What is the basis of these differences? The quantum-mechanical parameters in Table I suggest that it does *not* reflect differences in vibronic coupling. The two systems have essentially the same critical temperatures and reorganization energies, indicating that the frequency of the coupled composite oscillator and the extent of nuclear reorganization upon electron transfer are comparable in the photosynthetic system and in the hemoglobin hybrids. The difference in temperature dependences is associated with the difference in exothermicity for the two reactions; the classical, high-temperature activation energy, $E^{\dagger}$, for *C. vinosum* is ca. 1.5 that for the hybrid. The scale of the rates is set by the electron-transfer matrix element, H, which is much greater for the photosynthetic system: $H(C.\ vinosum)/H(\text{hybrid}) \sim 2 \times 10^3$. This large ratio of matrix elements would suggest either that the redox partners in *C. vinosum* are substantially closer than in the hybrids or that the influence of orientation and/or the protein medium facilitates electron transfer in the photosynthetic system: the structure of the reaction center of *R. viridis* supports the latter, more interesting, possibility.[30]

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Molecular Motions of Alkoxysilanes Immobilized on Silica Surfaces: A Deuterium NMR Study

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Abstract: The motional dynamics of surface-attached chains have been studied by ^{2}H NMR. Deuterated alkoxysilanes were immobilized on silica gel and investigated both in the solid state and in the presence of solvents. In the solid state, the spectra exhibit motionally narrowed line shapes with the greatest narrowing and therefore the most motion being observed for the longest chains. The motions in the solid state persist to temperatures as low as 150 K and are likely isotropic in nature. Hexane and benzene have only a limited effect on the mobility of the alkoxysilanes. Methanol is able to solubilize a portion of the alkoxysilanes, but at least half of the chains are unaffected by the addition of methanol.

In the last several years there has been considerable growth in interest in the study of surface-modified silicas. These studies have been greatly facilitated by the application of magic angle spinning[1] and cross polarization[2] techniques to obtain high-resolution ^{13}C and ^{29}Si spectra of surface-immobilized species.[3-6] While these techniques allow substantial characterization of the surface, they do not give information on the nature of the motions which occur. Motional dynamics of surface-modified silicas have been probed by ^{13}C relaxation measurements,[7] and static ^{13}C chemical shift anisotropy patterns have given useful information on the molecular motions of surface-immobilized phenyl groups.[8] However, acquisition of this type of data is time-consuming and the results are open to some interpretation.

As an alternative approach, it is also possible to probe molecular motions by wide-line ^{2}H NMR. This technique has several advantages for studies of molecular motion: Since the quadrupole interaction, which dominates the spectra, is essentially axially symmetric, the spectral line shapes are simple and dependent upon the amplitude and symmetry of the molecular motions. As well, by synthetic incorporation of deuterium, the technique is sensitive and usually much less expensive than a comparable incorporation of a ^{13}C label. In addition, the technique is completely nonperturbing. Studies of molecular motion by ^{2}H NMR have, to date, been essentially limited to biological membranes[9] and some polymers,[10] but they have yielded incisive results in these areas.

In order to probe the molecular motions occurring on surfaces, we have undertaken a ^{2}H NMR study of several deuterium-containing alkoxysilanes, chemically bonded to silica. The surface-immobilized alkoxysilanes, which contained completely deuterated alkoxy groups and ranged from one carbon to sixteen carbons in length, are shown in Figure 1. The motional behavior of these surface-modified silicas has been probed in the solid state. As well, since these compounds are models for chromatographic materials, the influence of various solvents on the mobility of the alkoxy groups has also been studied.

Experimental Section

Dimethyldichlorosilane was obtained from Petrarch Systems Inc. (Levitown, PA) and the deuterated alcohols were purchased from MSD Isotopes, Montreal, Canada. Fisher S-157 silica gel (28-200 mesh) was predried by heating to 200 °C on a vacuum line.

