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Near-UV Photoionization of $[Ru(bpy)_3]^{2+}$: A Catalytic Cycle with an Excited Species as Catalyst**

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Photoionization of the tris-2,2′-bipyridyl ruthenium(II) ion $[Ru(bpy)_3]^{2+}$ is the archetype of a class of reactions that might effect photochemical water splitting:[1] the ejected electron $e^{\bullet-}_{aq}$ reacts with H^+, ultimately yielding hydrogen,[2] and the remaining oxidized complex $[Ru(bpy)_3]^{3+}$ is thermodynamically capable of oxidizing OH^- to oxygen,[1] although in practice this has only been realized with additional cocatalysts[3] or in microheterogeneous environments.[4] Herein, we identify the excited metal-to-ligand charge-transfer (MLCT) complex $^*[Ru(bpy)_3]^{2+}$ as a catalytic intermediate of this photoionization. Near-UV light (308 or 355 nm) drives both the ionization of this species and the reduction of $[Ru(bpy)_3]^{3+}$, which then regenerates the ruthenium(II) complex in its excited state.

Despite its model character, the mechanism of photoionization in this system has received very little attention. On the basis of flash-lamp experiments with polychromatic light (300–360 nm, 17 μs flash duration) and indirect detection of $e^{\bullet-}_{aq}$, a sequential reaction (Scheme 1) with a very low quantum yield of the ionization proper (0.0015) was proposed.[5a] Later studies using nanosecond laser flash photolysis, with optical detection of $e^{\bullet-}_{aq}$, gave somewhat contradictory results for the dependence of the electron yield on the excitation intensity,[5b, c] and focused mainly or exclusively[5d] on the effect of surface-active molecules on the electron yield.

$$[Ru(bpy)_3]^{2+} \xrightarrow[(\kappa_1)]{h\nu} {}^*[Ru(bpy)_3]^{2+} \xrightarrow[(\kappa_2)]{h\nu} [Ru(bpy)_3]^{3+} + e^{\bullet-}_{aq}$$

Scheme 1. Linear reaction sequence for photoionization of $[Ru(bpy)_3]^{2+}$.

To elucidate the mechanism and determine the relevant photokinetic parameters, we decided to investigate the intensity dependence of the yield not only for the final product $e^{\bullet-}_{aq}$ but also for the presumed intermediate $^*[Ru(bpy)_3]^{2+}$. Such an approach obviously provides much more information about a reaction that is expected to have multiple steps. Laser flash photolysis with different excitation wavelengths and detection of luminescence or optical absorbance was performed (see Experimental Section).

Figure 1 a shows the dependence of the concentrations of $^*[Ru(bpy)_3]^{2+}$ and $e^{\bullet-}_{aq}$, relative to the starting concentration c_0 of $[Ru(bpy)_3]^{2+}$, on the excitation intensity at 308 nm. A high turnover can be achieved; at our highest laser intensity the electron concentration approaches 50 % of c_0.

