation for some DHB experiments.

Photodissociation experiments were performed to determine if the $[\text{Ru}(\text{bpy})_3]^{1+}$ ions could be decomposed in the gas phase by the 355 nm light. In the case of ions generated using DHB as matrix, 30

Fig. 2. FTMS spectra of $[\text{Ru}(\text{bpy})_3]^+$ ions (A) before and (B) after the optical detection event.

pulses of broad beam laser light produced $[\text{Ru}(\text{bpy})_2]^+$ at m/z 414 as seen in Fig. 4. Since $[\text{Ru}(\text{bpy})_2]^+$ could be produced by photodissociation, its gas phase emission properties were also examined and while some light scattering was detected, no emission was observed. Photodissociation experiments where $[\text{Ru}(\text{bpy})_3]^+$ was generated by SA did not show any signs of photodissociation even after 100 laser shots.

4. Discussion

Transient emission data have been obtained for species best described as $[\text{Ru}(\text{bpy})_3]^+$ and control experiments have been performed which strongly indicate that the transient emissions are not artifacts

Fig. 3. Fluorescence lifetime transients: (A) background prior to transfer of ions to optical detection cell, (B) from ions generated using DHB as matrix, and (C) from ions generated using SA as matrix.

Fig. 4. FTMS spectrum showing photodissociation of $[\text{Ru}(\text{bpy})_3]^{1+}$ (m/z 570.11) to form $[\text{Ru}(\text{bpy})_2]^{1+}$ (m/z 414.04) after 30 laser shots. Ions were generated using DHB as matrix.

of the experiment. Based on solution experiments, emission from $[\text{Ru}(\text{bpy})_3]^{1+}$ may seem unexpected; however, weak emission from ruthenium (I) polypyridines have been observed in frozen matrices where the solvent effects are minimized [29]. In the gas phase, there is no solvent to couple to the vibrational and rotational modes of $[\text{Ru}(\text{bpy})_3]^{1+}$ and quench fluorescence.

Based on previous work [18,30], it is possible that two ruthenium species are generated by MALDI that differ by one hydrogen atom as illustrated in reaction Scheme 1. A metal–nitrogen bond in structure A, $[\text{Ru}(\text{bpy})_3]^{1+}$, is broken to produce structure B. Rotation of a pyridine ring and re-formation of an ortho-metallated complex by a metal–C bond then produces structure C with concomitant loss of a

Scheme 1.

hydrogen atom. Loss of one H to produce structure C is consistent with stabilization of the ruthenium complex by following the $18e^-$ rule. The most likely candidates for fluorophores are excited states of structures A and C. Even in the higher resolution FTMS spectra, the isotopic patterns for structures A and C would overlap and be difficult to distinguish [18]. Additionally, there may be other conformations present that also fluoresce because very little is known about the behavior of large molecular ions, especially inorganic species, in the gas phase.

A caveat to remember is that the lifetime signal is an average of all fluorophores present that are excited by 355 nm light. The variability in the observed lifetime transients suggests that the identity and relative concentration of fluorophores present was not consistent from one experiment to the next. Besides the different structural conformations, fluorescent neutrals that enter the cell and fluorophores of the same conformation but existing at different energy levels may produce potential fluorescent signals. Light scattering from ions and/or neutrals could also contribute to the overall signal; however, the low pass filters should eliminate most of the scattered light.

Because more stable ions are generated by MALDI using SA compared to DHB, it is reasonable that distributions in energy levels are produced and account for some of the variability in the observed fluorescence signals. In solution, the energy levels of $[\text{Ru}(\text{bpy})_3]^{2+}$ drop to the singlet state in picoseconds before fluorescing because of solvent interaction with vibrational and rotational states of the metal complex [31,32]. In the gas-phase, there are no solvent relaxation modes. While there may be some relaxation due to collisions, at a pressure of 10^{-8} Torr the calculated collision rate for $[\text{Ru}(\text{bpy})_3]^{1+}$, assuming a molecular radius of 6.1 Å [33], is approximately 0.2 s^{-1} [34]. However, the actual efficiency of collisional relaxation would depend on the size of the neutral involved in the collision [28]. Therefore, molecular ions may be produced and trapped at multiple energy levels.

5. Conclusion

The results presented illustrate the powerful potential of combining mass spectrometry with gas-phase optical detection. While the mass spectra may indicate that only one species is present, the multi-exponential nature of the emission lifetimes suggests the presence of at least two optically active species. Using MALDI to generate the ions complicates interpretation because multiple structural conformations with a broad energy distribution can be created. Future experiments should utilize electrospray ionization

(ESI) to generate ions to hopefully produce a single conformation with a narrower energy distribution. Additionally, ESI would allow production of the multiply-charged species $[\text{Ru}(\text{bpy})_3]^{2+}$, which could be compared directly to solution experiments. Besides the ability to generate a well-defined population of large molecular ions, other technological challenges exist for the gas-phase spectroscopic study of molecular ions. For example, solution spectroscopy takes advantage of Beer's law. In the gas phase, Beer's law is difficult or impossible to apply because it is a non-trivial task to define the volume or determine the exact number of optically active ions; hence, extinction coefficients remain unknown. In essence, the study of the optical properties of molecular ions in the gas phase is at an embryonic stage similar to condensed-phase spectroscopic studies in the early 1900's.

Acknowledgements

JEH would like to thank the INEEL ACE Fellowship program for funding. The authors also gratefully acknowledge support from the United States Department of Energy, under contract DE-AC07-99ID13727 BBWI.

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