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Absorption spectrum of isolated tris(2,2′-bipyridine)ruthenium(II) dications *in vacuo*

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ABSTRACT

Here we report the gas-phase action spectrum of tris(2,2′-bypyridine)ruthenium(II) dications, $Ru(bipy)_3{}^{2+}$, recorded over a broad wavelength region from 210 nm to 650 nm. Ions formed by electrospray ionization were thermalized in collisions with helium buffer gas at room temperature in a 22-pole ion trap. A bunch of ions was then accelerated to keV-kinetic energies and injected into an electrostatic ion storage ring in which they circulated with a revolution time of 69 microseconds. After several milliseconds to allow for the decay of metastable ions, the ions were photoexcited and their decay monitored in time. Dissociation was found to occur on the microsecond time scale. Based on the time spectra, the initial number of photoexcited ions was estimated at each wavelength (relative and not absolute numbers). This approach circumvents the problem of kinetic shifts often encountered when dissociation is sampled within a finite time interval in the case of finite length time-of-flight instruments. The obtained absorption spectrum is found to be similar to the solution phase spectrum (acetonitrile solvent) but with a blueshift of the lowest energy metal-to-ligand charge transfer transition. This finding indicates a localized electronic transition in solution involving only one of the bipyridine ligands. There are small differences in the relative intensities of the bands between the gas-phase and solution-phase spectra. Finally, our gas-phase spectrum serves as a reference to benchmark theoretical calculations of excited states.

1. Introduction

Tris(2,2′-bipyridine)ruthenium(II), $Ru(bipy)_3{}^{2+}$, has become a text-book case for coordination chemistry. It is one of the most extensively studied and widely used transition metal complexes due to its interesting photophysical and photochemical properties [1–3]. The ground state of the complex is a singlet, and the highest occupied molecular orbitals are predominantly localized on the metal whereas the lowest unoccupied molecular orbitals are on the ligands. Electronic transitions can be categorized as metal-centered (dd), ligand-centered ($\pi\pi^*$), metal-to-ligand (ML) and ligand-to-metal (LM) charge transfer (CT). The transition energies depend on the metal and ligand orbitals and the coupling between them, and they may be perturbed by a chemical environment such as a solvent. Owing to its stability, high extinction coefficients and long-lived excited states, $Ru(bipy)_3{}^{2+}$ is suitable as a light-harvesting antenna, applicable in dye-sensitized solar cells and in artificial photosynthesis [4–7].

While the complex that belongs to the D_3 point group has zero dipole moment in its electronic ground state, it may have a permanent dipole moment in an excited state if the excitation is localized, that is, if the photoactive electron is localized on a single ligand rather than delocalized over all three. The molecular symmetry is then reduced from D_3 to C_2, *cf.* $[Ru(III)(bipy)^-(bipy)_2]^{2+}$. Experiments in different solvents have been performed to elucidate the character of the transitions, and it was found that the lowest energy band was slightly sensitive to solvent which implies a non-zero dipole moment in the excited state [8–10]. Raman experiments point in the same direction [11,12] whereas evidence has been found in solid matrices for the photoexcited electron to be delocalized among the ligands [13,14]. Femtosecond time-resolved absorption anisotropy measurements revealed time dependence in nitrile solutions attributed to initial delocalization followed by charge localization [15].

Information on the nature of the excited state can also be obtained from a comparison between the absorption spectrum of the bare ion isolated in vacuum and that of the ion in bulk solution. The difference is expectedly larger than that between different solvents. An obstacle, however, is that the binding energy of the bidentate bipyridine ligand is high, and it is therefore difficult to identify photofragmentation within the limited sampling time interval of for example time-of-flight instruments. Previous work by Posey and co-workers [16–19] was focused on microsolvated $Fe(bipy)_3{}^{2+}$ and $Fe(terpy)_2{}^{2+}$ (terpy = 2,2′,2″-terpyridyl) ions

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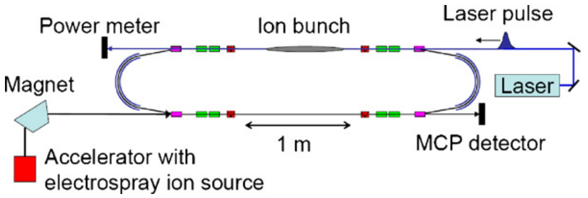

Fig. 1. Schematic layout of the electrostatic ion storage ring ELISA.