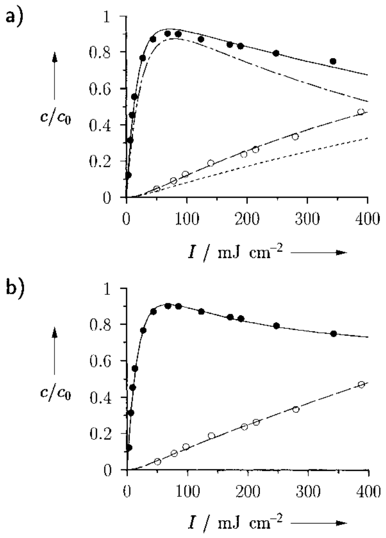

Figure 1. Photoionization of 3×10^{-5} M $[Ru(bpy)_3]^{2+}$ with light of wavelength 308 nm. The concentrations c, relative to the substrate concentration c_0, of $^*[Ru(bpy)_3]^{2+}$ (●) and $e^{\bullet-}_{aq}$ (○) are shown as functions of the laser intensity I. a) The fit curves refer to the mechanism of Scheme 1: —— shows a fit of Equation (1) to the experimental data for $^*[Ru(bpy)_3]^{2+}$, which yields the best-fit parameters $\kappa_1' = 5.68 \times 10^{-2}$ cm²mJ⁻¹, $\kappa_2' = 1.03 \times 10^{-3}$ cm²mJ⁻¹, ---- the curve calculated with κ_1' and κ_2' for $e^{\bullet-}_{aq}$ [Eq. (2)]. --- is the best fit of Equation (2) to the experimental data for $e^{\bullet-}_{aq}$, yielding $\kappa_1'' = 4.21 \times 10^{-2}$ cm²mJ⁻¹, and $\kappa_2'' = 1.69 \times 10^{-3}$ cm²mJ⁻¹, and -•- is the calculated result with κ_1'' and κ_2'' for $^*[Ru(bpy)_3]^{2+}$ [Eq. (1)]. b) The curves refer to the mechanism of Scheme 2, and are simultaneous fits of Equation (3) to the experimental data for $^*[Ru(bpy)_3]^{2+}$ (——) and of Equation (4) to those for $e^{\bullet-}_{aq}$ (----). Best-fit parameters are $\kappa_1 = 5.73 \times 10^{-2}$ cm²mJ⁻¹, $\kappa_2 = 1.52 \times 10^{-3}$ cm²mJ⁻¹, and $\kappa_3 = 3.19 \times 10^{-3}$ cm²mJ⁻¹.

Because the concentrations of $^*[Ru(bpy)_3]^{2+}$ and $e^{\bullet-}_{aq}$ are measured immediately after the end of the 308 nm pulse, the whole reaction sequence leading to photoionization must be completed within about 25 ns. On that time scale, bimolecular steps involving two ruthenium-based species, or one such species and $e^{\bullet-}_{aq}$, are negligible at the low concentrations used. As our solutions were optically thin, all the absorption steps can be described as first-order processes.[6] For a simple two-step photoreaction according to Scheme 1, that is, for the mechanism proposed in the literature, the intensity dependences of the observed species would be given by Equations (1) and (2). These expressions are valid for random shapes of the laser pulse, and depend only on its total intensity I

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$$\frac{*[\mathrm{Ru(bpy)_3}]^{2+}}{c_0} = \frac{\kappa_1}{\kappa_1 - \kappa_2}(\mathrm{e}^{-\kappa_2 I} - \mathrm{e}^{-\kappa_1 I}) \tag{1}$$

$$\frac{\mathrm{e}^{\bullet -}_{\mathrm{aq}}}{c_0} = 1 - \frac{\kappa_1 \mathrm{e}^{-\kappa_2 I} - \kappa_2 \mathrm{e}^{-\kappa_1 I}}{\kappa_1 - \kappa_2} \tag{2}$$

(see ref. [6]). The constants κ_1 and κ_2 correspond to the rate constants in formal kinetics but have a reciprocal-intensity dimension ($\mathrm{cm^2\,mJ^{-1}}$ in our case).

However, attempts to fit the two Equations (1) and (2) to the data reveal that the kinetic model in Scheme 1 must be wrong, or at least incomplete. While acceptable fits can be obtained for each species alone (by fitting Equation (1) to the intensity dependence of the triplet concentration, and independently fitting Equation 2 to that of the intensity dependence of the electron concentration), the curves calculated from the resulting best-fit parameters κ_1 and κ_2 for the respective other species strongly deviate from the experimental data, as seen in Figure 1 a. Any explanation must account for the fact that with increasing intensity (I), the electron concentration increases almost twice as much as the triplet concentration decreases.

