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Spectroscopic Confirmation of the Tetrahedral Geometry of $\text{Ag}(\text{H}_2\text{O})_4^+$

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Ultraviolet absorption studies of aqueous solutions of the tosylate, sulfate, perchlorate, and tetrafluoroborate salts of Ag^+ show that three bands at 225, 210, and 192 nm are attributable to isolated Ag^+ ions. These bands are believed to emanate from the parity-forbidden $(4d^9 5s) {}^1D \leftarrow (4d^{10}) {}^1S$ excitation of Ag^+ , subject to ligand field effects of the primary hydration sphere. These bands have essentially temperature-independent oscillator strengths, which suggests that the static ligand field does not have a center of inversion. A tetrahedral arrangement of four water molecules in the primary hydration sphere, proposed earlier as a result of ESR studies, is consistent with these temperature-independent optical data. These same Ag^+ bands appear (red shifted) in methanol solutions, which is again consistent with ESR studies showing a primary solvation sphere of four molecules and suggests that these molecules are arranged tetrahedrally. The absence of these bands in acetonitrile solutions corroborates the Dewar-Chart bonding mechanism proposed to explain the preferential solvation of Ag^+ by acetonitrile over water. The oscillator strength of the 225-nm band increases dramatically and linearly as the mole percent of ethanol in water/ethanol solvent is increased. These observations suggest that solvation of Ag^+ by ethanol has a local symmetry that is less than tetrahedral and that the "preferential solvation" effect observed at 13 mol % ethanol by ESR is attributable to a polycrystalline glass transition.

Introduction

The ultraviolet spectrum of aqueous Ag^+ has received very little attention, although the structure of the primary hydration shell of Ag^+ has been studied intensively. This paper presents and characterizes the ultraviolet absorption bands of aqueous Ag^+ at wavelengths >185 nm. The multiplet structure and the temperature dependence of the oscillator strength are interpreted in terms of ligand field effects as they relate to the symmetry of the primary hydration shell. A comparative study of this ultraviolet Ag^+ multiplet in methanol, ethanol, aqueous ethanol, and acetonitrile permits the interpretation of these optical results to be directly correlated with solvation analyses based upon a variety of ESR experiments.

The only previously published study of the optical properties of aqueous Ag^+ appears to be that of Fromherz and Menschick,¹ who reported a single band at 210 nm for concentrated aqueous AgClO_4 solutions. The spectra of substitutional Ag^+ ions in solid-state matrices, however, have been extensively studied.² The corresponding multiplets are believed to emanate from the Laporte-forbidden $(5s4d^9) {}^1D, {}^3D \leftarrow (4d^{10}) {}^1S$ intraionic excitation. The observed oscillator strength is borrowed from higher lying Laporte-allowed transitions either by vibronic coupling with odd-parity phonons or by static coupling with crystal fields having no inversion center. The vibronic and static intensity borrowing mechanisms can be discerned experimentally by measuring the temperature dependence of the oscillator strength. The oscillator strength of a Laporte-forbidden transition increases with increasing temperature if a vibronic mechanism is operating. In the static borrowing case the oscillator strength remains constant with increasing temperature. The primary hydration of Ag^+ has, until recently, been considered to be low. Vapor pressure,³ isotope fractionation,⁴ polarizability,⁵ and nuclear magnetic resonance were used to deduce primary hydration numbers of 2 or less for aqueous Ag^+ .⁶⁻⁹ In the

past several years, however, electron spin resonance has been used to deduce a primary hydration shell containing four water molecules, and there is now good agreement on this result among several laboratories.¹⁰⁻¹³ Similar ESR techniques have been used to show that Ag^+ solvation in methanol¹⁴ and in acetonitrile¹⁵ also contains four solvent molecules in the primary solvation sphere, that the primary solvation shell in ethanol has fewer than four molecules,¹⁶ and that Ag^+ in aqueous ethanol shows a preferential (ethanol) solvation effect¹⁶ in solutions >13 mol % ethanol.