The deuterated silating reagents were prepared by slowly adding a deuterated alcohol (30 mmol) to dichlorodimethylsilane (28 mmole) with the reaction mixture maintained at 0 °C. The resulting product, which

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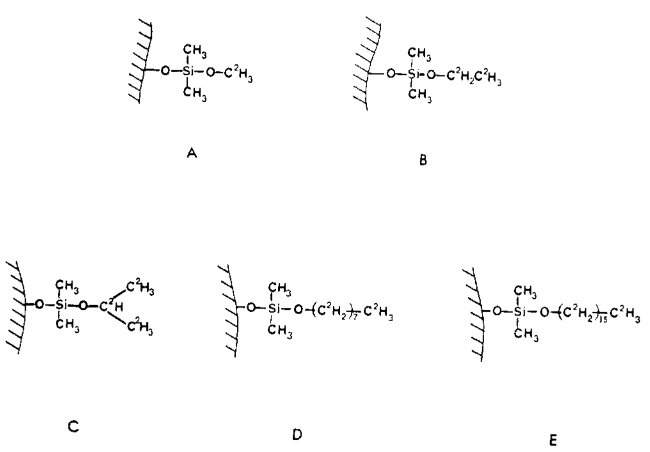


Figure 1. Structures of the silica-immobilized alkoxysilanes.

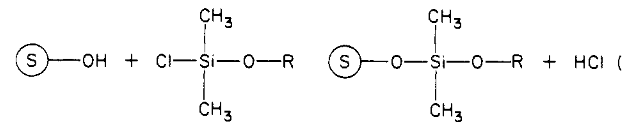
contains primarily the alkoxychlorodimethylsilane as well as small amounts of dialkoxydimethylsilane, was added to 10 g of dried Fisher S-157 silica gel and 20 mL of dry toluene.[6] The mixture was heated to 130 °C for 12 h with stirring. Following the reaction the mixture was washed repeatedly with toluene and dried under vacuum at 100 °C. Silane loading levels were typically 150–200 mg/g of silica.

The ^2H NMR experiments were carried out on a Bruker CXP-200 operating at 30.72 MHz. Spectra were acquired with a 500-kHz spectral width with use of the quadrupole echo sequence (11) with phase cycling of the radio frequency pulses. Typically, $\pi/2$ pulses of 5 μs, with 40 μs pulse spacings, were used. The use of the echo technique can cause intensity distortions in isotropic lines. A limited number of single-pulse experiments were performed, but no significant distortions were noted. Dry samples were examined in sealed tubes under vacuum. For studies of the effect of solvents, a small excess of free liquid was always present and the samples were well equilibriated.

Quantitative solid-state ^{13}C spectra were acquired with magic angle spinning on a Bruker CXP-100 operating at 22.636 MHz. The spectra were obtained with high-power proton decoupling and a long recycle time to allow the carbon magnetization to relax. Quantitative high-resolution ^{29}Si spectra were obtained at 39 MHz with MAS, on a Bruker CXP-200, using a 25 kHz spectral width and a 120 s recycle time.

Results and Discussion

The surface-modified silicas prepared in this study were characterized by both ^{13}C and ^{29}Si high-resolution solid-state NMR spectra. Quantitative ^{13}C spectra indicated that the ratio of $SiCH_3$ groups to alkoxy groups is 2:1, and the ^{29}Si chemical shift of −5 ppm is also consistent with the formation of predominantly $(-O)Si(CH_3)_2(OR)$ groups[6] as indicated in eq 1. Solid-state ^{13}C studies of surface-bonded alkoxysilanes have shown that these species can react further to give immobilized $(-O)_2Si(CH_3)_2$ and an alkoxy group which, itself, can react in a secondary process with the silica surface.[6] However, in addition to the higher reactivity of the chlorine functionality, the absence of a ^{29}Si resonance at −14 ppm $[(-O)_2Si(CH_3)_2]$ and the observed ratio of methyl groups to alkoxy groups rules out the formation of any appreciable amount of byproduct of this type.



$$\textcircled{S}\text{—OH} + \text{Cl—}\overset{CH_3}{\underset{CH_3}{Si}}\text{—O—R} \quad \textcircled{S}\text{—O—}\overset{CH_3}{\underset{CH_3}{Si}}\text{—O—R} + HCl \quad (1)$$

Solid-State ^2H NMR Results

The alkoxysilane-functionalized silicas were all dried on a vacuum line for 12 h prior to acquisition of spectra. The ^2H NMR spectra of these surface-modified silicas at 20 °C are shown in Figure 2. It is immediately apparent that, while all of the spectra are narrowed from the rigid limit due to partial averaging of the quadrupole interaction, the amount of reduction varies with the sample. However, the still significant width of the patterns indicates that motional narrowing is inefficient.

