

Time-Resolved Photoselection of $[\text{Ru}(\text{bpy})_3]^{2+}$ -Exciton Hopping in the Excited State

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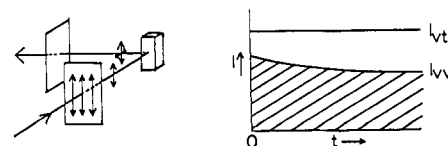
Measurements in this laboratory using the technique of time-resolved (TR) photoselection have revealed a time dependence in the maximum polarization (P_{max}) of $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) (Figure 1). The excitation polarization falls to the steady-state value¹ (0.23) rapidly after excitation with a rate which shows solvent dependence (Table I). This result implies *intrinsic*^{2,3,4} localization in the lowest excited states of the complex rather than a solvent-driven phenomenon.⁵⁻⁸

In the experiments reported here, pulsed excitation at 468 nm with a Molelectron UV-12 N₂-pumped dye laser (pulse width = 5 ns) was chosen to allow time resolution of the 580-nm emission by using a PAR 162 boxcar integrator (with digital storage) with a 5-ns gate. The laser scatter was eliminated with glass filters on the emission monochromator as verified by both solvent blank and scattering samples.

Photoselection experiments determine the polarization of emission from a compound excited by linearly polarized light.⁹ A polarization value near the high limit of 0.5 indicates one-dimensional absorption and emission oscillators which are oriented parallel or nearly parallel to one another. The maximum value possible for two planar oscillators is 0.14; consequently, P greater than 0.14 indicates that neither the emitting or absorbing oscillator can be degenerate.

Steady-state photoselection experiments for this complex produce a $P_{\text{max}} = 0.23$ emission polarization resulting from excitation on the low-energy side of the MLCT absorption maximum. This cannot be rationalized consistent with the occurrence of E modes and has been attributed to symmetry reduction caused by absorption into and emission from single chelate ring localized MLCT states. The $P_{\text{max}} \approx 0.23$ is found for a number of RuL_3^{2+} complexes at steady state.¹⁰ However, TR measurements show that at $t = 5$ -10 ns, P for $[\text{Ru}(\text{bpy})_3]^{2+}$ approaches that of a linear-linear oscillator as seen in $[\text{Ru}(\text{bpy})(\text{py})_4]^{2+}$, $P_{\text{max}} = 0.45$.¹¹

Since time-resolved studies^{6,7} show no time dependence for the emission or transient absorption of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, at any temperature, the time dependence of the polarization at 77 K must be explained by movement of the excitation among orbitally equivalent states differing only in spatial orientation. Such a model^{12,13} has been used to rationalize the electrochemically generated analogue $[\text{Ru}(\text{bpy})_3]^+$, believed to exist as $[\text{Ru}(\text{bpy})_2(\text{bpy}^-)]^+$. For this complex, temperature-dependent line broadening of the EPR signal has been attributed to "hopping" of the localized electron among the three ligands. A similar model has been proposed for $[\text{Ru}(\text{bpy})_3]^{2+}$ in its lowest electronic excited state based upon temperature-dependent steady-state photoselection results.^{1,3} Therefore, the rapid decrease of P after laser excitation is best explained by the randomization of exciton energy



$$P_{\text{max}}(t) = \frac{I_{VV}(t) - I_{VH}(t)}{I_{VV}(t) + I_{VH}(t)}$$

Figure 1. Diagram of photoselection experiment with equation defining P and graph showing dependence of vertical and total polarization components ($I_{VT} = I_{VV} + I_{VH}$) upon time. I_{VT} is total emission intensity with vertical (V) excitation.

Table I. P_{max} for $[\text{Ru}(\text{bpy})_3]^{2+}$ as $f(t)$ for Various Solvents

solvent	polarization at		
	5-10 ns	15-20 ns	300 ns
2:1 MeCl ₂ /Et ₂ O	0.24 ± 0.01	0.23 ± 0.02	0.22 ± 0.02
4:1 EtOH/MeOH	0.30 ± 0.01	0.25 ± 0.02	0.22 ± 0.02
4:1 MeOH/H ₂ O	0.37 ± 0.03	0.28 ± 0.03	0.22 ± 0.02

from the originally excited ligand-localized state to those states which are orbitally equivalent but of different orientation. The effect of this is to lower P by introducing a component in the transition moment of the emission which is perpendicular to the direction of the original excitation.

