Gas−Phase Hydration and Alcohol Addition Reactions of Complexes Composed of Ag^+ and a Single Alcohol Molecule

Dorothy Hanna,*,[†] Manohari Silva,[‡] Jennifer Morrison,[‡] Sammer Tekarli,[‡] Victor Anbalagan,[‡] and Michael Van Stipdonk*,[‡]

Department of Chemistry, Kansas Wesleyan University, Salina, Kansas 67401, and Department of Chemistry, Wichita State University, Wichita, Kansas 67260-0051

Received: December 21, 2002; In Final Form: May 12, 2003

The reactivity of mono-alcohol/Ag^+ complexes (methanol, ethanol, *n*-propanol, *n*-butanol, and *tert*-butyl alcohol) when stored, without collisional activation, in an ion trap mass spectrometer for periods ranging from 1 to 1000 ms was investigated. During the isolation/reaction time, association reactions between the complex ions and adventitious water and alcohol present within a He bath gas occurred to varying degrees. While the free Ag^+ ion was unreactive, complexes composed of Ag^+ coordinated by a single alcohol molecule demonstrated reactivity consistent with the following reactions: (1) formation of an adduct by the addition of a single water molecule, (2) formation of a bis-alcohol complex by the addition of a second alcohol molecule, and (3) formation of the bis-alcohol complex via the exchange of a water molecule for alcohol when investigated under similar experimental conditions. The trend in reactivity followed the order *n*-butanol > *n*-propanol > ethanol > methanol. To quantify observed trends in hydration reactivity, experimental kinetic plots were modeled stochastically. Reasonable fits to experimental reaction kinetic plots were achieved using a model that included forward and, in some cases, apparently reverse reactions, consistent with the addition of either water or alcohol in nondissociative fashion. Pseudo-first-order reaction rate constants were generated using stochastic kinetic simulations that provide insight into the relative reactivity of the mono-alcohol/Ag^+ complexes. To rationalize the observed trends in reactivity, the lowest energy conformations and molecular orbital geometries were determined using Hartree−Fock and density functional theory calculations. Our results show that the hydration and alcohol addition reactivity of Ag^+ may be influenced by the degree to which electron density can be delocalized within a coordinating ligand and to which the electron density within a hybridized orbital on Ag^+ is decreased by bonding to an alcohol molecule.

Introduction

The investigation of gas-phase ion/molecule reactions involving metal ions and metal ion/ligand complexes has long been an active area of research in mass spectrometry (MS). For example, Kebarle and co-workers investigated the ion/molecule chemistry and binding strengths of K^+ with benzene and water in a pioneering demonstration of cation-π interactions.[1] Metal ions have been used as chemical ionization agents[2] for the characterization of unsaturated organic molecules. Investigations of the intrinsic interactions and gas-phase reactions between metal ions and small molecules have contributed significantly to the understanding of the activation of C−H and C−C bonds in catalysis.[3] Collision induced dissociation (CID) and MS have been used to measure the affinity of crown ethers,[4] glymes,[5] cryptands,[6] calixarenes,[7] and amino acids[8] for metal ions, to probe metal ion binding sites on peptides[9] and oligosaccharides,[10] and to elucidate the novel dissociation pathways exhibited by the latter classes of molecules when metal cationized.

Complexes composed of metal ions and organic ligands have been shown to undergo association reactions with a range of small molecules in the gas phase. For example, Callahan, Vachet, and co-workers,[11] and later Vachet and co-workers,[12] have demonstrated that transition metal ions such as Ni(II), Cu(II), Zn(II), and Co(II), coordinated by a range of organic ligands containing nitrogen or oxygen heteroatoms, will react with species such as water, acetonitrile, and pyridine in the gas-phase environment of an ion trap mass spectrometer. The ion/molecule chemistry demonstrated was found to be sensitive to the intrinsic coordination structure of the complexes.[11] Several years earlier, Wu and Brodbelt demonstrated that Cu(I) and Ag(I) complexes (with ligands such as pyridine, bipyridine, and phenanthroline), when coordinatively unsaturated, will form water adducts in the ion trap.[13] Groenewold and co-workers have used ion trap mass spectrometry to investigate the gas-phase reactions of silicon and aluminum oxyanions with H_2O and H_2S[14] and have applied ab initio calculations to determine the most probable structures and stochastic kinetic simulations to derive relative reaction rate constants.