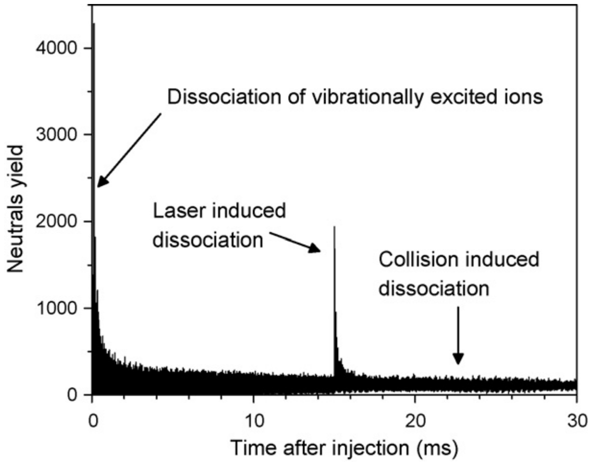

Fig. 2. Time spectrum of $Ru(bipy)_3{}^{2+}$. At early times, decay of vibrationally excited ions dominate over decay due to collisions with residual gas in the ring. Photoexcitation leads to an increased yield of neutrals.

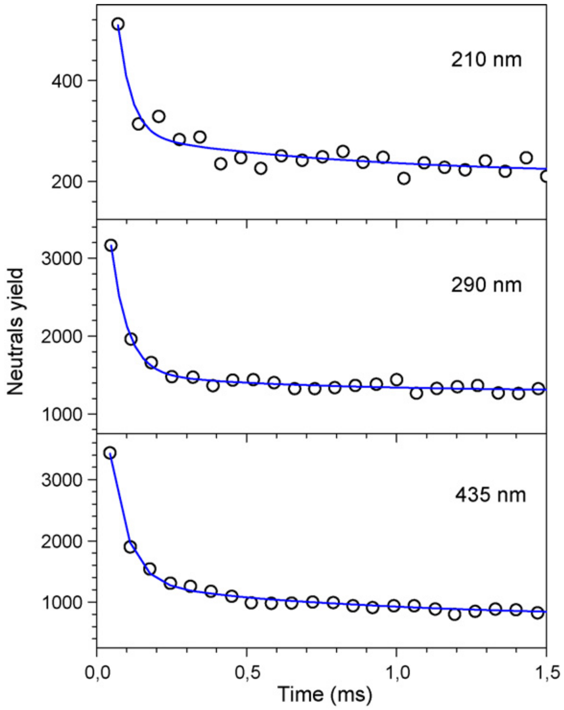

Fig. 3. Yield of neutrals as a function of time after photo-excitation. The sum of three exponentials was fit to the data. Time constants of about 50 μs and 500 μs were found for dissociation of photoexcited ions while dissociation due to collisions with residual gas in the ring occurred with a time constant of 100 ms.

for which solvent molecules readily evaporate after photoexcitation.

The problem of observing dissociation in action spectroscopy experiments is largely overcome in storage ring experiments or ion traps where fragmentation is monitored over a long time scale, in rings often from tens of microseconds to tens of milliseconds [20,21]. In the present work we have probed the influence of solvent on the energy of electronic transitions of the coordination complex $Ru(bipy)_3{}^{2+}$ from measurements on bare ions using the electrostatic ion storage ring in Aarhus (ELISA). The yield of photofragments was monitored from 210 nm to 650 nm.

2. Experimental

Experiments were carried out at the electrostatic ion storage ring in Aarhus (ELISA) (see Fig. 1) [22,23]. $[Ru(bipy)_3](ClO_4)_2$ was dissolved in MeOH to a concentration of about 10 mM and electrosprayed [24]. In this way $Ru(bipy)_3{}^{2+}$ ions were produced that were subsequently accumulated in a 22-pole ion trap and thermally equilibrated by collisions with a room temperature helium buffer gas therein. The ions were accelerated as an ion bunch to kinetic energies of 22 keV × q (q = charge state), and a bending magnet was used to select the appropriate ions. Following injection into the ring, the ions were stored for several milliseconds before being irradiated by a nanosecond light pulse from a tuneable, pulsed EKSPLA laser. This allowed for the decay of ions that were collisionally excited during the extraction from the ion trap or during injection into the ring (see Fig. 2). The laser is an Nd:YAG laser where the third harmonic (355 nm) pumps an optical parametric oscillator (OPO). The visible output from this OPO was frequency doubled in a crystal providing UV light with a beam diameter of about 5 mm. The repetition rate of the experiment was 10 Hz. Dissociation was a result of one-photon absorption (*vide infra*). In another experiment on $Fe(bipy)_3{}^{2+}$, where the ring was used as a mass spectrometer, it was found that a dominant fragmentation channel is loss of bipy, and likewise bipy loss has been observed in collision-induced dissociation experiments on $Ru(bipy)_3{}^{2+}$ [24,25]. Lifetimes were obtained from measurements of the yield of neutrals hitting the microchannel plate (MCP) detector located at the end of the straight section opposite to the side where photoexcitation was performed (*i.e.*, delayed dissociation experiment). The pressure in the ring was about 10^{-10} mbar.

