The Triamminecopper(I) Ion in Aqueous Solution. Spectral and Photochemical Evidence for CTTS Behavior

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The equilibrium constant for the stepwise formation of $Cu(NH_3)_3^+$ was determined at 1 M ionic strength, with a value of 0.050, and its ultraviolet spectrum was resolved in the 210–340-nm region. Gaussian resolution of the absorption spectrum gave weak bands at 295 and 270 nm, assumed to be CTTS bands, and a stronger band at 229 nm. Laser flash experiments at 266 and 308 nm yielded transients in solutions containing no electron scavengers with absorption spectra resembling that of the hydrated electron. Continuous-photolysis studies using ammonium ions as electron scavengers resulted in geminate-pair scavenging kinetics, which indicate that the ammonium ion is a much better scavenger than previously reported. The results of the dependence of quantum yield on temperature are consistent with a geminate pair consisting of oppositely charged species. The diamminecopper(I) species appears not to be photoactive in the 240–320-nm region. The action spectrum of the triammine complex conforms to the CTTS assignment of the 295- and 270-nm bands.

Introduction

Although the diamminecopper(I) ion has been known since 1901,[2] it is only recently that the existence of triamminecopper(I) has been observed. In 1984 we reported[3] that the molar extinction coefficient at 290 nm of solutions of $CuClO_4$ in aqueous ammonia increased linearly with molar ammonia concentration, at a constant ionic strength of 1 M, indicating the presence of the equilibrium

$$Cu(NH_3)_2^+ + NH_3 = Cu(NH_3)_3^+ \quad (1)$$
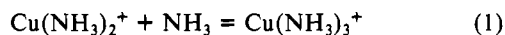
We estimated the equilibrium constant, K, to be no larger than 0.002 and published the ultraviolet absorption spectrum of the diammine complex and a qualitative spectrum of the triammine complex, i.e. $K(\epsilon_3 - \epsilon_2)$ vs wavelength, where ϵ_2 and ϵ_3 are the molar extinction coefficients of the di- and triammine complexes, respectively. Subsequently, Bjerrum showed,[4] using activity coefficients for aqueous ammonia obtained from Perman's vapor pressure data,[5] that our estimate of K was too small by about 1 order of magnitude. Since Bjerrum used ammonia activities in low and variable ionic strength solutions for the determination of equilibrium constants in systems that were at ionic strengths of about 0.5 M, we felt it was necessary to remeasure K, using our spectrophotometric data at 1 M ionic strength and ammonia activities that we would determine at the same ionic strength. This would then allow us to resolve the spectrum of $Cu(NH_3)_3^+$.

Our interest in the resolved spectrum of $Cu(NH_3)_3^+$ stems from the fact that irradiation of an equilibrated solution of the two complexes in the ultraviolet region results in photooxidation of copper in the presence of hydrated-electron scavengers such as N_2O and NH_4^+,[3] suggesting that the absorption bands may be charge-transfer-to-solvent (CTTS) in nature. We have already established the CTTS nature of UV bands in the anionic halocuprates $CuCl_2^-$, $CuCl_3^{2-}$,[6,7] $CuBr_2^-$, and $CuBr_3^{2-}$.[8] The theory of CTTS transitions has been extensively developed for anions,[9] but, except for some Ru(II) complexes studied by Ford et al.,[10,11]

few cations have shown CTTS behavior. This report, then, presents spectral and photochemical evidence that the UV absorption of $Cu(NH_3)_3^+$ in the 240–340-nm region may be attributed to CTTS transitions.