We have recently investigated the tendency for Ag^+ complexes with amino acids to form water and methanol adducts when stored in an ion trap mass spectrometer.[15] While Ag^+ cationized aliphatic amino acids such as alanine, valine, and *tert*-leucine formed adducts, amino acids with aromatic side groups (phenylalanine, tyrosine, and tryptophan) were found to be unreactive when compared under similar experimental conditions.[15a] For the latter group, semiempirical and ab initio calculations suggested that the lowest energy, and therefore most likely, gas-phase conformation included coordination by the aromatic ring of the side group along with the amine nitrogen and carbonyl oxygen atoms. Because the donation of π electron density to the Ag^+ ion was a likely determining factor in coordination by the side group, and thus the inhibition of complex reactivity, we investigated the influence of *para*-position substituents to the aromatic ring on the formation of

---

* To whom correspondence should be addressed.

[†] Kansas Wesleyan University.

[‡] Wichita State University.

10.1021/jp027797w CCC: \$25.00

the water adducts.[15b] With respect to the substituent, adduct ion intensities followed the trend $-NO_2 > -Br > -F > -OH > -H$, consistent with a weakening in the interaction between the ring and the metal ion due to the decrease in ring electron density, and an increased probability for the displacement of the ring from the coordination sphere by a water molecule. The tendency to form gas-phase water adducts was also used by our group as supporting evidence for the formation of Ag^+ cationized phenylacetaldehyde as the major CID product from Ag^+ cationized phenylalanine.[15c]

During preliminary investigations we noticed significant differences in the tendency to form water adducts to complexes composed of Ag^+ and a single aliphatic amino acid and that the trends suggested reactivity increases with the size of the substituent at the α-carbon position. To explore this issue further, we decided to investigate the influence of the size of the alkyl groups using Ag^+ complexes with simpler molecules and, in particular, ones with a single coordinating heteroatom. Motivating our efforts are the emerging indications that gas-phase hydration reactions may provide information about the conformation and electronic structure of gas-phase complexes and, in particular, ones composed of metal ions coordinated by model molecules of biological relevance.[11,14,15] Our experiments have initially focused on the Ag^+ ion, which, while lacking significant biological or industrial function, is of interest to us for the following reasons: (1) the tendency to form H_2O by association reactions is observed only when the metal ion is coordinated by a ligand (thus allowing us to elucidate ligand attributes that lead to reactivity), and (2) Ag^+ serves as a convenient test system for the development of analytical methods and protocols for gas-phase hydration reactions. Our ultimate goal is to use the tendency to form water adducts to biomimetic metal ion/biomolecule complexes to provide insight into the influence of the coordination environment on the activity of metalloenzymes, such as liver alcohol dehydrogenase, that feature water molecules at the metal center of their active site. In addition, examining the intrinsic hydration reactions may benefit the development of artificial enzymes that utilize metal centers to activate water and/or bonds for the hydrolysis of peptides, proteins, and oligonucleotides. We also note that the Ag(I) ion has become an attractive "reagent" ion for the sequencing of peptides in the gas phase by multiple-stage tandem mass spectrometry, thus motivating in-depth investigations of intrinsic Ag(I)/biomolecule interactions.[16]

In this study, we prepared Ag^+ cationized alcohols ($[M + Ag]^+$, where M is methanol, ethanol, *n*-propanol, *n*-butanol, and *tert*-butyl alcohol) by the CID of bis-alcohol complexes with Ag^+ ($[2M + Ag]^+$) generated by ESI. The $[M + Ag]^+$ ions were then isolated and stored in an ion trap ion mass spectrometer for periods ranging from 1 to 1000 ms. During the imposed isolation/reaction time, the ions were subject to association reactions with adventitious water and alcohol present within the He bath gas. Pseudo-first-order reaction rate constants were generated using a stochastic kinetic simulation to quantify the trends in hydration reactivity. To provide insight into $[M + Ag]^+$ and hydrated complex structures and rationalize apparent trends in reactivity, the various species lowest energy conformations and electron density distributions were calculated using ab initio methods. Several factors that may contribute to the exhibited trends in reactivity are presented.

Experimental Section

Mass Spectrometry. Methanol, ethanol, *n*-propanol, *n*-butanol, *tert*-butyl alcohol, and silver nitrate were purchased from Aldrich Chemical (St. Louis, MO) and used as received. A stock solution (1×10^{-3} M) of the metal nitrate was prepared by dissolving the appropriate amount of solid material in deionized H_2O.