Experimental Section

Materials. Spectrograde methanol, ethanol, and acetonitrile were obtained from Kodak Laboratory Chemicals. AgClO_4 and LiClO_4 were obtained from Alfa, AgBF_4 was obtained from Chemical Procurement Laboratories, and NaBF_4 was obtained from Baker and Adamson. These materials were used without further purification. The concentrations of stock solutions of the hygroscopic AgClO_4 and AgBF_4 were calibrated by potentiometric titration with standard KCl. Ag_2SO_4 and K_2SO_4 were obtained from Baker and Adamson, and $\text{Ag}(\text{pts})$ and $\text{Na}(\text{pts})$ (pts^- = tosylate anion) were obtained from Kodak Laboratory Chemicals. Ag_2SO_4 , K_2SO_4 , $\text{Ag}(\text{pts})$, and $\text{Na}(\text{pts})$ were recrystallized from hot distilled water. Ag_2SO_4 and $\text{Ag}(\text{pts})$ were recrystallized in the dark, and the hot $\text{Ag}(\text{pts})$ solution was treated with decolorizing carbon and filtered before recrystallization.

Spectroscopy. UV spectra were recorded on a Perkin-Elmer 330 spectrophotometer. The monochromators were purged with nitrogen. Sample and reference solutions were placed in quartz cuvettes with 0.1- or 1.0-cm path length. Variable-temperature spectra were obtained by using

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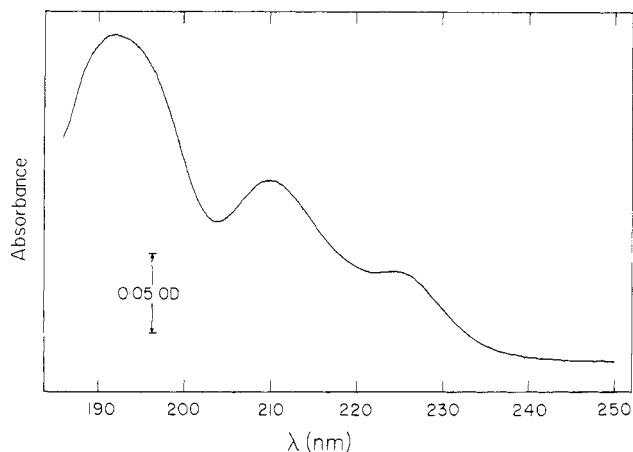


Figure 1. Aqueous Ag^+ UV band system at 25 °C. This spectrum was obtained for 1.33×10^{-3} M sample and reference solutions, respectively, of AgBF_4 and NaBF_4 in 0.1-cm path length cells.

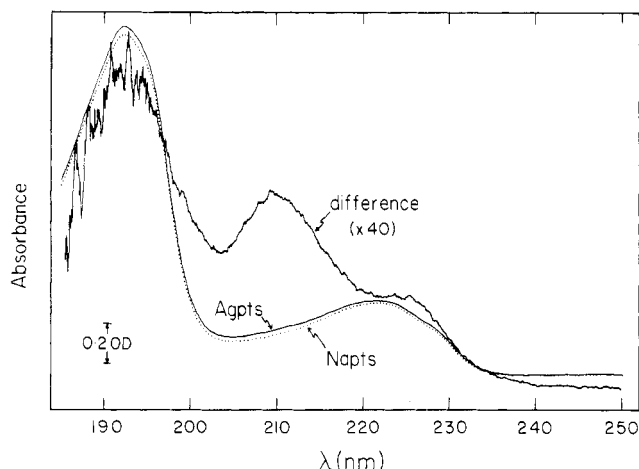


Figure 2. Illustration of the aqueous Ag^+ UV band system obtained by difference between 3.176×10^{-4} M $\text{Ag}(\text{pts})$ and $\text{Na}(\text{pts})$ solutions in 0.1-cm pathlength cells. The $\text{Ag}(\text{pts})$ and $\text{Na}(\text{pts})$ spectra, in which the absorption of pts^- dominates, were recorded against a water reference.

thermostated cuvette holders and a Braun-Frigomix circulating system.