Experimental Section

Determination of Ammonia Activities and the Equilibrium Constant. Solutions of varying ammonia concentration at 1 M ionic strength were prepared by mixing concentrated aqueous ammonia solution with a concentrated standard $NaClO_4$ solution and diluting to a desired volume. Such solutions were placed in a 250-mL flask in a water bath thermostated to 25 °C and pumped off for about 5 min to remove all air. The vacuum line was closed and the system allowed to equilibrate for about 10 min, after which the vapor pressure was measured by using a closed mercury manometer. An aliquot was then taken from the flask and titrated with standard hydrochloric acid to determine the molar ammonia concentration. The measured vapor pressures were corrected for the vapor pressure of water by subtracting the vapor pressure measured in a 1 M ionic strength solution containing no ammonia. A plot of ammonia vapor pressure versus concentration (Figure 1) is linear up to a concentration of about 2 M, yielding a Henry's law constant, K_H, of 12.4 Torr M^{-1}. A polynomial fit to all the vapor pressure data in Figure 1 up to 12 M ammonia concentration yields the expression (where c is the ammonia concentration)

$$p = 1.58 + 12.4c - 1.66c^2 + 0.937c^3 - 0.119c^4 + 0.00529c^5 \quad (2)$$

from which any ammonia activity, a, within this concentration range can be calculated by using

$$a = p/K_H \quad (3)$$

Using the extinction coefficients at 290 nm from our previous study[3] and the expresson for the measured extinction coefficient in terms of individual extinction coefficients, equilibrium constant, and free ammonia activity

$$\epsilon = \epsilon_3 + (\epsilon_2 - \epsilon_3)/(1 + Ka) \quad (4)$$

we calculated the value of K that gives the best linear fit. From this, and the spectra at different free ammonia activities, the resolved spectra were calculated. The free ammonia actvity was calculated for each solution by correcting the total added ammonia concentration for the ammonia bound in the two copper complexes and then applying eq 2 and 3. Digitized spectra were obtained on a Beckman ACTA M-VI or Hewlett-Packard 8451 spectrophotometer.

Continuous Photolysis. The photolysis setup has been described previously.[6] Hydrogen evolution rates were measured with a recording gas volumeter.[12] Because inner-filter effects from the Cu(II) formed during photolysis can be significant in photolysis of these ammine complexes,[3] a 10-cm quartz cuvette with a volume of about 30 mL was used so that during a typical run the amount of Cu(II) remained small compared to the total amount of copper in solution, resulting in nearly constant gas evolution rates. The long cuvette, which was stirred by a reciprocating magnetic stir bar, also ensured that nearly 100% of the incident light was

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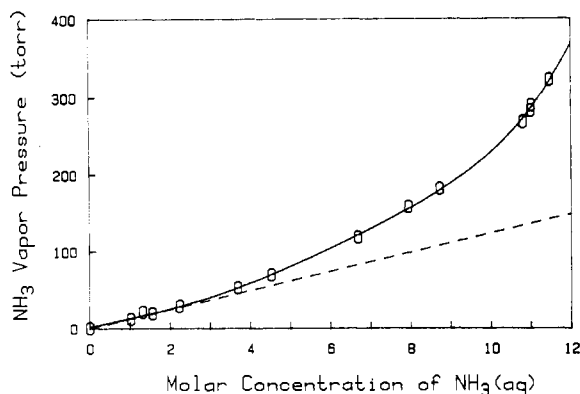(8) To be submitted for publication.
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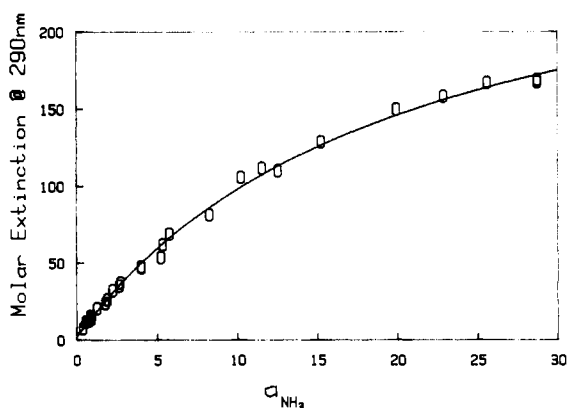(10) Matsubara, T.; Ford, P. C. *Inorg. Chem.* **1978**, *17*, 1747.

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Figure 1. Vapor pressure of NH_3 at 25 °C for aqueous ammonia solutions at 1 M ionic strength ($NaClO_4$) versus concentration (M) of $NH_3(aq)$. The dashed line is a Henry's law plot.