ESI mass spectra were collected using a Finnigan LCQ-Deca ion trap mass spectrometer (Thermoquest Corporation, San Jose, CA). Mixtures (1:1 by volume) of the $AgNO_3$ solution and the respective alcohols were infused into the ESI-MS instrument using the incorporated syringe pump at a flow rate of 3−5 μL/min. The atmospheric pressure ionization stack settings for the LCQ (lens voltages, quadrupole and octapole voltage offsets, etc.) were optimized for maximum $[2M + Ag]^+$, M = alcohol, ion transmission to the ion trap mass analyzer by using the autotune routine within the LCQ Tune program. Following the instrument tune, the spray needle voltage was maintained at +5 kV, the N_2 sheath gas flow at 25 units, and the capillary (desolvation) temperature at 200 °C. The ion trap analyzer was operated at a pressure of $\sim 1.5 \times 10^{-5}$ Torr. Helium gas, admitted directly into the ion trap, was used as the bath/buffer gas to improve trapping efficiency and as the collision gas for CID experiments.

The studies of Ag^+ complex ion reactivity during storage within the ion trap mass spectrometer were performed as described previously.[15] The $[M + Ag]^+$ species were generated by the CID of the $[2M + Ag]^+$ complex ions that dominate the ESI mass spectrum (discussed below). To effect dissociation, the activation amplitude was set at 30−35% of the maximum 5 V "tickle" voltage available (chosen empirically), the activation Q setting at 0.30, and the isolation width at 10 *m*/*z* units. The activation time employed for dissociation was 30 ms. Following the dissociation step, product ions corresponding to the mono-alcohol/Ag^+ complexes were isolated for the association reaction studies.

The $[M + Ag]^+$ complexes were isolated for the kinetics studies by setting the parent mass between the ^{107}Ag and ^{109}Ag isotopic peaks. Ions were isolated and stored with minimal activation by setting the activation amplitude (the amplitude of the rf excitation energy applied to increase stored ion kinetic energy) at 0%. The isolation width and activation Q setting (as labeled by Thermoquest, used to adjust the frequency of the rf excitation voltage placed on the end cap electrodes) were set at 10 mass to charge (*m*/*z*) units and 0.500, respectively. For quantitative comparisons, the complex ions were isolated and stored within the ion trap for times ranging from 1 to 1000 ms, during which time reactions with H_2O and alcohol, present within the ion trap bath gas, occurred. Following the isolation period, the precursor and product ions were scanned out of the trap and detected as part of the automated mass analysis operation. To maintain the integrity of our LC-MS system, the LCQ-Deca has not been modified to allow the He buffer gas to be seeded with a known amount of neutral reagent gas. Vachet et al. have proposed that both water and methanol will accumulate, when used as solvents for ESI, in the vacuum system at partial pressures sufficiently high to conduct ion/molecule reactions with these reagents in an ion trap.[11] We have found, during experiments in which D_2O was used as solvent for ESI, that the principal adduct formed is generated by the attachment of H_2O.[16f] Similar observations have been made when acetonitrile or methanol are used without H_2O cosolvent (and both acetonitrile and methanol adducts are observed in lower abundance). This suggests that that H_2O adsorbed to the walls of the ion trap and/or vacuum chamber, or present as an impurity in the He buffer gas, is the *primary* source of H_2O reagent in our system. The amount of H_2O within the ion trap is expected to increase slightly when H_2O is used as a cosolvent for ESI. The alcohol reagent likely originates entirely from neutral flux introduced via the syringe pump and the ESI process; therefore, the alcohol concentration will be significantly less than that of the water reagent.

We have found that our reactivity profiles are fully reproducible when several experimental runs are conducted in the same day, indicating that the ambient concentration of water remains stable over at least a 24 h period. The data collected for the measurements of adduct ion formation represent the average of 15 isolation/reaction/scan sequences. The mass spectra shown are the result of the averaging of 10−30 analytical scans.

Kinetic Modeling. To quantify observed trends in hydration reactivity, kinetic modeling of the addition of H_2O or alcohol to the $[M + Ag]^+$ complexes was performed as follows. Fractional abundances of reactant and product ions were calculated by dividing the relative intensities of the precursor (complex) ion and adduct ions by the total ion abundance. The changes in fractional abundances with time were used to obtain relative values of the rate constants for the addition reactions using the Chemical Kinetic Simulator software package, a program available through a no cost license on the IBM Web site, which employs a stochastic algorithm to model the reacting system. Reactions involved in the system were assumed to be kinetically simple, having rate equations based upon reaction stoichiometry. Putative rate constants for the reactions in the model system were changed incrementally until the concentration curves generated by the model fit the observed changes in fractional abundances. To adequately fit the model to the experimental data, it was necessary to introduce into the model system reactions corresponding to the exchange of water for alcohol (providing an alternate route to the $[2M + Ag]^+$ species) and the elimination of water from the hydrated $[M + Ag]^+$ complex. Inclusion of the elimination reaction did not significantly alter the values obtained for the hydration reactions' modeled rate constants (which are primarily determined by the initial rate of change in fractional abundance of the $[M + Ag]^+$ and $[M + Ag{+}W]^+$ species) but was necessary to fit the experimental data at longer isolation times (IT > 200 ms) for the most reactive species.