Results

The band system of aqueous Ag^+ is illustrated in Figure 1 for an aqueous AgBF_4 sample. Three bands at 192 nm (6.46 eV), 210 nm (5.90 eV), and 225 nm (5.51 eV) are clearly resolved. The 192-nm band has a full width at half-maximum intensity of $\sim 3240 \text{ cm}^{-1}$ (0.4 eV), and the 210- and 225-nm bands have a combined width of $\sim 5000 \text{ cm}^{-1}$ (0.62 eV). The 192-nm band has an average peak extinction of $1430 \text{ M}^{-1} \text{ cm}^{-1}$ (cf. Figure 3) and hence an approximate oscillator strength of 0.02.¹⁷ The 210- and 225-nm bands have an average peak extinction of $625 \text{ M}^{-1} \text{ cm}^{-1}$ (cf. Figure 3) and therefore an approximate combined oscillator strength of 0.013.¹⁷ The band system as a whole therefore has an oscillator strength of about 0.033. The same three bands are observed in aqueous difference spectra of $\text{Ag}(\text{pts})$ and $\text{Na}(\text{pts})$ solutions (Figure 2) as well as in aqueous difference spectra of Ag_2SO_4 vs. K_2SO_4 and of AgClO_4 vs. LiClO_4 . Figure 3 summarizes the peak extinction coefficients measured for different concentrations of aqueous solutions of these argentous salts at 25 °C. The

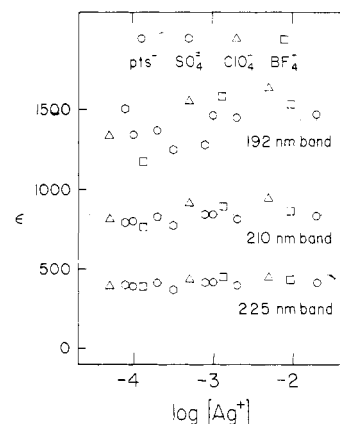


Figure 3. Illustration of the band maxima extinction coefficients measured for aqueous argentous tosylate, sulfate, perchlorate, and tetrafluoroborate solutions. The dotted lines illustrate the average values of 1430, 840, and $410 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, for the 192-, 210-, and 225-nm bands.

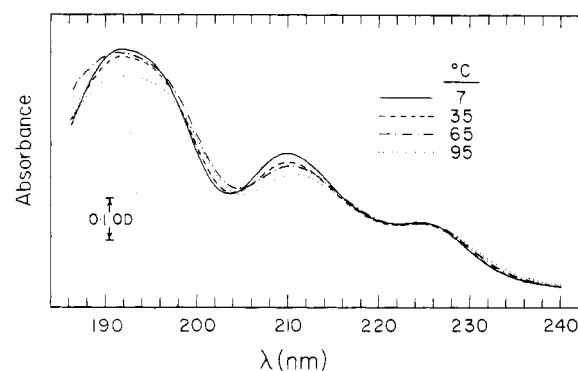


Figure 4. Temperature dependence of the aqueous Ag^+ UV band system. These spectra were obtained for a 4.01×10^{-4} M Ag_2SO_4 sample measured against 4.01×10^{-4} M K_2SO_4 in 1-cm path length cells.

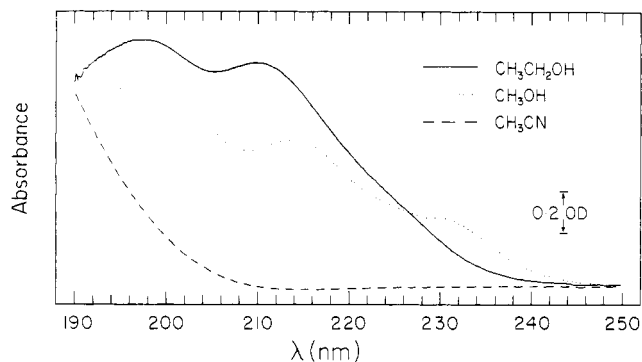


Figure 5. Illustration of the Ag^+ UV band system obtained in three nonaqueous solvents at 25 °C. AgClO_4 sample solutions were run against LiClO_4 reference solutions in 0.1-cm path length cells. The solution concentrations were 7.7×10^{-3} , 7.0×10^{-3} , and 7.2×10^{-3} M in $\text{CH}_3\text{CH}_2\text{OH}$, CH_3OH , and CH_3CN , respectively.

averages of the measured extinction coefficients (dotted lines) are 1430, 840, and $410 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, for the 192-, 210-, and 225-nm bands. The temperature dependence (7–95 °C) of this band system is illustrated in Figure 4 for an aqueous Ag_2SO_4 (K_2SO_4) sample (reference). There appears to be a slight decrease in the overall intensity with increasing temperature. Increasing temperature also appears to impart a slight red shift to the entire system.