Figure 2. Molar extinction coefficient at 290 nm, 25 °C, for 0.02 M solutions of $CuClO_4$ at 1 M ionic strength versus activity of $NH_3(aq)$.

absorbed. Photolytes were prepared by dissolving a weighed amount of CuCl (which does not form chlorocuprates in these solutions[3]) in an argon-bubbled solution containing the requisite amounts of $NaClO_4$, NH_3, and $HClO_4$ to give the desired ionic strength and NH_3 and NH_4^+ concentrations and to give copper concentrations of about 0.02 M. The tris(oxalato)ferrate(III) actinometer[13] was used to determine the light intensities at the various wavelengths.

Laser Flash Photolysis. Flash experiments were carried out at the Radiation Laboratory of the University of Notre Dame, utilizing the frequency-quadrupled Nd–YAG laser output at 266 nm or the 308-nm output from a XeCl excimer laser. Both laser systems have the capability of measuring transient absorbance and luminescent lifetimes and time-resolved spectra at delay times greater than about 10 ns. Solutions used were similar to those described above.

Results and Discussion

Equilibrium Constant and Resolved Spectra. Figure 2 shows a plot of extinction coefficient at 290 nm taken from our earlier paper[3] versus ammonia activity, along with a plot of eq 4 in which the optimum value of K at 1 M ionic strength is 0.050, $\epsilon_2 = 1.8$, and $\epsilon_3 = 290$, all with 10% error limits. These values are in reasonable agreement with those obtained by Bjerrum;[4] i.e., 0.038 $\leq K \leq$ 0.046, $\epsilon_2 = 1.3$, and 269 $\leq \epsilon_3 \leq$ 343. The resulting spectra of $Cu(NH_3)_2^+$ and $Cu(NH_3)_3^+$ are shown in Figure 3, and these are consistent with those published earlier.[3]

It is interesting that while the diammine complex has almost no spectral features in the 220–340-nm range, the triammine complex shows at least three absorption bands. The features of these bands, summarized in Table I, were obtained by replotting the spectrum of $Cu(NH_3)_3^+$ in terms of wavenumber rather than wavelength and computer-resolving into four Gaussian bands,[7] as shown in Figure 4. It is perhaps worth comparing this spectrum with that of $CuCl_3^{2-}$, since the ligands in both complexes have similar electronic structures, i.e., no π electrons, which might cause some MLCT behavior. The main spectral features of the trichloro

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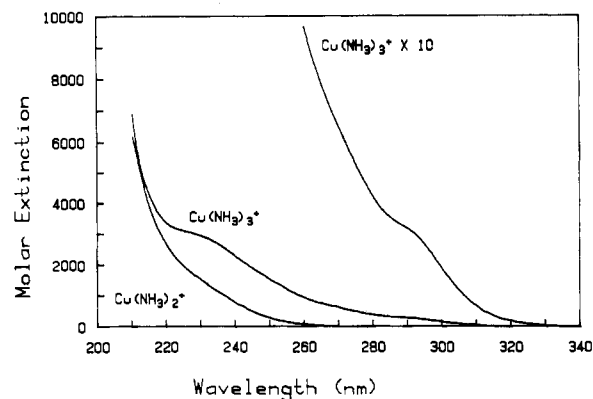
Figure 3. Resolved UV spectra of $Cu(NH_3)_2^+$ and $Cu(NH_3)_3^+$ at 1 M ionic strength.
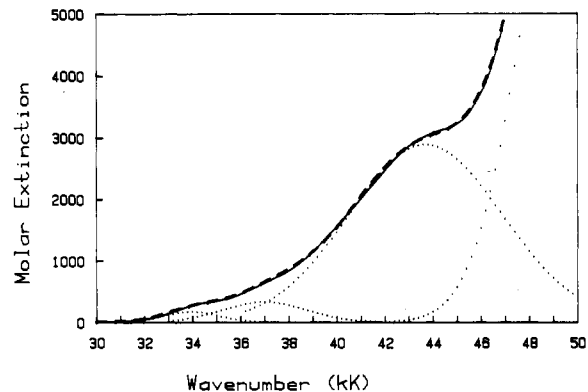
Figure 4. Gaussian components of the wavenumber spectrum of $Cu(NH_3)_3^+$.