The reaction schemes and associated rate constants used for kinetic modeling are shown below. Our primary interest was to describe and rationalize qualitative trends in the relative values of the hydration rate constants, k_2, by examination of relative values of the modeled rate constants obtained for hydration reactions for the series of $[M + Ag]^+$ complexes. Under pseudo-first-order conditions, such trends in relative values of k_2 will be independent of the concentration of water within the ion trap.

$$[M + Ag]^+ + M => [2M + Ag]^+ \qquad k_1, k_1' = k_1[M],\ [M] = \text{molecules/cc}$$

$$[M + Ag]^+ + W => [M + Ag + W]^+ \qquad k_2, k_2' = k_2[W],\ [W] = \text{molecules/cc}$$

$$[M + Ag + W]^+ + M => [2M + Ag]^+ \qquad k_3, k_3' = k_3[M],\ [M] = \text{molecules/cc}$$

$$[M + Ag + W]^+ + E => E + [M + Ag]^+ + W \qquad k_{-2}\ (E = \text{collision gas atom or molecule})$$

The exchange of water was independently observed by isolating the hydrated complex, $[M + Ag + H_2O]^+$, in the ion trap, holding it under conditions of minimal activation energy (activation amplitude set equal to zero), and observing the appearance of the $[2M + Ag]^+$ species. The elimination reaction was not independently observable. Although inclusion of the elimination reaction in the reaction scheme was necessary to fit the experimental data for longer isolation times (>200 ms) for the most reactive complexes, it did not significantly alter the relative values of the modeled rate constants of the hydration reaction, which are most sensitive to changes in reactant and hydration product concentrations at short isolation times (<100 ms), and had no effect on the qualitative trends observed for hydration reactivity.

Relative initial concentrations of reactant and product ionic species were obtained from the fractional abundances of the corresponding ions. The concentration of the water, which was kept constant for all reactions modeled, was estimated upon the basis of ambient conditions existing in the ion trap (298 K, 5×10^{-6} Torr) and resulted in rate constants for hydration which are consistent with the order of magnitude of the maximum rate constants predicted using the average dipole orientation (ADO) theory. ADO theory has been successfully employed to interpret kinetic data for other chemical systems investigated using ion trap mass spectrometers.[17] The concentration of the alcohol was set at 1 order of magnitude lower than the concentration of water. Because the rate constant for the hydration reaction is primarily determined by the initial rate of change of the relative abundances of parent and hydrated species, its value is relatively insensitive (<5%) to the value used for the concentration of the alcohol.

Although the concentrations of water and alcohol molecules in the ion trap cannot be precisely determined quantitatively, the temporal evolution of the reactant ion and adduct intensities indicates that our experiments were conducted under pseudo-first-order reaction conditions (large excess of H_2O and alcohol reagent relative to $[M + Ag]^+$); therefore, the relative values of the rate constants obtained for a given reaction will be independent of the concentrations of these neutral species. To further ensure that conditions were pseudo-first-order, we conducted trials with the automatic gain control (AGC) on the LCQ turned off. The AGC is used to set the ion inject time for the ion trap to optimize the number of ions (in this case the number of trapped metal/complex reagent ions) per analytical scan. We instead set the inject time manually to limit (decrease) the number of complex ions admitted into the ion trap and thus the number of complex ions isolated for reaction studies. Over a range of 2 orders of magnitude of trapped ion intensity, the reaction trends were reproducible. In addition, experiments in which water adducts were isolated and allowed to exchange for alcohol, which is introduced solely via the syringe pump, followed pseudo-first-order reaction profiles. The amount of H_2O as contaminant within the ion trap is likely one or more orders of magnitude greater than the concentration of alcohol resulting from the ESI process. This is supported by the preferential addition of water over alcohol at short isolation times. The assumption of pseudo-first-order behavior was supported by the independence of the observed kinetics on injection time for isolation times of 2 and 200 ms and by the apparent first-order behavior of $[M + Ag + W]^+$ with respect to ligand addition, indicated by a linear relationship of the log(fractional abundance of $[M + Ag + H_2O]^+$) to isolation time. Under these conditions, the relative values of rate constants for a given reaction modeled are independent of initial concentrations of alcohol or water molecules.

