higher than the absorption peak and a broader weaker tail. The ratio of the peak ΔA and peak A is 4.3×10^{-5}. The principal CD component was observed by Holzwarth et al. with much lower signal-to-noise ratio. The low energy tail was not observed.

Figure 3 shows the CD in the O-H stretching band. The sign is the same as in the C*-H band but the anisotropy ratio $\Delta A/A = 2.5 \times 10^{-5}$ is smaller by nearly a factor of 2. In this case the CD and absorption maxima correspond closely. No CD was reported in this band by Holzwarth et al.

The observation of vibrational CD with good signal-to-noise ratio in an unremarkable chiral molecule indicates that vibrational CD spectra should be generally observable with currently accessible instrumentation. Experiments are in progress to test this optimistic prognosis.

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The Effect of Ligand and Solvent Deuteration on the Excited State Properties of the Tris(2,2′-bipyridyl)ruthenium(II) Ion in Aqueous Solution. Evidence for Electron Transfer to Solvent

Sir:

Several recent studies have reported the use of $[Ru(bipy)_3]^{2+}$ to sensitize photoreactions in aqueous solution.[1-10] The quenching of the luminescence of this complex by other (presumably photoinert) molecules[11-16] has also been studied. Some authors postulate an electron transfer (photoredox) process involving excited state $[Ru(bipy)_3]^{2+}$ as a reducing agent[8-11] to explain the luminescence quenching, while others assume that a direct excitation energy transfer process occurs.[1-6,11-16] We wish to communicate observations of the luminescence lifetime and quantum yield of this ion in aqueous solution at 25°; conditions are typical of those employed in the references cited. In addition, the effect of deuteration of either the ligand, the solvent, or both, on the luminescence lifetime and quantum yield, was measured.

Commercial $[Ru(bipy)_3]Cl_2 \cdot 6H_2O$ (G. F. Smith Chemical Co.) was used without purification. The properties of this material were identical with those of samples which were synthesized and purified in this laboratory. The perdeuterated analog, $[Ru(bipy\text{-}d_8)_3]Cl_2 \cdot 6D_2O$, was prepared by the method of Burstall[17] using 60 mg of $RuCl_3 \cdot 3H_2O$ (Englehard Industries) and 176 mg of the deuterated ligand (Merck Sharp and Dohme of Canada, Ltd.) which was first purified by vacuum sublimation. The product of this synthesis was recrystallized from D_2O. The absorption and emission spectra of deuterated complex agreed with those of the parent complex.[18-20]

Table I. Measured Lifetimes, μsec (Quantum Yields)

Sample	$[Ru(bipy)_3]Cl_2$	$[Ru(bipy\text{-}d_8)_3]Cl_2$
Solvent,		
H_2O; 25°	0.58 ± 0.04[a] (0.042 ± 0.003)	0.69 ± 0.03 (0.047 ± 0.003)
D_2O; 25°	1.02 (0.070)	1.25 (0.079)
4:1 v/v EtOH:MeOH; 77°K	5.1 ± 0.1[b]	6.1 ± 0.1
	Free Ligand Lifetimes, sec	
	bipy-h_8	bipy-d_8
4:1, v/v EtOH:MeOH; 77°K	0.97	2.2

[a] References 8, 11, and 12 report values of 0.66, 0.60, and 0.65 μsec, respectively, under similar conditions. [b] Reference 27 reports a value of 5.21 μsec for this system.

Luminescence measurements were made on the complexes dissolved in H_2O (deionized and then distilled) or in D_2O (used as supplied by Thompson Packard Inc.). The solutions were deoxygenated with dried, chromous-scrubbed nitrogen. All solutions were prepared fresh daily.

Luminescence quantum yields were measured by a modified Parker Rees method.[21,22] Fluorescein, purified by the method of Orndorff and Hemmer,[23] was used as a standard with a yield of 0.90.[24] The samples were excited at 436 nm using a 1000-W Hanovia Hg-Xe lamp. The exciting light was filtered through 7 cm of $CuSO_4$ (150 g/l.), and the desired line was isolated with a Bausch and Lomb monochromator having a 250-mm focal length and a grating blazed at 300 nm. The bandpass was limited to 5 nm. The output of this monochromator was modulated with a PAR Model 181 chopper and stray light was filtered with two Corning 9-58, one Corning 0-52, and an Optics Technology 430 blue edge filter before entering the cuvet containing the sample. The samples were maintained at 25.0 ± 0.1° with a water-jacketed cuvet holder and a Forma Temp Model 2095-2 bath. The emissions were monitored with a Perkin-Elmer Model 98 monochromator and an RCA C31034A photomultiplier having a 128 spectral response. The output was amplified with a PAR Model 184 lock-in amplifier and fed into a RDK Model B161 strip-chart recorder. The system was calibrated with an NBS L-101 standard lamp to correct for variations in instrumental response with wavelength. Lifetimes were measured in the manner described previously,[25] using the cell holder and bath mentioned above and monitoring at 610 nm.