Table I. Spectral Features of Aqueous Solutions of $Cu(NH_3)_3^+$ in the 220–340-nm Range

| λ_{max}, nm	$\bar{\nu}_{max}$, 10^3 cm^{-1}	ϵ	half-bandwidth, 10^3 cm^{-1}	osc strength
295	33.95	170	2.7	0.0018
270	37	330	4.05	0.0043
229	43.7	2880	7.5	0.051

complex consist of two bands in this wavelength range: at 274 and 228 nm with oscillator strengths of about 0.059[7] and 0.025,[14] respectively. It thus appears that both of these trigonal complexes exhibit both bands at about the same energies, but the transition probabilities, as indicated by the oscillator strengths, differ. The nature of the higher energy transition, at 228–229 nm, which becomes more probable by about 2× for the triammine complex, is unclear. On the other hand, the band at 270–274 nm displays the properties of the CTTS transition seen in the trichlorocuprate species,[6] although its oscillator strength is considerably reduced. The weakest band in the triammine complex centered at 295 nm has not been observed in the trihalocuprate(I) complexes,[6,15] but that could be the result of the much stronger 274-nm band in those complexes overshadowing such a weak adjacent band. In fact, a 290-nm transition is observed with high oscillator strengths in tetrameric halocuprates such as $Cu_2Br_6^{4-}$ [8] and CuI_4^{3-},[15b] suggesting a strong dependence of this transition on geometry. These results suggest also that the charges of the complexes play a strong role in probabilities of the various CTTS transitions, with anions having higher oscillator strengths than cations.

Laser Flash Photolysis. Figure 5 shows the transient absorption at 680 nm of an aqueous solution containing 0.02 M CuCl and 2 M NH_3, bubble-degassed with argon, and flashed with the

(14) Unpublished results.
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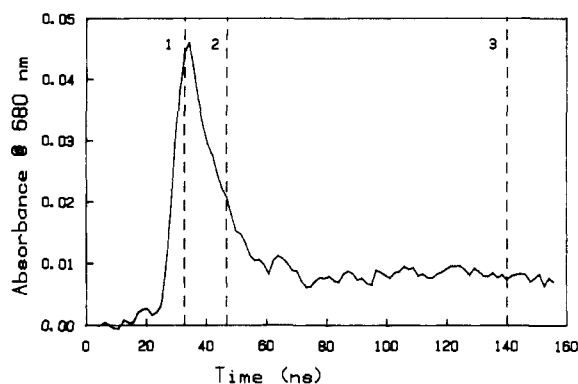
Figure 5. Decay of 680-nm absorbance after exposure to 10-ns laser pulse at 266 nm, for solution that is 0.02 M CuCl in 2 M NH₃ at 1 M ionic strength.
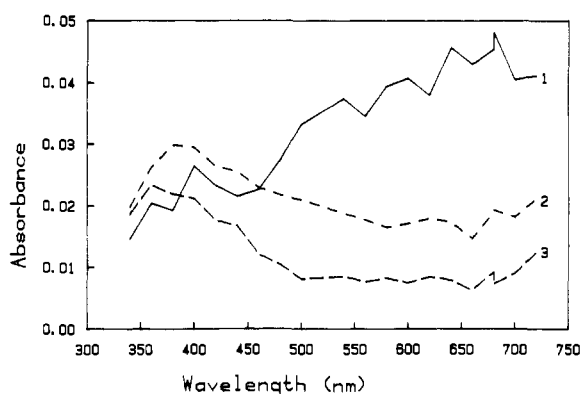

Figure 6. Time-resolved spectra of transients generated under the same conditions and at the time markers shown in Figure 5.

Figure 7. Difference between spectra 1 and 3 from Figure 6 (✻) and the normalized spectrum of hydrated electron (---).