Ab Initio Calculations. Ab initio calculations were performed using the Gaussian 98 group of programs.[18] Our interest

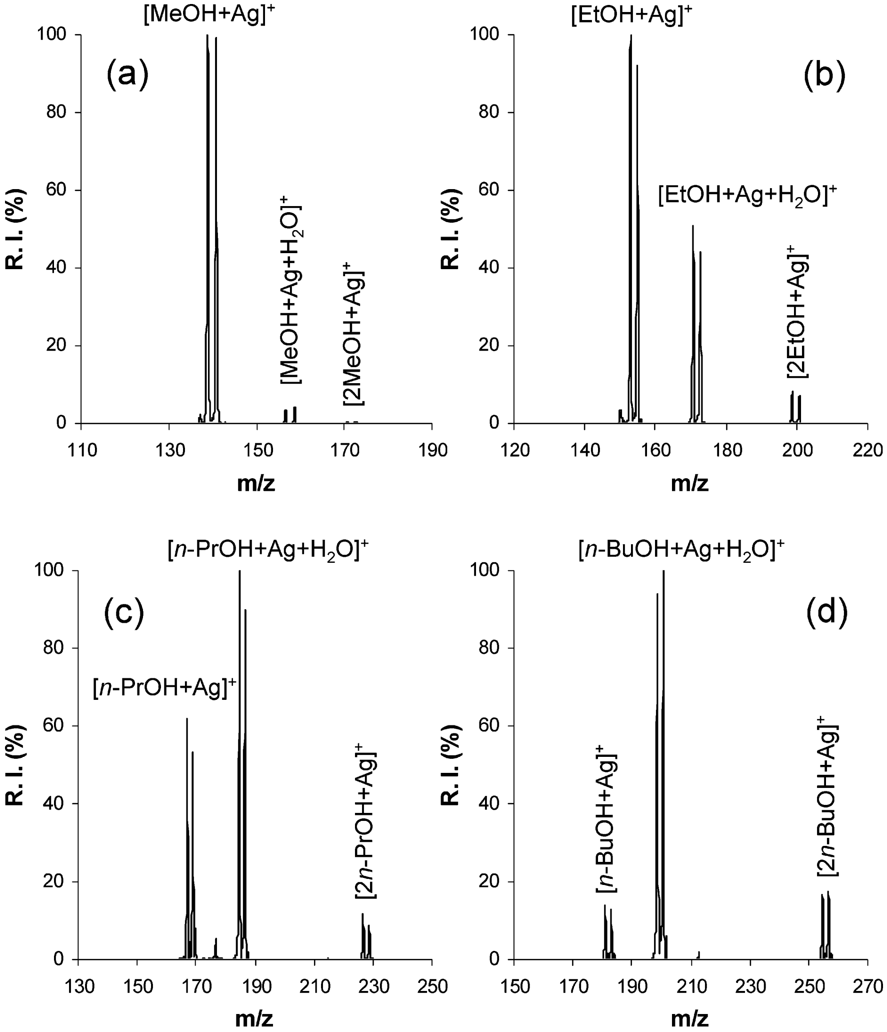

Figure 1. Mass spectra generated by isolation and storage of Ag^+ cationized (a) MeOH, (b) EtOH, (c) *n*-PrOH, and (d) *n*-BuOH. The $[M + Ag]^+$ species were generated from the $[2M + Ag]^+$ by CID as described in the Experimental Section. The isolation time for each spectrum was 300 ms.

was in trends in the various complexes' geometries and molecular orbital distributions rather than absolute energy, enthalpy, and free energy values. Methanol, ethanol, *n*-propanol, *n*-butanol, and *tert*-butyl alcohol were the ligands subjected to this investigation. Initially, the alcohol molecules were modeled using Gauss View, and the resulting conformations were then optimized at the AM1 level. The AM1 optimized geometries were then used as starting geometries for Hartree−Fock (HF) calculations employing the 3-21G* basis set. The HF optimized geometries were then used as starting geometries for density functional theory (DFT or B3LYP) calculations employing the 3-21G* basis set.

Following optimization and the determination of the lowest energy conformation, the Ag^+ ion was added to each of the DFT optimized alcohol geometries, with coordination of the metal ion by the oxygen atom. The $[M + Ag]^+$ structures were optimized using HF/3-21G* and then reoptimized using B3LYP/3-21G*. Upon optimization of the $[M + Ag]^+$ complex geometries, one H_2O ligand was added to the DFT optimized complexes, coordinating the Ag^+ ion such that the complex was linear with respect to the $O-Ag^+-O$ bond. The hydrated complexes were then optimized using HF/3-21G* and reoptimized using B3LYP/3−21G*. The molecular orbital distribution images for $[M + Ag]^+$ complexes and $[M + Ag + H_2O]^+$ were generated using the Gauss View program.