Spectra of AgClO_4 solutions in ethanol, methanol, and acetonitrile at 25 °C are illustrated in Figure 5. The band system observed in methanol is nearly identical with that

(17) Approximate oscillator strengths are obtained from the formula $f = 4.3 \times 10^{-9} \epsilon \Delta\nu_{1/2}$ where ϵ is the peak extinction coefficient in units of $\text{M}^{-1} \text{ cm}^{-1}$ and $\Delta\nu_{1/2}$ is the full width at half-maximum in units of cm^{-1} .

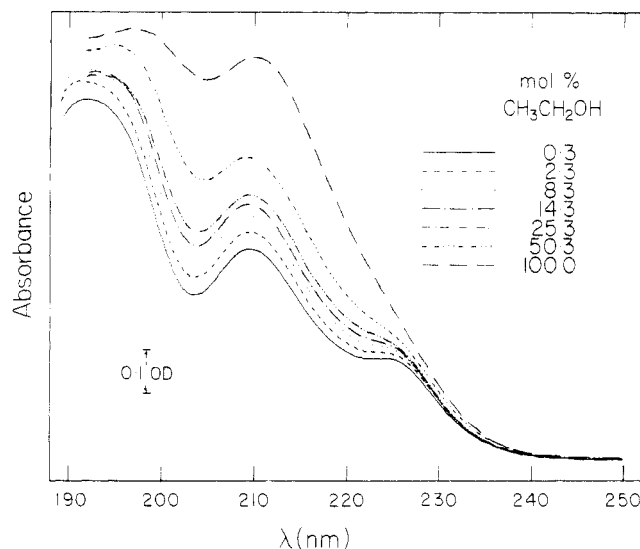


Figure 6. Illustration of the Ag^+ UV band system at 25 °C in mixed $\text{H}_2\text{O}/\text{CH}_3\text{CH}_2\text{OH}$ solvents; 6.5×10^{-4} M AgClO_4 and LiClO_4 solutions in 1-cm path length cells were used in the sample and reference beams, respectively.

observed in water. This spectrum as a whole, however, is red shifted by about 800 cm^{-1} relative to the aqueous spectrum. The band peaks in methanol occur at 197, 214, and 231 nm with approximate extinction coefficients of 1400 , 990 , and $460 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The band system observed in ethanol is similar to those in water and in methanol, except that the relative intensity of the middle band ($\epsilon_{210} \sim 1400 \text{ M}^{-1} \text{ cm}^{-1}$) is close to that of the high-energy band ($\epsilon_{197} \sim 1420 \text{ M}^{-1} \text{ cm}^{-1}$), and the low-energy band appears as an unresolved shoulder. In the acetonitrile solution, only a high-energy absorption edge is observed. At $\sim 214 \text{ nm}$, the acetonitrile solution of AgClO_4 is slightly less dense optically than the LiClO_4 reference solution.

The effects of changes in aqueous ethanol solvent composition on the Ag^+ UV band system are illustrated in Figures 6 and 7. No sudden changes in the spectra are observed at 13–14 mol % $\text{CH}_3\text{CH}_2\text{OH}$.

Discussion and Conclusions

The data in Figure 3 show that the 192-, 210-, and 225-nm bands are attributable to isolated aqueous Ag^+ ions, because the band positions and extinctions are independent of the counterion and the concentration. Fromherz and Menschick¹ did not report data at wavelengths below 200 nm, and they did not report a band at 225 nm. They did observe the 210-nm band and measured its extinction as $\epsilon_{210} = 822 \pm 80$. This value is in good agreement with our own value of $\epsilon_{210} = 840 \pm 50$.

The temperature dependence illustrated in Figure 4 shows that the intensities decrease slightly rather than increase with increasing temperature. This decrease can be accounted for, within experimental error, by the thermal expansion of the dilute sample solutions, although part of the decrease may be due to thermal dissociation of a small fraction of the aqueous Ag^+ complexes. The interpretation of this temperature effect is unambiguous insofar as the local symmetry of the aqueous Ag^+ is concerned, because the oscillator strength does not increase with increasing temperature. The primary hydration sphere therefore lacks a center of inversion symmetry (cf. discussion in Introduction) and the observed oscillator strength for this $5s \leftarrow 4d$ excitation is borrowed by a static, ligand-field-induced mechanism. The simplest such geometries to envision would involve trigonal (D_{3h}) or tetrahedral (T_d)