Figure 8. Dependence of quantum yield at 274 nm for reaction 5 in 2 M NH₃, 1 M ionic strength solution as a function of $[NH_4^+]^{1/2}$.

266-nm output of the Nd–YAG laser. At this irradiating wavelength the two complexes absorb light in a 3:2 ratio for the triammine-compared to the diamminecopper(I) ion. The dashed lines show markers used to generate the time-resolved spectra shown in Figure 6. Both figures indicate that at least two transients are formed: a short-lived one with maximum absorbance at about 680 nm and lifetime of about 10–15 ns and a long-lived species with maximum at 380 nm and a lifetime determined in a separate experiment to be 9200 ns. Spectrum 1 in Figure 6 suggests the spectrum of a hydrated electron,[16] which has a maximum absorbance at 680–700 nm, but the absorbance in the short wavelength portion of the transient is too high to give a good match. On the other hand, if we assume that the long-lived species (spectrum 3) forms very quickly and parallel to the short-lived species, as suggested by the lack of an isosbestic point in the three spectra, then it is reasonable to a first approximation to subtract spectrum 3 from spectrum 1 to get a clearer picture of the spectrum of the short-lived species. Figure 7 shows the result along with the normalized published spectrum of a hydrated electron,[16] giving reasonable agreement except for the somewhat high absorbance in the 480–600-nm region. The short-lived transient spectrum obtained from the excimer laser at 308 nm, where the only absorber is $Cu(NH_3)_3^+$, similarly displayed a peak at about 680 nm but with considerably more noise because of the low absorbance of the solution at this laser wavelength.

When a solution with the same copper and ammonia concentration, but containing 1 M NH_4^+, was flashed with the 308-nm laser, a transient different from that seen in the solution, above, was produced, with a lifetime of about 20 ns and an aborbance peak at about 590 nm. Although this spectrum resembled that of the NH_2 radical, which has a maximum absorption at 530 nm with $\epsilon = 81$,[17] its first-order decay and rather high absorbance suggest an intermediate with a much larger extinction coefficient. Without speculating about the nature of this transient species,
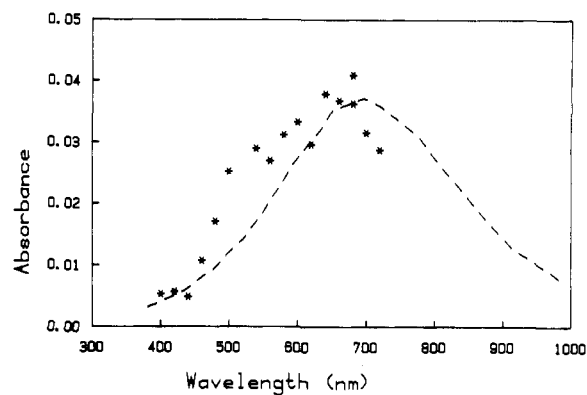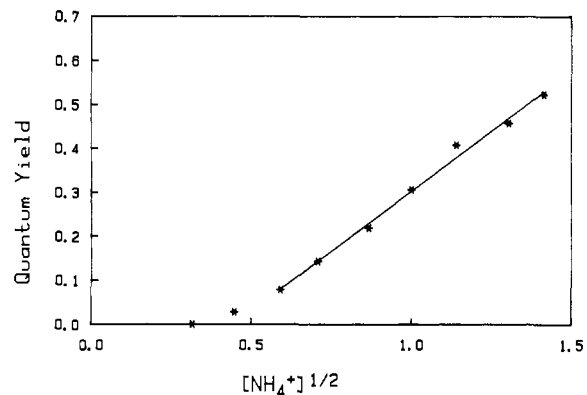
we can assume that its presence would be expected in flashed aqueous ammonia solutions because of their small NH_4^+ concentrations and could explain the bump in the hydrated electron spectrum of Figure 7.