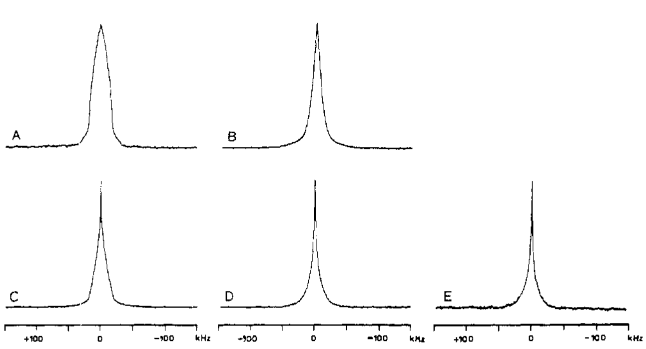


Figure 2. ^2H NMR spectra of the immobilized alkoxysilanes at 293 K: (A) $(-O)Si(CH_3)_2(OC^2H_3)$, (B) $(-O)Si(CH_3)_2(OC^2H_2C^2H_3)$, (C) $(-O)Si(CH_3)_2(OC^2H(C^2H_3)_2)$, (D) $(-O)Si(CH_3)_2(O(C^2H_2)_7C^2H_3)$, and (E) $(-O)Si(CH_3)_2(O(C^2H_2)_{15}C^2H_3)$.

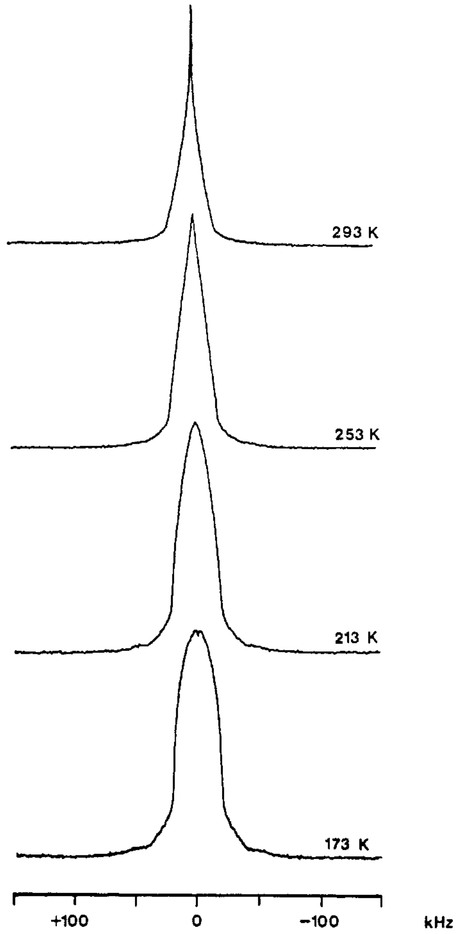


Figure 3. Temperature dependence of the ^2H NMR spectra of the $(-O)Si(CH_3)_2(OC^2H(C^2H_3)_2)$ species in the solid state.

The $(-O)Si(CH_3)_2(OC^2H_3)$ sample (A) shows a pattern with a width of approximately 30 kHz, but with a substantial amount of extra intensity in the center. Cooling of the sample to 150 K gives a quadrupole pattern with a quadrupole splitting of 40 kHz, which is the expected value for a methyl group undergoing rapid rotation about the C_3 axis.

Both the $(-O)Si(CH_3)_2(OC^2H_2C^2H_3)$ and $(-O)Si(CH_3)_2(OC^2H(C^2H_3)_2)$ species show a pattern somewhat narrower than that seen for the $(-O)Si(CH_3)_2(OC^2H_3)$ species (A). However, both of the former compounds have spectra which show spectral intensity extending out to at least 125 kHz. This intensity represents the partially averaged quadrupole pattern of the methylene and methyne deuterons. These deuterons would be expected to give a quadrupole pattern with a splitting of approximately 125 kHz in the rigid limit.