Photoionization of the starting material by a parallel route that bypasses the triplet state is highly unlikely because, on excitation of $[\mathrm{Ru(bpy)_3}]^{2+}$, the triplet state forms within 300 fs[7], with a quantum yield of one.[8, 9b] Because of the very high redox potential of the $\mathrm{Ru^{III}/Ru^{IV}}$ couple,[10] all routes leading to $[\mathrm{Ru(bpy)_3}]^{4+}$ must be discounted for thermodynamic reasons; this includes subsequent monophotonic or biphotonic ionization of $[\mathrm{Ru(bpy)_3}]^{3+}$, formed by the pathway in Scheme 1, as well as the ejection of two electrons from a higher excited state of the starting material, in a parallel reaction.

The only remaining possibility is regeneration of the substrate or its triplet-excited form from $[\mathrm{Ru(bpy)_3}]^{3+}$, the by-product of photoionization of the triplet species. This reaction is exergonic even for ground-state $[\mathrm{Ru(bpy)_3}]^{3+}$, but much too slow to account for the observed effect.[3] However, irradiation of $[\mathrm{Ru(bpy)_3}]^{3+}$ at 660 nm was reported to lead to an increased rate.[3] As the 308 nm pulse carries more than twice the energy per photon, it seemed conceivable that it might induce a much faster photoreaction. This hypothesis was verified by two-pulse experiments on the oxidized complex $[\mathrm{Ru(bpy)_3}]^{3+}$ (Figure 2).

A 532 nm laser pulse provides a convenient analytical tool that is only sensitive to $[\mathrm{Ru(bpy)_3}]^{2+}$: it converts $[\mathrm{Ru(bpy)_3}]^{2+}$ into its MLCT triplet species $*[\mathrm{Ru(bpy)_3}]^{2+}$, which is detected by its characteristic luminescence. However, it does not produce any luminescence from $[\mathrm{Ru(bpy)_3}]^{3+}$ at all, nor does it lead to any chemical change of this compound.

Confirmation of the photoinduced transformation of $[\mathrm{Ru(bpy)_3}]^{3+}$ into $*[\mathrm{Ru(bpy)_3}]^{2+}$ or $[\mathrm{Ru(bpy)_3}]^{2+}$ was given by use of a 532 nm pulse followed by a 308 nm pulse (top trace in Figure 2). After the first pulse, no luminescence was detectable, which shows that, initially, our solution of $[\mathrm{Ru(bpy)_3}]^{3+}$ did not contain any $[\mathrm{Ru(bpy)_3}]^{2+}$. The second pulse gave an intense luminescence of $*[\mathrm{Ru(bpy)_3}]^{2+}$, which must have been formed either directly from $[\mathrm{Ru(bpy)_3}]^{3+}$ or by conversion of $[\mathrm{Ru(bpy)_3}]^{3+}$ into $[\mathrm{Ru(bpy)_3}]^{2+}$, and subsequent excitation of the latter species by the same pulse. When we reversed the sequence of the two pulses in a second experiment (bottom trace in Figure 2), the initial 308 nm pulse produced the expected luminescence, but the subsequent 532 nm pulse also did so, which provides additional confirmation of the formation of a ruthenium(II) species by 308 nm light, rather than an unknown emissive ruthenium(III) species.

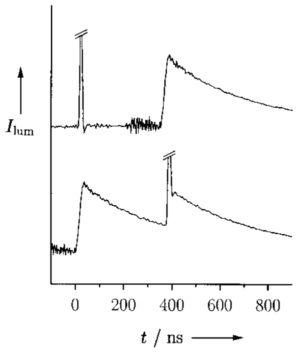
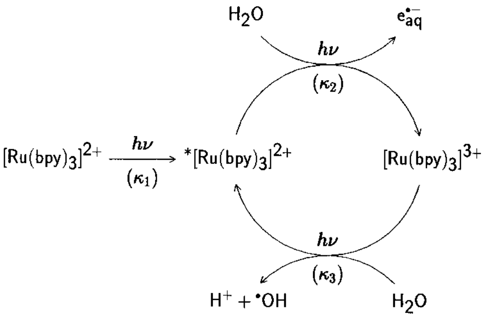