Continuous Photolysis. Quantum yields were determined for the net reaction

$$Cu(NH_3)_3^+ + NH_4^+ \rightarrow Cu(NH_3)_3^{2+} + \tfrac{1}{2}H_2(g) + NH_3 \quad (5)$$

We were rather surprised to observe quantum yields for these studies that are considerably higher than the qualitative results we observed earlier,[3] but these experiments are much more reliable because of the minimization of inner-filter effects. Dependence of the quantum yield at 274 nm on the square root of the ammonium ion concentration at 2 M ionic strength (Figure 8) shows that there is a concentration region in which the system obeys geminate-pair recombination-scavenging kinetics, as modeled by Noyes[18,19] and Jortner et al.[20] Both models equate the slope of such a plot, $d\Phi/dS^{1/2}$, in a system in which a member of a radical geminate pair is reactively scavenged, to the quantity $2a(\pi k_s)^{1/2}$, where k_s is the second-order rate constant for scavenging and a is a diffusion parameter with a value of about 1.6×10^{-6} s$^{1/2}$. The Jortner model also adds a factor of 2Γ to the slope, where Γ is a leveled-off or diffusion-limited quantum yield at high scavenger concentration, a value not reached in Figure 8. Using the Noyes model, and assuming that the mechanism, below, for reaction 5 doubles the quantum yield by requiring a thermal oxidation of copper(I) for each light-initiated oxidation, as is the case in the chlorocuprate(I) photolysis,[21,22] we estimate from the slope of this plot a value of k_s of about 2.3×10^9 M^{-1} s^{-1}. This value is about 1 order of magnitude smaller than the rate constant for reaction of e_{aq}^- by H_3O^+[23] but considerably larger than the value of $3 \times$

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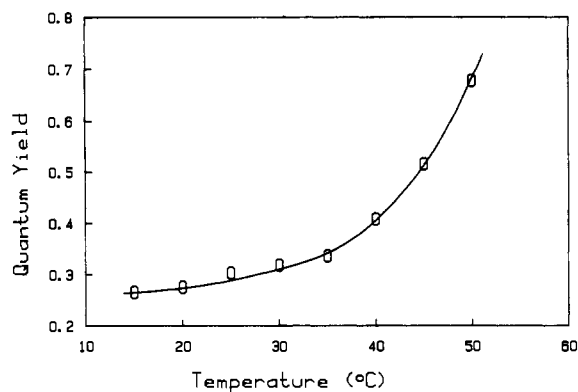(17) Pagsberg, P. B. *RISO-256 Rep.* **1972**, 209.

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Figure 9. Temperature dependence of quantum yield for reaction 5 at 274 nm in solutions that are 1 M NH₄ClO₄, 2 M NH₃, and 0.015 M CuCl at 1 M ionic strength.

10^6 M^{-1} s^{-1} reported for ammonium ion.[24] Thus, our results suggest that if dihydrogen is produced by ammonium ion scavenging of hydrated electrons, then ammonium is a much better electron scavenger than previously thought.

It seems reasonable to suppose that the geminate-pair scavenging reaction is

$$Cu(NH_3)_3^{2+}\cdots e_{aq}^- + NH_4^+ \rightarrow Cu(NH_3)_3^{2+} + NH_4 \quad (6)$$
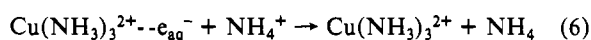
followed by the formation of a hydrogen atom

$$NH_4 \rightarrow NH_3 + H^\bullet \quad (7)$$

The formation of dihydrogen might result from the reaction of ammonium ions with a copper(II) hydride intermediate formed by reaction of H$^\bullet$ with other copper(I) species, similar to the chlorocuprate photolysis mechanism[21] or from the reaction of copper(I) with H$_2^+$ formed by the reaction of ammonium ions and H$^\bullet$.