Cooling of these samples results in a very gradual broadening of the line shape and the eventual appearance of a rigid line shape at temperatures below 150 K. Figure 3 shows the temperature dependence of the ^2H NMR spectra of the $(-O)Si(CH_3)_2(OC^2H(C^2H_3)_2)$ species. Even at temperatures as low as 170 K

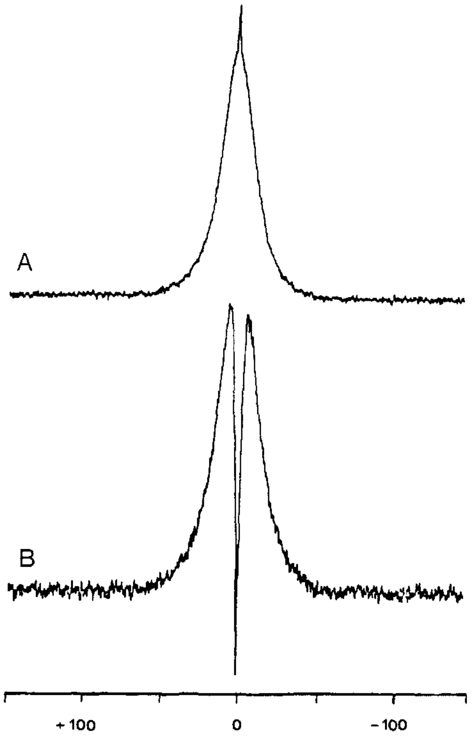


Figure 4. Partially relaxed spectra of $(-O)Si(CH_3)_2(O(C^2H_2)_7C^2H_3)$ acquired with an echo following a π-DA-sequence: (A) using DA = 100 ms and (B) DA = 50 ms.

there is still motional narrowing.

The silica-immobilized $(-O)Si(CH_3)_2(O(C^2H_2)_7C^2H_3)$ and $(-O)Si(CH_3)_2(O(C^2H_2)_{15}C^2H_3)$ species (Figure 2D,E) both show much narrower spectra than those discussed above, but some spectral intensity still extends out to 125 kHz. Variable-temperature studies show that both of these compounds exhibit motionally narrowed lineshapes down to temperatures of 120 K. As well, the spectra of both of these samples show contributions from two components, one broad and one narrow. Partially relaxed spectra, acquired following a π pulse and a short delay (Figure 4), indicate that the narrow component has a T_1 of approximately 140 ms while the broad component has a T_1 of approximately 15 ms.

In all of these silica-immobilized silanes, the ^2H NMR line shapes are considerably narrowed from the rigid limit. If a $C-^2H$ bond is subjected to motions which are fast compared to the quadrupole interaction ($>10^5$ s^{-1}) and have appropriate symmetry, there will be an averaging of the quadrupole interaction and a narrowing of the spectral line shape. Therefore, from the room temperature ^2H NMR spectra of the immobilized silanes, it is clear that motional narrowing has occurred. It is also apparent that the extent of the motional narrowing varies between samples, with the longest chains showing the greatest narrowing and, therefore, the most motion.

While there is clear evidence of substantial motional narrowing, the actual molecular motions which are occurring are not well defined. The motions are not simple, single correlation motions, such as "kink-3-bond" motions or "crankshaft-5-bond" motions which have been characterized in polyethylene chains.[10,12] For the long-chain silanes, one can also rule out a model in which the chains are fully extended and lined up parallel to each other, as is found for the hydrocarbon chains in a biological membrane.[9] Rather, the chains are likely randomly intertwined similar to the amorphous region of a polymer. The motions are therefore likely to be a combination of torsional motions about the O–Si, O–C, and the various C–C bonds, with, perhaps, increasing amplitudes of motion as the chain length increases.

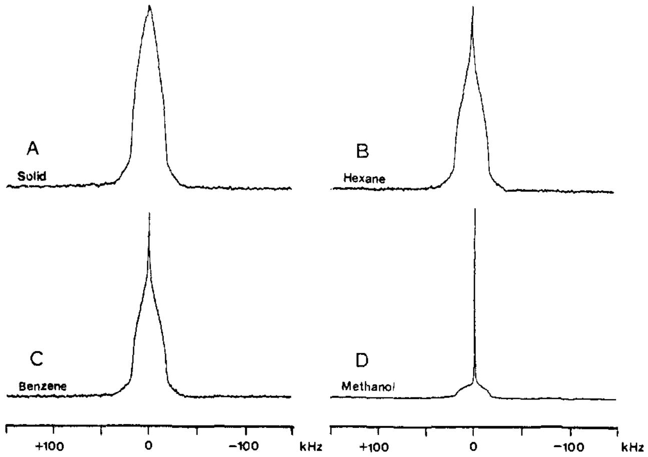


Figure 5. The influence of solvents on the ^2H NMR spectra of $(-O)Si(CH_3)_2(OC^2H_3)$: (A) solid; (B) excess hexane added; (C) excess benzene added; and (D) excess methanol added.