Solution-phase absorption spectroscopy was carried out using a Thermo Spectronic heλlios α instrument. The $[Ru(bipy)_3](ClO_4)_2$ salt was home-made and dissolved in acetonitrile.

3. Results and discussion

Time spectra taken at three different excitation wavelengths are shown in Fig. 3. Three exponentials are required to satisfactorily describe the decays. Photon absorption leads to dissociation on the microsecond time scale while dissociation due to collisions with residual gas in the ring occurs on the hundred millisecond timescale. The smallest time constant increases with wavelength from 45 μs at 210 nm to 62 μs at 435 nm in accordance with statistical dissociation. The second time constant is about 500 μs for all three wavelengths, and finally the third time constant is 100 ms.

The yield of photofragments increases linearly with the number of photons in the laser pulse (see Fig. 4 for 430-nm excitation), which implies that the dissociation is due to absorption of one photon. The requirement of two time constants to account for the decay due to photon absorption is most likely a consequence of the width of the internal energy distribution; not all ions have exactly the same energy after photoexcitation [26,27]. In principle there would be a time constant associated with each internal energy determined by the activation energy and preexponential factor for the dissociation process but since two are sufficient we decide against using more exponentials. Another interpretation of the long life-

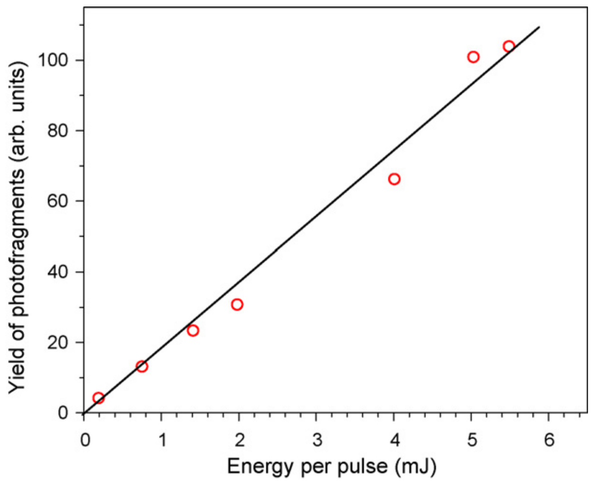

Fig. 4. The yield of photofragments as a function of energy of the laser pulse. The wavelength of the light was 430 nm.

time component is trapping in a long-lived electronically excited state that acts a bottleneck to the dissociation (*vide infra*).

Based on the exponentials, we estimated the initial number of photoexcited ions (relative numbers) at each wavelength. These numbers were divided by the average number of photons in the pulse and corrected for differences in ion beam intensities to provide values for absorption. The signal from collision induced dissociation serves as a measure of the ion beam intensity. A clear advantage of this method is that we correct for variations in dissociation lifetimes after photoexcitation, which is an issue when dissociation is sampled in a too short time interval.

In our experiment, we can only identify absorption if it leads to fragmentation (action spectroscopy), and neutrals have to be formed. Light emission would result in cold ions that do not have enough excess energy for dissociation. To equate the action spectrum with the absorption spectrum, it is therefore an assumption that the luminescence quantum yield is the same for all excitation wavelengths. It is known for $\mathrm{Ru(bipy)_3}^{2+}$ that radiationless deactivation to the lowest excited state, ^{3}MLCT, occurs quickly with a quantum yield close to unity [1]. This state does not undergo fast radiationless decay to the ground state, and it is highly luminescent (quantum yield of about 0.4). The radiative lifetime of the excited complex in a rigid alcoholic glass is 13 μs but both the emission lifetime and quantum yield decrease with temperature as thermally activated radiationless deactivation can occur via upper-lying metal-centered excited states (dd) [1]. Since vibrational cooling does not occur for isolated ions *in vacuo* neglecting infrared emission, the excited-state lifetime and luminescence are likely smaller than in solid phase. Still we caution that the luminescence quantum yield may change with excitation wavelength though most likely not very much within a band. Also if dissociation occurs promptly in an electronically excited state or two singly charged ions are formed in a Coulomb explosion process, we are blind to it. High-energy collision experiments (keV energies) that lead to broad internal energy distributions and that often involve electronically excited states, however, reveal that the formation of $\mathrm{[Ru(bipy)_2\text{-}H]^+}$ and $\mathrm{bipyH^+}$ is a minor process compared to loss of bipy [25].