The implication of this exciton hopping for the emitting state is important to the origin of the 0-, ~9-, and ~60-cm⁻¹ states postulated by Crosby and co-workers^{14,15} from temperature-dependent lifetime and quantum yield measurements. The recent report by Yersin and co-workers of such emission transitions for pure single crystals verifies, in general, the Crosby postulate. However, Yersin and co-workers¹⁶ have suggested that the states have E , E , and A symmetry (within D₃ classification). The occurrence of two similar symmetry states within 10 cm⁻¹ is unlikely. Moreover, the two states apparently have very different radiative and nonradiative properties, a fact difficult to reconcile if they have the same symmetry. Finally, recent excited-state ESR results at liquid He temperatures for $[\text{Ru}(\text{bpy})_3]^{2+}$ measure a very small zero field splitting parameter ($D \sim 0.1$ cm⁻¹) for the excited state.¹⁷ Such a result implies that the spin-orbit interaction may not be the origin of the emitting state splitting. We suggest that the three low lying levels are nondegenerate orbital states resulting from an exciton interaction and an additional vibronic interaction. Thus, these three states likely retain spin degeneracy (are spin triplets).^{18,19} Such a rationale does require further study.

Recent controversy about the description of the lowest excited states of $[\text{Ru}(\text{bpy})_3]^{2+}$ has centered upon the mechanism of the localization of exciton energy with two limiting cases: (1) intrinsic to the molecule¹⁻⁴ or (2) caused by extrinsic factors such as preferential solvation.⁵⁻⁸ The argument in favor of solvent-induced localization has been presented recently by Krausz using excited-state resonance Raman⁵ (ERR) and Tazuke⁶ and Ferguson^{7,8} using time-resolved emission. Most recently, Kligler and co-workers²⁰ have produced temperature-dependent excited-state absorption to demonstrate that the interpretation of ref 5-8 cannot be correct. This evidence for the triplet single ring localization and the earlier work of Carlin and DeArmond,¹ giving solid solution photoselection data, reveal unequivocally that the localization of the emitting state can occur at 77 K in glassy solvents.

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The current results are evidence that a hopping (dephasing) rather than overlapping absorption bands is the origin of some of the decrease in P_{\max} for the tris vs. the mono bpy complex. Consistent with this result for the tris complex is the time-resolved P_{\max} of the $[\text{Ru}(\text{bpy})\text{py}_4]^{2+}$ for which no change in P_{\max} as a function of T can be measured at even the shortest time possible. This result verifies that the data for $[\text{Ru}(\text{bpy})_3]^{2+}$ are not instrumental artifacts. Relative rates of exciton hopping as a function of solvent are obtained (Table I). Qualitative analysis shows there to be a dependence of hopping rate upon solvent.

In addition to exciton hopping of the emitting state, the TR photoselection experiment provides detail relating to nonradiative relaxation. For information on the original excitation to be retained, the original excitation must be into a localized state and a relaxation pathway must exist between absorbing and emitting states that does not cause the loss of the polarization properties of the absorption. Therefore, in addition to the emitting state, the absorbing singlet state must possess spatially isolated orbitals. This is in agreement with absorption studies performed by Meyer and co-workers.²¹

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Subfemtomole Quantitation of Molecular Adsorbates by Two-Step Laser Mass Spectrometry