The results of the temperature dependence of quantum yield at 274 nm (Figure 9) are consistent with a geminate pair consisting of oppositely charged ions, since the electrostatic attraction would tend to impart a positive enthalpy of dissociation. These results are to be contrasted to the opposite temperature effect observed in the photolysis of the chlorocuprate(I) system[6] which forms a geminate pair of two anions in the case of CuCl$_3^{2-}$ or a neutral species and an anion in CuCl$_2^-$.
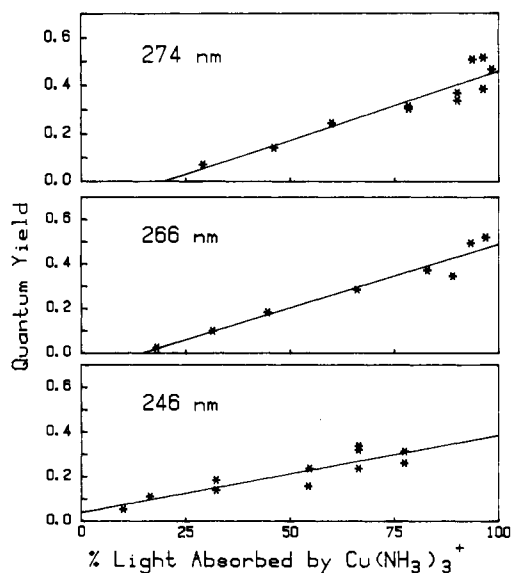
The dependence of quantum yield on ammonia activity allows the computation of the individual quantum yields, Φ_2 and Φ_3, of the two species in equilibrium, since they are related to the observed quantum yield, Φ, through the fractions of light absorbed by each complex, f_2 and f_3

$$\Phi = f_2\Phi_2 + f_3\Phi_3 \quad (8)$$

where $f_2 = \epsilon_2 c_2/(\epsilon_2 c_2 + \epsilon_3 c_3)$ and c_2 and c_3 are the equilibrium concentrations of the two species. It can be shown that this equation becomes

$$\Phi = \Phi_2 + (\Phi_3 - \Phi_2)\epsilon_3 Ka/(\epsilon_2 + \epsilon_3 Ka) \quad (9)$$

Application of this expression was rather successful at the three irradiating wavelengths, 246, 266, and 274 nm, in which all the light was absorbed by the sample, as shown in Figure 10. Within experimental error, one can deduce that the diammine complex is not photoactive at these three wavelengths. The quantum yield

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Figure 10. Quantum yield versus % light absorbed by Cu(NH₃)₃⁺ at three wavelengths, in solutions that are 1 M NH₄ClO₄, 0.015 M CuCl, 1 M ionic strength, and variable ammonia concentration.
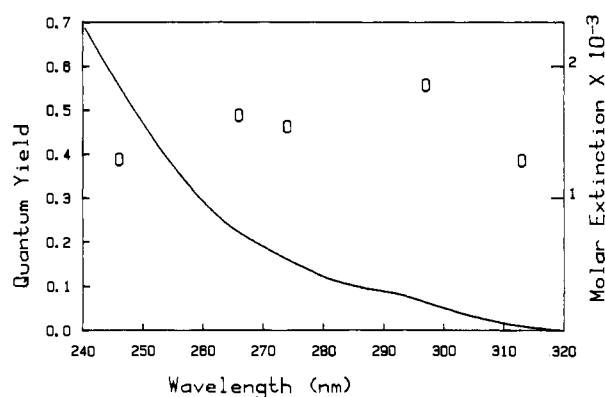
Figure 11. Quantum yield for photooxidation of Cu(NH₃)₃⁺ versus wavelength, in solutions that are 1 M NH₄ClO₄, 0.015 M CuCl, 1 M ionic strength, and variable ammonia concentration. The absorption spectrum of Cu(NH₃)₃⁺ is shown for comparison.

of Cu(NH₃)₃⁺ is obtained by extrapolation to 100% light absorbed by this complex. At the two longer wavelengths, 297 and 313 nm, the lack of complete absorption by the sample except in the most concentrated ammonia solutions did not allow such linear plots, but since the absorbance of the diammine complex is essentially zero at these wavelengths, the observed quantum yield can be assumed to be that of the triammine complex. Thus, an action spectrum (Figure 11) was plotted, along with the absorption spectrum of the triammine complex, to show the correlation between them. These results are very similar to those obtained earlier[3] for the N₂O-scavenging studies, and they lend further support to the assertion that the 240–320-nm region of the triamminecopper(I) absorption spectrum is CTTS.