Decay is first sampled 35 μs after photoexcitation which is longer than the excited-state lifetime of 13 μs, and we assume that most of the ions at this time are in their electronic ground state. The attribution of the second time constant to long-lived triplet-state excited ions is therefore less likely.

The action spectrum is shown in Fig. 5, top panel. The uncertainties in the data points are dominated by fluctuations in laser pulse

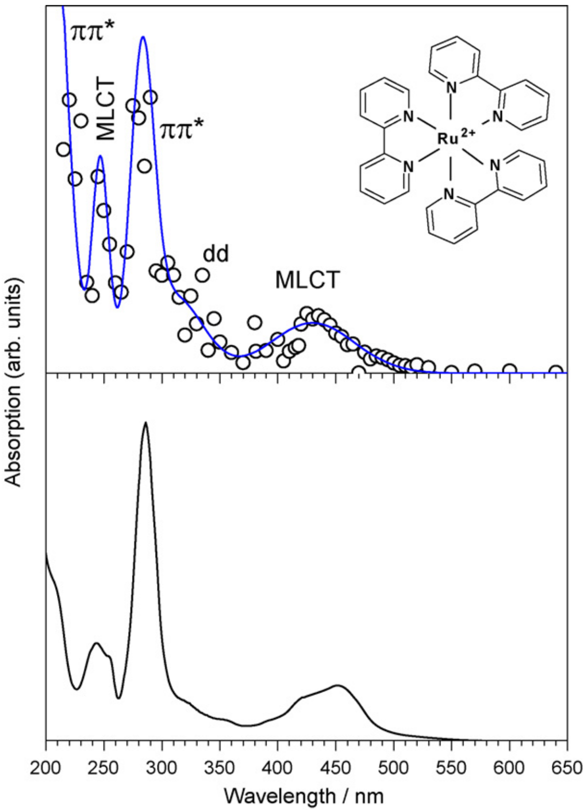

Fig. 5. Absorption spectra of $\mathrm{Ru(bipy)_3}^{2+}$ isolated in vacuum (top panel) and in acetonitrile solution (lower panel). Band assignments are taken from [2]. The blue line is drawn to guide the eye. (For interpretation of the references to color in the caption of this figure, the reader is referred to the web version of the article.)

Table 1
Absorption band maxima (in nm) of $\mathrm{Ru(bipy)_3}^{2+}$.

Transition	LMCT	dd	ππ*	LMCT	ππ*
In vacuo	430	310	283	247	<210
In acetonitrile solution	452	319	286	243	195

energies and are estimated to be less than 10%. Bands are assigned to MLCT transitions at 430 nm and 247 nm, ligand-centered ππ* transitions at 283 nm and 210 nm, and a metal-centered dd transition at 310 nm, see [2]. For comparison, the solution-phase spectrum taken in acetonitrile is shown in the lower panel of the figure. The band maxima are summarized in Table 1. The band positions are almost identical with the exception of a significant redshift of the 430-nm band to 452 nm upon solvation. This can be explained by charge localization introduced by the solvent which decreases the energy of the charge transfer from the metal to the ligand. The MLCT bands are known to be most sensitive to solvent effects [9]. For comparison, Posey and co-workers [17] measured the red edge of the MLCT band of $\mathrm{Fe(bipy)_3}^{2+}$ and found that methanol caused a redshift in the absorption band, which reflects a more favorable interaction between the excited state of $\mathrm{Fe(bipy)_3}^{2+}$ and the methanol molecules relative to its ground state. In the case of $\mathrm{Ru(bipy)_3}^{2+}$, the ground state is nonpolar whereas the MLCT excited state is highly polar; a value for the excited-state dipole moment of 14.1 ± 6.1 D has been reported by Meyer and co-workers [8]. Our data are consistent with the formulation of the excited state as localized, $\mathrm{Ru(bipy)_2}^{3+}\mathrm{(bipy)^-}$, and not delocalized having the promoted electron confined to the π* orbital over all three bipy ligands. Interestingly, a redshift was not measured for the 247-nm band, which indicates that in this case the excited state has more delocalized character.

Small differences are seen in the relative intensities of the bands where the high energy band is much larger in the gas phase than in solution. Also the dd transition is more pronounced in the gas phase. These differences could be related to wavelength-dependent luminescence.

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