Measurements on a Cary Model 118C spectrophotometer indicated that *the absorbance of 10^{-7} M oxygen-free solutions of the complexes was about 20% less than in air-saturated solutions.* The decrease in absorbance upon deoxygenation was uniform throughout the visible-uv region, and the original spectrum could be regenerated by reaerating the solution. We know of no previous report of this effect in transition metal systems, although dissolved oxygen is known to enhance the intensity of $T_1 \leftarrow S_0$ absorptions of aromatic hydrocarbons.[26] This effect of dissolved oxygen requires an additional precaution in the quantum yield measurements; i.e., absorbances as well as emission intensities must be determined on oxygen-free solutions or the measured absorbance will be high, resulting in a measured quantum yield which is lower than the true value.

The results summarized in Table I show a remarkable effect. Deuteration of the free ligand causes the measured lifetimes, τ_m, to more than double, consistent with the theories developed for organic systems.[28,29] The effect of ligand deuteration is mitigated in the complex; but now a large isotope effect is observed for the solvent. *Deuteration of the solvent causes the radiationless lifetime to almost double while deuteration of the ligand causes only a 20–25% increase in* τ_{nr} *for the complex.* Quantum yield measurements indicate that the radiative lifetime, τ_m/Q, is invariant, within experimental error, for all the 25° measurements. The measured lifetimes of the complexes were found to be independent of pH or pD; thus structures involving base hydrolysis of the ligand[30] seem unlikely as possible explanations of the large solvent deuterium effect.

The effect of solvent deuteration may be explained in terms of an excited state model involving partial charge transfer to solvent (CTTS) when viewed in the light of the "active H-atom" theory of Robbins and Thomson.[31] These authors point out that the electronic part of the expression for the radiationless decay rate, $J^{ko}(m,n)$, may be expressed as

$$J^{ko}(m,n) \propto \int \zeta_{mn}(r) \frac{dV}{dQ_k} dr \qquad (1)$$

where dQ_k refers to the nuclear coordinates of the promoting mode, V is the one-electron nuclear-electron interaction and $\zeta_{mn}(r)$ is the electric transition density ($\psi_m \rightarrow \psi_n$). They go on to show that this integral will be significant only when $\zeta_{mn}(r)$ is large in the region of the vibrating nuclei responsible for the perturbing force. They argue that increased electron density in the region of the atoms whose vibrations act as promoting modes should lead to greater efficiency of radiationless relaxation. These conclusions are supported with data on a variety of systems, including: a series of ammine complexes and β-diketone complexes of Cr(III), ligand-substituted bipyridyl and phenanthroline complexes of Ru(II) and Os(II), and solvent deuterium effects in aqueous solutions of rare earth chelates.

The interpretation of the present work in terms of a CTTS model is a logical extension of the work of Robbins and Thomson. If the excited state of $[Ru(bipy)_3]^{2+}$ were purely charge transfer to ligand (CTTL), as is commonly assumed, then one would expect a larger increase in τ_{nr} upon deuteration of the ligand. The fact that the most pronounced effect is observed upon deuteration of the solvent is strong evidence for increased electron density in the region of the solvent. Thus the luminescent state of $[Ru(bipy)_3]^{2+}$ may be thought of as having some CTTS character, which may be important in electron-transfer quenching mechanisms.

We have noticed that both the lifetime and quantum yield are sensitive to the temperature of the solution and we are presently conducting a study of this temperature dependence in order to determine activation parameters for the system.[32] We also plan to further test the "active H-atom" theory by using mixtures of H_2O–D_2O and other appropriate solvent systems.

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A Kinetic Investigation of the Reaction of 2-Bromooctane with Silver Perchlorate, a Second-Order Dependence in Silver Ion

Sir:

Nucleophilic substitution reactions of alkyl halides are known to be markedly accelerated by electrophilic metal ions such as silver ion. The stereochemical course of the reaction of optically active 2-iodooctane with silver nitrite[1a] and 2-bromooctane with silver nitrate has been shown by Pocker[1b] and Kornblum[1c] to proceed with inversion of configuration regardless of the solvent. A solvent dependency on the stereochemistry of the reaction of silver salts with α-phenylethyl chloride was observed.[1a] On the basis of salt effects, the fact that silver nitrate was more reactive than silver perchlorate, and the relatively low reactivity of neopentyl iodide, Hammond also suggested that these reactions had significant S_N2 character.[2]

Since the initial kinetic investigation[3] of the reaction between alkyl halides and silver salts, there have been numerous attempts to define the rate law for this reaction.[4] It has been established that the contribution of the alkyl halide to the order of the reaction is always close to unity. However, all attempts to elucidate the contribution of the Ag^+ and its counterion have led to fractional orders. For example, the reaction of $AgNO_3$ with ethyl iodide, isopropyl iodide, and neopentyl iodide in acetonitrile solvent at 25° did not fit a constant integral order but fell between second and third order.[2] Similar kinetic behavior was observed for the reaction of 2-bromooctane with $AgNO_3$ and $AgClO_4$ in acetonitrile.[1b] The stereochemical[1] and kinetic evidence[1b,2] prompted the suggestion that both silver cation and its accompanying anion participated in the rate limiting step (eq 1). Our interest in the kinetic behavior of these reactions was stimulated by the observation that we found it necessary to

$$NO_3^- + RI + Ag^+ \longrightarrow \underset{\text{transition state}}{[NO_3\text{-}RIAg]} \longrightarrow \text{products} \qquad (1)$$