Results and Discussion

Mass spectra resulting from the isolation and storage of the $[M + Ag]^+$ complexes derived from methanol, ethanol, *n*-propanol, and *n*-butanol are shown in Figure 1. For each case, the imposed isolation time was 500 ms with the activation amplitude set equal to zero. The spectra in Figure 1 show the stored precursor complex ion $[M + Ag]^+$, the hydrated complex $[M + Ag + H_2O]^+$, and the bis-alcohol complex $[2M + Ag]^+$ formed by association reactions that occur during the isolation period. Figure 2 shows the experimentally determined change in relative peak intensity, and fits generated by kinetic modeling, for Ag^+ cationized ethanol and *n*-propanol. Values of rate constants for each $[M + Ag]^+$ complex obtained through kinetic modeling, and the corresponding pseudo-first-order rate constants, are shown in Table 1. The relative values of the modeled rate constants for a given reaction are independent of the values used for the intital concentration of the neutral species, as would be expected under pseudo-first-order conditions. The modeling is fairly insensitive to minor adjustments in the rate constants (5%−20%), but larger changes create significant deviation of the modeled concentration curves from the observed fractional abundances. Precision in the rate constants obtained varies according to the apparent contribution of a given reaction to the overall kinetics observed. Rate constants for the addition of a second alcohol ligand to $[M + Ag]^+$ follow the order expected from hard−soft acid−base (HSAB) theory,[19] *n*-butanol

TABLE 1: Relative Rate Constants Obtained through Kinetic Modeling of Temporal Changes in Ion Abundances[a]

	AM + M => AR2		AM + W => AMW		AMW + M => AM2 + W		AMW => AM + W
alcohol	k_1	k_1'	k_2	k_2'	k_3	k_3'	k_{-2}
methanol	$<3 \times 10^{-12}$	$< 8.4 \times 10^{-6}$	4.80×10^{-12}	1.3×10^{-4}	5.00×10^{-10}	1.4×10^{-3}	$<1 \times 10^{-3}$
ethanol	6.00×10^{-11}	1.7×10^{-4}	4.80×10^{-11}	1.3×10^{-3}	4.90×10^{-11}	1.4×10^{-4}	6.00×10^{-4}
n-propanol	3.00×10^{-10}	8.4×10^{-4}	1.35×10^{-10}	3.8×10^{-3}	1.00×10^{-12}	2.8×10^{-6}	9.50×10^{-4}
n-butanol	3.80×10^{-10}	1.1×10^{-3}	3.20×10^{-10}	9.0×10^{-3}	7.00×10^{-11}	2.0×10^{-4}	1.00×10^{-3}
tert-butyl alcohol	1.03×10^{-11}	2.9×10^{-5}	1.40×10^{-10}	3.9×10^{-3}	1.00×10^{-10}	2.8×10^{-4}	$<1 \times 10^{-3}$

[a] The reactivity of $[ROH-Ag]^+$ complexes toward addition of water or a second alcohol ligand increases with the length of ROH and decreases with branching. The reactivity of *tert*-butyl alcohol is comparable to that of *n*-propanol. A = Ag^+, M = alcohol, W = water. k = (molecules $AM/cm^3)^{-1}$ (molecules $AMW/cm^3)^{-1}$ s^{-1}. k' = (molecules $AM/cm^3)^{-1}$ s^{-1}.