The observation of two signals in compounds D and E, with different spin–lattice relaxation times, could arise from two different situations. First, the narrow line with the long T_1 could be the C^2H_3 group while the wide component with the short T_1 could arise from the methylenes. This is also supported by the relative intensities of the two components which agree with those expected from the C^2H_2/C^2H_3 ratio. The longer T_1 for the C^2H_3 group is a result of being in the fast motion regime (confirmed by shorter T_1's at lower temperatures). The resulting T_1 values would therefore be quite similar to those measured for fatty acid chains in membranes.[13] The second possibility is that some portion of the chains is in a different, more mobile environment and this is reflected with methylene resonances giving a narrower line. However, this would likely have a shorter T_1, again assuming the short correlation regime. Further, the possibility of two distinct sites seems unlikely. If there were more than one environment, a large distribution of environments would seem most probable and this would give a distribution of T_1 values.

Influence of Solvents on the ^2H NMR Spectra

The addition of solvents to these surface-immobilized species results in substantial changes in the spectral line shapes. The addition of hexane or benzene to immobilized $(-O)Si(CH_3)_2(OC^2H_3)$ (Figure 5) results in the appearance of a narrow line, which is superimposed on a line shape similar to that seen for the solid. When methanol is added a narrow component is again present and contributes a substantial (30%) amount of the total spectral intensity. It is now much narrower, indicating essentially isotropic motion of that portion of the immobilized species. All of the other immobilized species show similar line shape changes when solvents are added. In all cases methanol caused the most pronounced spectral changes and the clearest differentiation between the two components.

The appearance of a very narrow spectral component superimposed on the broad component, when solvents are added to the $(-O)Si(CH_3)_2(OC^2H_3)$, suggests that the solvent "solubilizes" only a portion of the surface silane species which are present. The remaining surface species are left unchanged by the solvent and retain the line shape which is observed in the absence of solvent. The larger narrow line noted when methanol is added suggests that the surface of these modified silicas is still fairly polar. In the case of the $(-O)Si(CH_3)_2(O(C^2H_2)_{15}C^2H_3)$ and $(-O)Si(CH_3)_2(O(C^2H_2)_7C^2H_3)$ immobilized species the increased "solubilization" noted for methanol, compared to hexane or benzene, is rather surprising. This suggests that despite the presence of the long hydrocarbon chains, the surface is still fairly polar.

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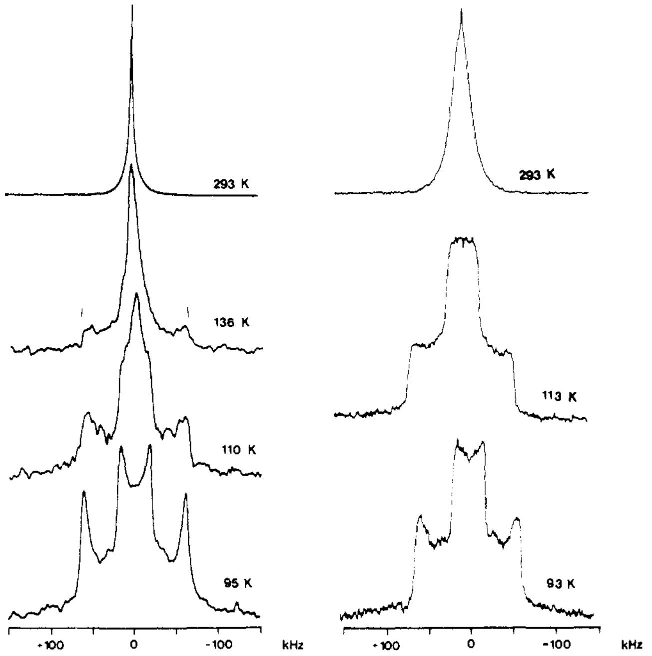

Figure 6. Temperature dependence of the ^2H NMR spectra of $(-O)Si(CH_3)_2(O(C^2H_2)_7C^2H_3)$ with excess hexane at the temperatures indicated together with those of the unsolvated material for comparison (right-hand spectra).

