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Publication Date

2000-06-30

Ultrafast Solvent Induced Charge Localization in Tris-[2,2'-Bipyridine] Ruthenium(II)

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Abstract. Two distinct excited state processes are resolved in tris-[2,2'-bipyridine] ruthenium(II). Time resolved anisotropy measurements reveal a solvent dependent depolarization indicative of charge localization. Transient absorption measurements resolve wavepacket motion on the excited state surface(s) independent of solvent.

Tris-(2,2'-bipyridine)ruthenium (II) or $[Ru(bpy)_3]^{2+}$ is the prototype to study the photoinduced properties of transition metal charge transfer complexes. $[Ru(bpy)_3]^{2+}$ has been extensively studied and much is known about the properties of its lowest-energy metal-to-ligand charge transfer (MLCT) state[1]. The electronic properties of this MLCT state have been found to depend on the molecule's environment. For example, evidence has been found in solid matrices for the photoexcited electron to be delocalized among the ligands in the MLCT state[2, 3]. In solution, however, Raman experiments[4, 5] observe an excited state with charge localized on a single ligand. Previous work from this lab focused on time-resolving the evolution of the Franck-Condon state to the ^{3}MLCT excited state using transient absorption pump-probe measurements[6]. The excited state absorption spectrum for $\Delta t \geq 300$ fs matched spectra acquired on the nanosecond time scale. This was an indication that the formation of the ^{3}MLCT state occurs with a time constant of $\tau \sim 100$ fs. Although this study defined the overall time scale for excited-state formation, it left unanswered a number of important, fundamental questions concerning the nature of the initial photoexcited state, as well as the role of the solvent in the evolution of the charge-transfer state. We have addressed both of these issues by examining the time dependence of the anisotropic absorption of the molecule.

The point group of $[Ru(bpy)_3]^{2+}$ is D_3. The principal axis of symmetry is three-fold orthonormal to the plane bisecting all three bipyridine ligands. The ligands themselves are each bisected by a C_2 axis thereby rendering all three bipyridine ligands indistinguishable in the ground state. Upon photoexcitation, an electron is promoted from the metal to the ligand(s). In the case of initial delocalization of the electron among the ligands, the transition moment will be doubly degenerate with (x,y) polarization and each ligand will remain indistinguishable from each other. However, if the electron is localized to a single bipyridine ligand, the degeneracy of the transition moment is reduced with the reduction in molecular symmetry from D_3 to C_2. This situation can be realized upon photoexcitation or may occur as the result of excited-state

dynamics from a delocalized Franck-Condon state to a localized state on a single ligand. A time-resolved anisotropy measurement can distinguish among these possibilities.

Time dependent anisotropy of $[Ru(bpy)_3]^{2+}$ in a nitrile solvent series $(CH_3(CH_2)_nCN,$ n=0,1,2) is shown in Figure 1. The initial anisotropy in all three solvents is r ~ 0.55 and
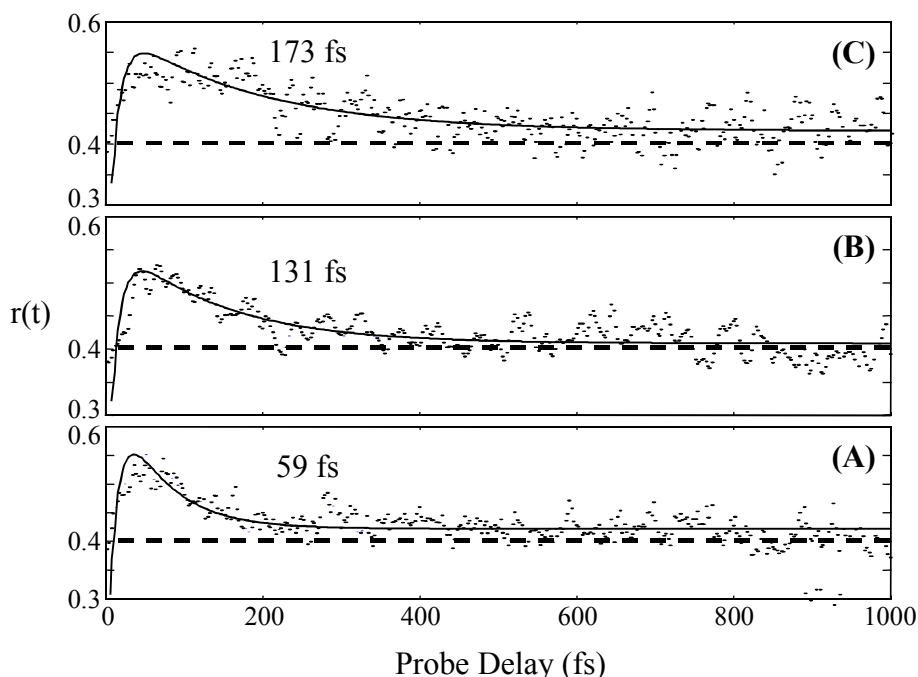

Figure 1 Solvent dependence of time-resolved anisotropic absorption measurements of $[Ru(bpy)_3]^{2+}$ in CH_3CN (A), CH_3CH_2CN (B) and $CH_3CH_2CH_2CN$ (C).

depolarizes to a value of r = 0.4. The value of r = 0.55 indicates the initial transition moment must be at least two-fold degenerate, implying an excited state symmetry of C_3 or higher. This is consistent with a doubly degenerate excited state as expected from the D_3 symmetry of the molecule. The depolarization of the anisotropy to r = 0.4 indicates a change in symmetry of the transition moment. Specifically, the value of r = 0.4 indicates the formation of a singly degenerate state but not an orthonormal state within the D_3 symmetry of the molecule. The conclusion is that there must be a reduction in symmetry that lifts the two-fold degeneracy of the excited state. The anisotropy data reflect a change in the symmetry of the MLCT transition moment consistent with charge localization from an initially delocalized excited state.

As seen in Figure 1, the rate of charge localization is observed to be dependent upon solvent. The nitrile solvents are polar and prior to excitation will solvate the dicationic $[Ru(bpy)_3]^{2+}$ in such a way as to screen charge. Thus, the negative end of the solvent dipole will be oriented toward the solute in the ground state. This electrostatic condition is changed dramatically with the introduction of additional negative charge density on the periphery of the chromophore upon photoexcitation. The initial response to this new charge distribution will most likely be dictated by non-diffusive inertial motion of the solvent. The driving force for charge localization is postulated to be the minimization of the number of unfavorable solvent-solute interactions in the excited state.

Magic angle transient absorption measurements were made to assess the correlation between population dynamics and the time scale for charge localization. As seen previously in

CH_3CN[6], the differential spectra evolve out to 300 fs with a time constant of $\tau \sim 100$ fs for ^{3}MLCT state formation. This is approximately the time scale of charge localization observed in this solvent. Charge localization in $CH_3CH_2CH_2CN$ is a factor of three slower than in CH_3CN. A change in the population dynamics of this magnitude should be clearly evident in the spectral evolution. No difference in the rate of spectral evolution was observed in $CH_3CH_2CH_2CN$. Once sensitivity to anisotropy is removed from the experiment, the dynamics of excited state evolution in $[Ru(bpy)_3]^{2+}$ appear to be independent of solvent. This suggests that the wavepacket motion associated with population dynamics is largely governed by intramolecular factors and occurs relatively independent of environmental forces. In contrast, the symmetry of the excited state is strongly influenced by the response of the surrounding medium to the metal-to-ligand charge-transfer.

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