Figure 2. Two-pulse experiments on 3×10^{-5} M $[\mathrm{Ru(bpy)_3}]^{3+}$ at pH 0. The uncalibrated luminescence intensities I_{lum} are displayed as functions of the time t. Top trace: 532 nm pulse ($540\ \mathrm{mJ\,cm^{-2}}$) followed by 308 nm pulse ($340\ \mathrm{mJ\,cm^{-2}}$); bottom trace: sequence reversed. The spikes caused by unsuppressed stray light from the 532 nm pulses have been cut off.

A criterion allowing a distinction in this photoreaction between direct formation of $*[\mathrm{Ru(bpy)_3}]^{2+}$ from $[\mathrm{Ru(bpy)_3}]^{3+}$, and indirect formation (that is, via ground state $[\mathrm{Ru(bpy)_3}]^{2+}$ as an intermediate) is provided by the initial slope in a plot of the luminescence as a function of the intensity of the 308 nm pulse. In the case of direct formation of $*[\mathrm{Ru(bpy)_3}]^{2+}$, this initial slope must be nonzero, whereas in the case of indirect formation an induction period would result. Our experiments provide good evidence for the former, so 308 nm photolysis of $[\mathrm{Ru(bpy)_3}]^{3+}$ produces an electronically excited ruthenium(II) complex.

The mechanism of thermal reduction of $[\mathrm{Ru(bpy)_3}]^{3+}$ to $[\mathrm{Ru(bpy)_3}]^{2+}$ is complex, and involves more than one molecule of $[\mathrm{Ru(bpy)_3}]^{3+}$.[3, 4] In contrast, the photoinduced reduction observed in this work must be much simpler: because it is fast on the time scale of our laser pulses, it cannot comprise bimolecular steps with species other than water; the situation is thus comparable to that of isolated reactant molecules, for example, in a microheterogeneous environment. When the interactions between $[\mathrm{Ru(bpy)_3}]^{3+}$ molecules were suppressed in zeolite cages, $^{\bullet}\mathrm{OH}$ radicals were detected in the thermal reduction,[4] while they were never reported in the homogeneous phase. The formation of radicals in our photoinduced reduction of $[\mathrm{Ru(bpy)_3}]^{3+}$, but not in the homogeneous thermal reduction, was confirmed by scavenging experiments with benzoic acid. Benzoic acid is converted by $^{\bullet}\mathrm{OH}$ radicals into salicylic acid,[2] which can be monitored by the fluorescence of the salicylate anion at a pH higher than 4. When a 6×10^{-5} M solution (stable at pH 0) of $[\mathrm{Ru(bpy)_3}]^{3+}$ that contained 5×10^{-3} M of benzoic acid was made basic with NaOH, the thermal reduction occurred instantaneously, but only an insignificant background signal arising from salicylic acid was recorded in the fluorescence spectrometer. When, however, the same solution was irradiated *before* adding the base with a few laser flashes at 308 nm, such that the UV spectrum indicated complete conversion into $[Ru(bpy)_3]^{2+}$, a substantial fluorescence signal of the salicylate anion was detected, which was comparable to the luminescence signal of the regenerated ruthenium(II) species.

The overall photoionization mechanism of $[Ru(bpy)_3]^{2+}$ is thus cyclic, with $^*[Ru(bpy)_3]^{2+}$ acting as a catalyst (Scheme 2); this mechanism is also in perfect accordance with the experimental results (Figure 1). Because all three steps of this mechanism are photoreactions that are driven by the same laser pulse, the pulse shape does not play any role in the intensity dependences, and the total intensity I is the only variable determining the concentrations of $^*[Ru(bpy)_3]^{2+}$ and $e_{aq}^{\bullet -}$ after the pulse. The results are given in Equations (3) and (4).