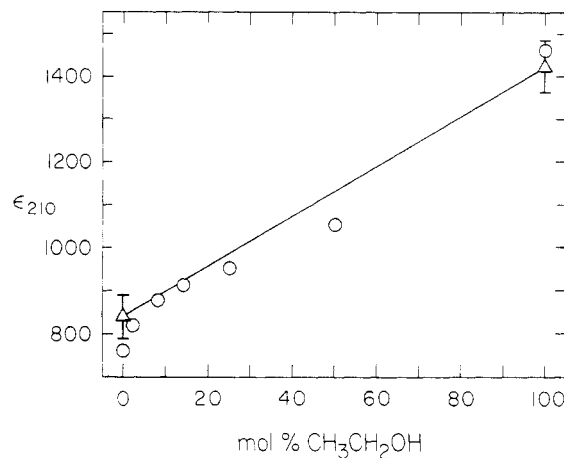


Figure 7. (O) Illustration of the relatively linear dependence of ϵ_{210} on mol % $\text{CH}_3\text{CH}_2\text{OH}$ for the spectra illustrated in Figure 6. (Δ) The line connecting the triangles is given by $\epsilon_{210} = 840(1 - x) + 1420x$, where x is the mole fraction of $\text{CH}_3\text{CH}_2\text{OH}$, $840 \pm 50 \text{ M}^{-1} \text{ cm}^{-1}$ is the average aqueous 210-nm extinction (cf. Figure 3), and $1420 \pm 60 \text{ M}^{-1} \text{ cm}^{-1}$ is the average 210-nm extinction measured in neat ethanol (cf. Figures 5 and 6).

configurations. The small red shift of the band system with increasing temperature is $\sim 150 \text{ cm}^{-1}$ and is simply the result of increasing excitation from more highly vibrationally excited ground-state levels.

The overall oscillator strength of ~ 0.033 for the aqueous Ag^+ band system deserves further comment, because oscillator strengths of 0.2–0.5 have been observed for Ag^+ in trigonal (C_{3v}) coordination in solid-state matrices.^{18–20} The interaction of Ag^+ with its nearest neighbors or ligand field is a charge–charge interaction in the solid-state matrices and a charge–dipole interaction in the aqueous case. A charge–charge interaction at a separation of 3 \AA amounts to $5 \times 10^{-10} \text{ C/m}$, and the charge–dipole interaction between a charge and the dipole of molecular water is about $0.7 \times 10^{-10} \text{ C/m}$ at a 3-\AA separation. The average of these interactions over the unperturbed wave function is, to first order in perturbation theory, what governs the static admixture of odd-parity wave functions into the nominally $5s$ orbital. The observed decrease by a factor of ~ 10 in the oscillator strength on going from an ionic to a dipolar matrix is therefore not surprising.

All of these optical features are consistent with a tetrahedral primary hydration sphere. This tetrahedral model was first put forward on the basis of ESR experiments involving proton spin-flip¹⁰ and electron spin-echo modulation¹¹ studies. These ESR data could be fitted best by a model that involved eight radially equidistant protons (or deuterons) in the frozen-in hydration shell. The data were not¹¹ critically discussed in terms of competitive T_d and D_{4h} possibilities, albeit the D_{4h} configuration would seem to be a less likely candidate. Our temperature-dependent data support the T_d symmetry assignment over the D_{4h} configuration, because a D_{4h} complex retains inversion symmetry. Furthermore, the $\text{Ag}(\text{H}_2\text{O})_4^+$ complexes are thermally stable at even 95°C . These optical data therefore provide an independent corroboration of the tetrahedral model of Ag^+ hydration put forward earlier on the basis of ESR studies.^{10–13}

The spectrum of Ag^+ in methanol (Figure 5) is nearly identical with that of aqueous Ag^+ . The overall similarity in the band envelope shapes and the oscillator strengths

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suggests that local Ag^+ solvation geometries are nearly identical in these two systems, and hence the primary solvation shell in methanol contains four molecules arranged tetrahedrally. Again, the optical data corroborate electron spin-echo modulation studies¹⁴ of Ag^+ solvation in CH_3OD and in CD_3OH . These spin-echo results showed that the frozen-in Ag^+ solvation shell consisted of four molecules oriented with the oxygens closest to Ag^+ and an average Ag–O distance of 3.3 Å. This distance is 0.1–0.2 Å greater than that found in water¹¹ (D_2O) by spin-echo modulation. Although this difference is small, it is consistent with the optically detected 800-cm^{-1} red shift of the band system in methanol relative to that in water. Such a red shift could arise as a result of a lower effective symmetric-field repulsion of the excited state caused by longer Ag–O distances in methanol than in water. Longer Ag–O distances would allow for more free volume expansion in the $4d^95s$ excited state, and therefore lower repulsion and transition energies would result.