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We report the quantitative analysis of molecules adsorbed on a surface using a two-step laser methodology. Here the first laser pulse causes virtually complete desorption of the molecules by rapid heating of the substrate surface. Then a second laser pulse, suitably delayed in time so as to intercept the maximum number of desorbed molecules, causes selective multiphoton ionization of the molecules in a time-of-flight (TOF) mass spectrometer. The difficulty in analyzing nonvolatile and thermally labile molecules by conventional mass spectrometry is mainly caused either by thermal decomposition during evaporation or by strong fragmentation accompanying ionization. Several methods using laser desorption¹⁻¹² have been developed to obtain mass spectra without significant fragmentation. These techniques are celebrated for their powers of identifying complex molecules but not for their ability to measure relative or absolute molecular concentrations.¹³ To achieve quantitation of molecular substances, mass spectrometry usually has to be interfaced with a quantitative analytical method, e.g., gas chromatography or liquid chromatography.^{14,15}

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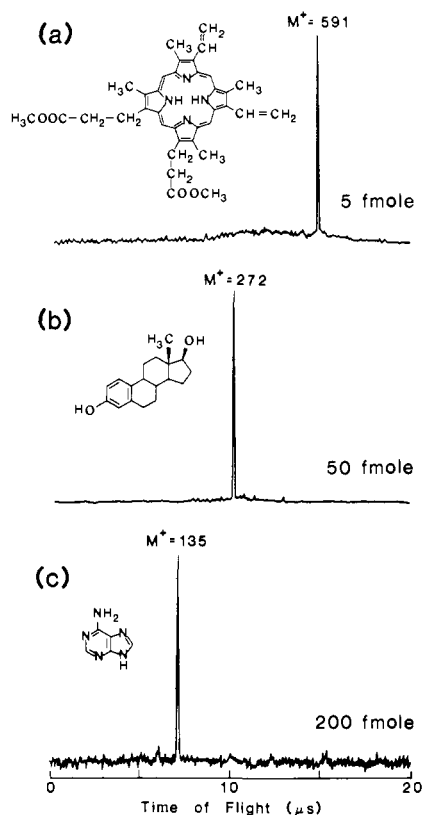


Figure 1. Laser desorption/multiphoton ionization mass spectra of (a) protoporphyrin IX dimethyl ester, (b) β -estradiol, and (c) adenine. The amount of each sample desorbed by a CO_2 laser pulse is 5, 50, and 200 fmol, respectively. Operating conditions: CO_2 laser fluence ~ 400 mJ/cm^2 , Nd:YAG laser fluence ~ 3 mJ/cm^2 , duty cycle = 10 Hz, and signal averaging time = 20 s.

Our two-step laser methodology is intended to overcome the problems mentioned above. For a number of molecules studied, e.g., protoporphyrin IX dimethyl ester, β -estradiol, and the four bases of DNA, the mass spectra obtained are dominated by the parent ion peak. Moreover, the ion signal is found to be linear with surface coverage over more than 5 orders of magnitude from nanomole to subfemtomole amounts per new target area exposed by consecutive laser shots. A detection limit ($S/N = 2$) of 4×10^{-17} mol of protoporphyrin IX dimethyl ester, corresponding to $\sim 10^{-5}$ of a monolayer, is obtained.

In our previous work the two-step laser methodology has been described and applied to the quantitation of the 20 phenylthiohydantoin (PTH) amino acids.¹⁶ Improvements in the reduction of chemical and electrical interference permit the sensitivity to be increased by at least 3 orders of magnitude while maintaining linear response. In the first step of our methodology, the pulsed output of a CO_2 laser (10.6 μm ; ~ 10 mJ/pulse ; 10- μs pulse width; 10-Hz repetition rate) is directed onto a thin film of the sample deposited on the inner surface of a rotating glass cup or tube. Neutral molecules escape from the surface in a rapid laser-induced thermal desorption process. It has been argued¹⁷⁻¹⁹ that the heating rate is so rapid (10^8 K/s) that internally lukewarm intact molecules are desorbed, even though more traditional heating rates (10 K/s or less) cause extensive molecular decomposition on the surface. After an appropriate time delay (70-90 μs) the fourth harmonic (266 nm) of a Nd:YAG laser (~ 1 mJ/pulse ; 10-ns pulse width; 10-Hz repetition rate) causes 1 + 1 resonance-enhanced multiphoton ionization (REMPI) of the desorbed molecules in an interaction region located about 1 cm from the surface. The

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