Scheme 2. Cyclic-photoionization mechanism of $[Ru(bpy)_3]^{2+}$.

$$\frac{*[Ru(bpy)_3]^{2+}}{c_0} = \frac{\kappa_3}{\kappa_2+\kappa_3} - \frac{(\kappa_1-\kappa_3)\,e^{-\kappa_1 I}}{\kappa_1-\kappa_2-\kappa_3} + \frac{\kappa_1\kappa_2 e^{-(\kappa_2+\kappa_3)I}}{(\kappa_2+\kappa_3)\,(\kappa_1-\kappa_2-\kappa_3)} \tag{3}$$

$$\frac{e_{aq}^{\bullet -}}{c_0} = \frac{\kappa_2}{\kappa_2+\kappa_3}\left[\left(\frac{\kappa_2}{\kappa_2+\kappa_3} - \frac{\kappa_3}{\kappa_1}\right) + \kappa_3 I\right] + \frac{\kappa_2}{\kappa_1-\kappa_2-\kappa_3}\left[\frac{\kappa_1-\kappa_3}{\kappa_1}e^{-\kappa_1 I} - \frac{\kappa_1\kappa_2}{(\kappa_2+\kappa_3)^2}e^{(\kappa_2+\kappa_3)I}\right] \tag{4}$$

This kinetic model represents the intensity dependences very accurately, as the successful simultaneous fit of Equation (3) to the triplet data and of Equation (4) to the electon data shows (Figure 1b). The ionization quantum yield ϕ_{ion} of the MLCT triplet species is linearly related to the constant κ_2 divided by the known[9a] extinction coefficient ε_T of $^*[Ru(bpy)_3]^{2+}$.[6] However, to eliminate inner-filter effects we used the excitation of $[Ru(bpy)_3]^{2+}$, for which the quantum yield is one,[8, 9b] as a chemical actinometer, and calculated ϕ_{ion} from the best-fit constants κ_1 and κ_2, ε_T, and the ground-state extinction coefficient ε_G with Equation (5). In this way, we arrived at a value of $0.016 \pm 10\%$ for ϕ_{ion}. Ionization of the MLCT-triplet species $^*[Ru(bpy)_3]^{2+}$ is thus an order of magnitude more efficient than previously thought.[5a]

$$\phi_{ion} = \frac{\kappa_2 \varepsilon_G}{\kappa_1 \varepsilon_T} \tag{5}$$

With light of 355 nm wavelength, quite similar results were obtained. Because the absorption properties are more favorable at this wavelength, the turnover was as high as 70%. The quantum yield of ionization was found to be comparable to that at 308 nm. When 308 and 355 nm irradiation wavelengths are used in conjunction, the electron yield exceeds 100% relative to c_0. The system does not saturate under these conditions; even above 100%, the electron concentration increases linearly with the laser intensity. Both observations are further evidence of a catalytic cycle.

The photoreaction investigated provides an interesting example of a mechanism in which an electronically excited species, $^*[Ru(bpy)_3]^{2+}$, acts as a catalyst. As a consequence of the cyclic mechanism, the yield of electrons is not limited by the exhaustion of their precursor $^*[Ru(bpy)_3]^{2+}$. The reported[5b–d] increase by a factor of 2–3 in the electron yield, when $[Ru(bpy)_3]^{2+}$ is photolyzed in a micellar environment, might well be caused by an analogous photoreaction of $[Ru(bpy)_3]^{3+}$ with a sodium dodecylsulfate molecule instead of a water molecule. Also, the recently reported short-time (<5 ns) anomaly of the luminescence decay of $^*[Ru(bpy)_3]^{2+}$ at high light intensities, which is characterized by an additional rising component and was attributed to formation of a dd excited state,[11] would find a natural explanation in the described photoreaction of $[Ru(bpy)_3]^{3+}$—the presence of which is unavoidable under these circumstances—to give $^*[Ru(bpy)_3]^{2+}$.