The inability of the solvents, particularly hexane and benzene, to solubilize the surface-immobilized species is also demonstrated by the low-temperature ^2H NMR spectra. Figure 6 shows the ^2H NMR spectra of the $(-O)Si(CH_3)_2(O(C^2H_2)_7C^2H_3)$ species (D), in the presence of hexane, at a variety of temperatures together with these in the absence of hexane for comparison. At 136 K it is possible to detect a quadrupole pattern for the methylene deuterons with a width of 122 kHz; however, there is still a substantial narrow central component. By 95 K, however, the pattern is fully rigid with a quadrupole splitting of 122 kHz for the methylene deuterons and almost 40 kHz for the C^2H_3 group. The presence of substantial motional narrowing at temperatures well below the freezing point of the solvent (178 K) suggests that there is only a limited penetration of the solvent molecules into the surface-immobilized species.

Conclusions

The current study has demonstrated that ^2H NMR is a useful technique for probing the motions of surface-immobilized species. The deuterated alkoxysilanes exhibit motionally narrowed ^2H NMR spectra down to temperatures of 150 K, indicating that even in the solid state the alkoxy groups are reorienting quickly ($>10^5$ s^{-1}), with the longer chains showing the most motion. Increased motion for longer surface immobilized chains has also been inferred from a solid-state ^{13}C NMR relaxation study.[7] The ^2H line shapes are not characteristic of any single anisotropic motion but likely represent an isotropic reorientation of the chain with varying torsional motions about the Si–O, C–O, and C–C bonds.

The addition of solvents to the surface-bonded silanes results in further ^2H NMR line shape changes. Hexane and benzene induce the formation of a small mobile component whose spectrum is superimposed on a wide line pattern similar to that found in the solid state. However, addition of methanol results in the formation of a larger and essentially isotropic component. Low-temperature studies show that the ^2H NMR spectra were still motionally narrowed at temperatures well below the freezing point of the bulk solvent. These observations indicate that hexane and benzene penetrate only to a limited degree into the surface region, while methanol is able to penetrate much more efficiently. Even for the immobilized species with the C_{14} chain, at what are relatively high loading levels, the surface appears to be still quite polar.

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Registry No. $ClSi(CH_3)_2(OC^2H_3)$, 100840-07-1; $ClSi(CH_3)_2(OC^2H_2C^2H_3)$, 100857-95-2; $ClSi(CH_3)_2(OC^2H(C^2H_3)_2$, 100840-08-2; $ClSi(CH_3)_2(O(C^2H_2)_7C^2H_3)$, 100840-09-3; $ClSi(CH_3)_2(O(C^2H_2)_{15}C^2H_3)$, 100857-96-3.

Formation of Electronically Excited Products in Electron-Transfer Reactions: Reaction of Polypyridine Complexes of Cobalt(I) and Ruthenium(III) in Acetonitrile

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Abstract: The yields of the metal-to-ligand charge-transfer excited state of poly(pyridine)ruthenium(II) complexes ($^*RuL_3^{2+}$) produced in the reaction of RuL_3^{3+} with poly(pyridine)cobalt(I) complexes in acetonitrile have been measured by use of a combination of continuous flow methods and chemical actinometry. The $^*RuL_3^{2+}$ yields are high, ranging from 0.31 ± 0.04 for the most exergonic system ($Ru(bpy)_3^{3+}$ and $Co(4,4'-(CH_3)_2bpy)_3^+$) to 0.07 ± 0.02 for the least exergonic system studied ($Ru(4,7-(CH_3)_2phen)_3^{3+}$ and $Co(bpy)_3^+$). The results are interpreted in terms of competing electron-transfer channels yielding primarily $^*RuL_3^{2+} + CoL_3^{2+}$ and $RuL_3^{2+} + {}^*CoL_3^{2+}$ (^2T), with the formation of entirely ground-state products being negligible. A new actinometer consisting of $Os(terpy)_2^{2+}$ and $Co(NH_3)_5Cl^{2+}$, for use at wavelengths up to ~720 nm, is described.

Electron-transfer reactions that are highly exergonic may yield electronically excited rather than ground-state products.[1,2] If the decay of an excited product to its ground state occurs radiatively, then the electron transfer may be accompanied by light emission (chemiluminescence): the intensity of this emission, in turn, provides a convenient measure of the yield of electronically excited products. The relative yields of ground- and excited-state products in highly exergonic reactions is a subject of considerable interest. Not only do the excited-state yields have important implications for electron-transfer theories[2] but also highly exergonic reactions provide a means of generating and characterizing

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