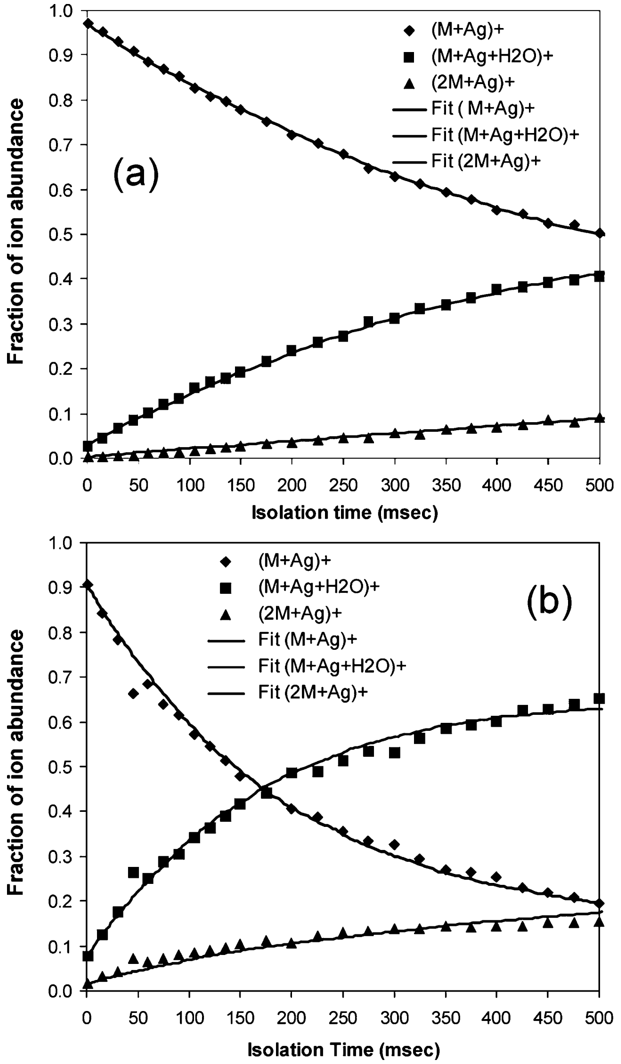

Figure 2. Experimentally measured change in fraction of ion abundance, and fits produced by kinetic modeling, for the reactivity of (a) $[EtOH + Ag]^+$ and (b) $[n\text{-}PrOH + Ag]^+$.

> *n*-propanol > ethanol > methanol. The rate constants for the hydration of $[M + Ag]^+$ and for the exchange of the water ligand for a second alcohol ligand follow the same order of reactivity. The rate constants for the elimination of water as a ligand to re-form $[M + Ag]^+$ are relatively insensitive to changes in the alcohol ligand and are large compared to the other rate constants, though generally an order of magnitude smaller than the pseudo first-order-rate constant for the forward hydration reaction. These observations suggest that the "reverse" reaction is of an assisted nature via nonthermal collisions with the helium gas, in which energy transferred to the hydrated complex stimulates the elimination of water, rather than being truly unimolecular.

Our primary interest in this study was to observe and rationalize ligand effects on the hydration reaction of Ag^+ in the gas phase; however, the inclusion of the reaction corresponding to the elimination of water from the hydrated complex requires further comment, in part because of what initially may appear to be incongruously large rate constants for this reaction. The initial rate of the elimination reaction is negligible, despite the large rate constant, because of the low initial concentration of the hydrated species and the high concentration (expressed as molecules/cm^3) of H_2O: the high H_2O concentration causes the hydration reaction to dominate the system initially. Acceptable fits for the experimental data could be obtained for the less reactive Ag^+ cationized methanol and ethanol complexes for isolation times up to 500 ms without inclusion of the elimination reaction. For the more reactive propanol and butanol complexes, inclusion of the elimination reaction significantly affects the fit of the modeled curves to the experimental data only for longer isolation times (>200 ms) and has little effect on the modeled rate constants obtained for the hydration reactions, which are most sensitive to *initial* changes in relative ion abundance. The observed pattern in the experimental data could, alternately, be explained by the existence of a second, less reactive, complex of Ag^+ with the same mass/charge ratio as that of the $[M + Ag]^+$ species whose product species are indistinguishable from those of $[M + Ag]^+$; however, we have no evidence from experimental data or ab initio modeling for the presence of such a species.

The order of reactivities found for the addition of the second alcohol ligand is consistent with the expected trend of the Lewis base strength and polarizability of the coordinating alcohol oxygen and reflects the well-known preference of the Ag^+ ion for "soft" electron donors.[20] The reactivity toward water, however, is surprising. In the solid state and in solution, Ag^+ is known to be resistant toward hydration, behavior which is generally attributed to the "soft" nature of the Ag^+ ion and the "hard" nature of oxygen as an electron donor in the water molecule. It might then be expected that electron donation by the coordinating alcohol would cause the electron density on the silver ion to increase and the affinity for a coordinating water ligand to be further decreased; however, the opposite trend in hydration is clearly present. There is no evidence for the presence of the singly coordinated $[Ag + H_2O]^+$ ion forming from free silver ion in the ion trap, an observation which is consistent with the solution chemistry of the Ag^+ ion.[20] However, when the metal ion is coordinated to an alcohol, it shows an affinity toward water which increases with an increase in the carbon chain length of the alcohol.

Factors which might be expected to influence the relative hydration tendencies of the $[M + Ag]^+$ ion include the following: (1) the Lewis acid character of the Ag^+ ion, affected by the electron donor ability of the alcohol ligand; (2) steric hindrance of the approach of the water molecule to the Ag^+