Experimental Section

Laser flash photolysis was performed with an excimer laser at 308 nm, pulse width 25 ns, and/or an Nd:YAG laser at 355 or 532 nm, pulse width 5 ns. Our setup[12] allows one- and two-pulse (i.e., two-color) experiments and very high excitation intensities. Aqueous solutions of $[Ru(bpy)_3]^{2+}$ (typically, 3×10^{-5} M) at neutral pH were degassed and used under argon in a flow cell.

At 532 nm, the only photochemical reaction (even at our highest laser intensity, about 540 mJ cm^{-2}) is formation of $^*[Ru(bpy)_3]^{2+}$, which reveals its presence by its luminescence (emission range 540–760 nm, maximum at 610 nm) and quantitatively decays to the ground state $[Ru(bpy)_3]^{2+}$.[1] At 308 or 355 nm, photolysis of $[Ru(bpy)_3]^{2+}$ is accompanied by exactly the same luminescence spectrum, so $^*[Ru(bpy)_3]^{2+}$ is the only emitting species in our system. The absolute concentration of $^*[Ru(bpy)_3]^{2+}$ was obtained from the measured luminescence intensity at 610 nm by a calibration adapted from the literature.[9b] Inner-filter effects on the luminescence were not observed.

Absorption measurements gave no evidence for the occurrence of species other than $[Ru(bpy)_3]^{2+}$, $^*[Ru(bpy)_3]^{2+}$, the oxidized complex $[Ru(bpy)_3]^{3+}$, and $e_{aq}^{\bullet -}$ in our reaction. The absolute concentration of $e_{aq}^{\bullet -}$ was measured at 830 nm, where its extinction coefficient is still high, but no $^*[Ru(bpy)_3]^{2+}$ luminescence interferes. ε_{830} was determined relative to the absorption maximum, for which the extinction coefficient was taken from ref. [2]. Difference experiments were necessary because $^*[Ru(bpy)_3]^{2+}$ also absorbs weakly at 830 nm.[9b] After recording a series of intensity-dependent measurements, the solution was saturated with nitrous oxide, and the series was then immediately repeated with all other parameters kept constant. The electron absorption is the difference of two corresponding experiments at the same excitation intensity, one with N_2O and the other without. In N_2O saturated solution, the electrons are scavenged within a few nanoseconds, and converted into nonabsorbing species; the reaction is not otherwise affected, as shown by the unchanged luminescence of $^*[Ru(bpy)_3]^{2+}$.

$[Ru(bpy)_3]^{3+}$ was prepared and purified according to the literature method.[3] Alternatively, it was prepared in situ by oxidation of $[Ru(bpy)_3]^{2+}$ with lead(IV) dioxide or cerium(IV),[13] with a slight excess of the oxidant. It was used in acidic solution (pH 0), in which it is sufficiently stable for our measurements. Protons rapidly scavenge $e_{aq}^{\bullet -}$,[2] but do not influence our photoreaction in any other way. This was ascertained by control experiments on $[Ru(bpy)_3]^{2+}$, which gave practically the same intensity dependence of the triplet luminescence, regardless of pH.

The scavenging experiment with benzoic acid had to be carried out in aerated solution, because the reaction stops at a cyclohexadienyl radical in the absence of oxygen. The luminescence was measured with a Perkin-Elmer LS50B spectrometer (excitation wavelength, 300 nm).

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Characterization and Photochemistry of the Silane – Aluminum Complex $Al\cdot SiH_4$ and Its Photoproducts $HAlSiH_3$ and $AlSiH_3$ in a Solid Argon Matrix**