ESR studies have also shown that acetonitrile solutions of Ag^+ have four molecules in the primary solvation shell and that Ag^+ is preferentially solvated by acetonitrile over water.¹⁵ The “back-Chatt” effect was invoked to explain this preferential bonding. Figure 5 shows that the acetonitrile solution has no multiplet structure whatsoever. This finding constitutes optical proof of the Dewar–Chatt effect²¹ insofar as the absence of absorption bands characteristic of the $5s \leftarrow 4d$ excitation is consistent with this excitation being pushed to higher transition energies by the repulsion of the overlapping nitrile π -bonding electrons with the virtual $5s$ and $5p$ orbitals of Ag^+ . An analogous phenomenon has been observed optically when gaseous ethylene is exposed to trigonally coordinated Ag^+ in zeolite,¹⁸ in which case the reversible removal of the ethylene restores the $5s \leftarrow 4d$ excitation multiplet. The slight negative absorbance observed at 214 nm in the acetonitrile solution is also a consequence of electrostriction of the $\pi^* \leftarrow \pi$ nitrile excitation by Ag^+ for those solvent molecules complexed to Ag^+ . In this case the filled $4d$ orbitals of Ag^+ overlap with the empty π^* orbital of acetonitrile, and this back-donation increases the $\pi^* \leftarrow \pi$ excitation energy by an analogous repulsion mechanism.²¹

The spectrum of Ag^+ in ethanol (Figure 5) differs from those in water and in methanol in that the middle band is considerably more intense and the low-energy band appears only as a shoulder. On the basis of the close similarity of the Ag^+ spectra observed in water and in methanol, the optical data for Ag^+ in ethanol suggest an

effective local solvation symmetry that is lower than tetrahedral. Primary solvation spheres of C_{3v} symmetry containing three or four ethanol molecules are likely candidates for consideration, in view of the gross similarities among the spectra in ethanol, methanol, and water and the higher oscillator strength observed in ethanol.

A particularly interesting suggestion has been made concerning the preferential solvation of Ag^+ by ethanol in aqueous ethanol at >13 mol % ethanol.¹⁶ In that ESR study,¹⁶ a discontinuous (step-function) change in the isotropic hyperfine splitting of ^{109}Ag at 4 K was observed on going from 13 to 14 mol % ethanol. It was also pointed out that this phenomenon may be “associated with a change in phase from a predominantly polycrystalline environment to a predominantly glassy environment”,¹⁶ which was observed to occur over the same short interval in composition. The spectra in Figure 6 show that the transition from the aqueous spectrum to that in neat ethanol is gradual. The 210-nm extinctions plotted in Figure 7 show that, to within experimental uncertainties, the measured extinctions are a linear function of the mole percent of ethanol. Such a plot does not constitute proof that a given fraction of Ag^+ ions are solvated by water and the remaining are solvated by ethanol. The existence of mixed complexes cannot be ruled out. These data do show that the optically derived symmetry effects change gradually as the aqueous ethanol composition is changed. We therefore conclude that the alternative suggestion¹⁶ of the polycrystalline-to-glassy environmental change at 13–14 mol % ethanol is responsible for the observed isotropic hyperfine splitting behavior.

Optical studies of Ag^+ solvation appear to nicely complement a variety of ESR studies. Interpretations involving symmetry have been directly corroborated for solvation by water and by methanol. Furthermore, the optical study of the aqueous ethanol system has allowed an unambiguous choice to be made between competitive explanations for an anomalous hyperfine splitting phenomenon.

Note Added in Proof. Tanaka and Iwasaki²² recently reported the spectrum (200–250 nm) of hydrated Ag^+ in their study of AgCl nucleation.

Acknowledgment. We thank Dr. Alfred Marchetti for his criticisms and suggestions concerning this manuscript.

Registry No. $\text{Ag}(\text{pts})$, 39938-22-2; Ag_2SO_4 , 10294-26-5; AgClO_4 , 7783-93-9; AgBF_4 , 14104-20-2; $\text{Ag}(\text{H}_2\text{O})_4^+$, 79082-24-9; Ag^+ , 14701-21-4.

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