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The activation of C–H or Si–H bonds is an area of both fundamental and industrial interest.[1] The first transition metal complex with an η^2-bound SiH_4 group, *cis*-[$Mo(\eta^2\text{-}SiH_4)(CO)(R_2PC_2H_4PR_2)_2$] (**1**; R = Ph, *i*Bu, Et),[2] was synthesized in 1995. Remarkably, in solution **1** is in equilibrium with its tautomer [$MoH(SiH_3)(CO)(Et_2PC_2H_4PEt_2)_2$], which features a seven-coordinate Mo center, as evidenced by the results of variable-temperature ^1H and ^{31}P NMR spectroscopy. Since then other systems have been found such as [$(PR_3)_2H_2Ru(SiH_4)RuH_2(PR_3)_2$] (R = Cy, *i*Pr), in which the SiH_4 ligand bridges two dihydridobis(phosphane)ruthenium units.[3]

On the basis of these remarkable experimental results, such silane complexes have also attracted attention from theorists.[4] It is commonly agreed that the silane–metal bond comprises a dative bond involving the σ(Si–H) orbital and a vacant metal orbital of appropriate symmetry and a d(M)→σ*(Si–H) back donation (M = transition metal). However, for main group elements like Al such an interaction is not plausible; here only participation of p orbitals can be considered, and therefore one expects a much weaker bond between the metal atom and ligand. However, preliminary experiments suggested that such a complex might be of sufficient strength to allow its generation and investigation in solid inert gas matrices at temperatures near 10 K.[5] Here we report on the results leading to the detailed characterization of $Al\cdot SiH_4$ (**A**) and its photoproducts, the Al^{II} species $HAlSiH_3$ (**B**) and the Al^{I} species $AlSiH_3$ (**C**) in a solid Ar matrix at 12 K.

Al atoms generated in a Knudsen cell at 1100 °C were codeposited with argon gas doped with 0.1–5 % SiH_4 on a polished copper block kept at 12 K. The matrix was subsequently exposed to several photolysis cycles at different wavelengths and IR spectra were recorded before and after each photolysis. Since some of the observed product absorptions lie close to those of SiH_4, it proved important to run experiments with very low concentrations of SiH_4 in the matrix (0.1 % SiH_4 in Ar, Figure 1) to narrow widths of the SiH_4 bands. As low concentrations, however, lead to weak signals, experiments were also carried out with high (1.5 % SiH_4 in Ar, Figure 2) concentrations of SiH_4.

In addition to absorptions of SiH_4,[6] the spectrum taken upon deposition displayed bands of a spontaneously formed product **A** of the reaction of Al atoms with SiH_4 (Figure 1). These bands were located at 2181.1, 2174.5, 2131.4, 901.7, and 892.4 cm^{-1} (most intense). Some of these absorption bands are not visible in the original spectra because they are masked by SiH_4 absorptions; however, they are clearly visible in the difference spectra shown in Figure 1b. Photolysis at $\lambda \approx$ 410 nm resulted in the rapid disappearance of these bands, and the appearance of several new absorption bands at 2158.4, 2127.6, 2113.3, 1780.9, and 846.2 cm^{-1}, which all belong to a single second reaction product **B**. The strongest absorption at 1780.9 cm^{-1} lies in a region characteristic of ν(Al–H) stretching modes in Al^{II} species ($HAlNH_2$ 1761.1,[7] $HAlCH_3$ 1764/1746,[8] HAlH 1806.3/1769.5,[9] and $HAlPH_2$ 1768.2 cm^{-1}[10]). The absorption at 846.2 cm^{-1} lies in the expected region for δ(SiH_3) deformation modes ($HHgSiH_3$ 867.8/871.4 cm^{-1}[11]).[12]

Photolysis at $\lambda \approx 580$ nm resulted in the disappearance of the absorptions of **B** and the reappearance of those of **A**. Renewed photolysis, at $\lambda \approx 410$ nm, caused the absorptions of **A** to vanish again and those of **B** to regain most of their initial intensity. Thus **A** and **B** can be interconverted almost reversibly.

Photolysis of the matrix with broadband UV/Vis ($\lambda = 200$–800 nm) resulted in the decay of the absorptions of **B**. An increase in the concentration of **A** was not observed here, instead two new absorptions appeared at 836.2 and 2151.3 cm^{-1} (Figure 2), which can be assigned to the photo-

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