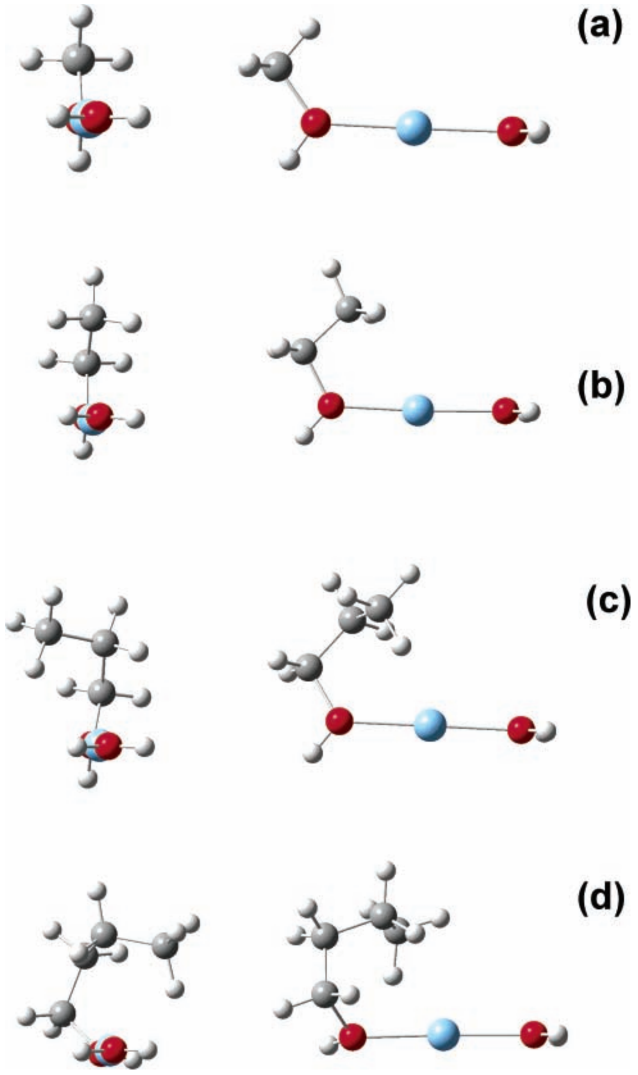

Figure 3. Lowest energy geometric structures for hydrated complexes, $[M + Ag + H_2O]^+$ with M = (a) MeOH, (b) EtOH, (c) *n*-PrOH, and (d) *n*-BuOH, as determined using ab initio calculations (DFT, B3LYP/3-21G*).

ion by the ligating alcohol; (3) hydrogen bonding between the water and the alcohol ligands; (4) distribution of excess energy from reactive collisions through internal vibrational modes within the alcohol ligand; (5) electronic effects on the Ag^+ ion due to atomic orbital hybridization and the formation of molecular orbitals to the alcohol ligand; (6) redistribution of electron density from the silver ion into the alcohol alkyl group.

The observed order of the hydration tendency of the $[M + Ag]^+$ is opposite to the trend that would be expected if electron density donation of the alcohol ligand to the Ag^+ ion and a corresponding decrease in Lewis acidity of the silver ion were the primary factors influencing the relative hydration tendencies. Structures of the $[M + Ag]^+$ obtained through ab initio calculations (B3LYP/3-21G* level) show the minimum energy configuration of the alcohol to be bent about the silver ion and the water in the hydrated species to be located opposite the alcohol ligand (Figure 3) for all the alcohol adducts. On the basis of the structures shown in Figure 3, there does not appear to be significant steric interference to hydration of $[M + Ag]^+$, nor is the observed order of relative rate constants consistent with the larger alcohols sterically hindering the approach of the water ligand. Hydrophobic effects due to the alcohol alkyl group may facilitate hydration by orienting the approach of the water molecule toward the opposite side of the silver ion.

During the interpretation of experimental results, the possibility of hydrogen bonding between H_2O and the metal-bound alcohol ligand was also considered. Such outer sphere interactions have been observed in theoretical studies of solvent/Ag^+ complexes. For example, molecular modeling of the Ag^+/methanol complexes by Armentrout and co-workers[21] has suggested than a $[M + Ag]^+ + M$ (M = methanol) complex involving a hydrogen-bonding interaction between Ag^+ cationized methanol and a free methanol molecule lies at a local energy minimum only a few kilojoules per mole higher in energy than a linear, bis-methanol Ag^+ complex. In the present study, a similar interaction involving a free water molecule could give rise to a means of entropically assisting hydration product formation by capturing the H_2O via hydrogen bonding to the alcohol prior to coordination of the water to Ag^+. To investigate this possibility, we modeled the $[M + Ag]^+ + H_2O$ complex, with a hydrogen bond between the oxygen atom of the H_2O molecule and the hydroxyl hydrogen atom of the bound methanol molecule. Of interest was the (possible) local energy minimum for this structure, and the $H_2O\cdots HOR$ (hydrogen) bond length: a stronger bond would be expected to facilitate hydration and enhance the reaction rate. The calculated electronic energies for the linear $[M + Ag + H_2O]^+$ species (shown in Figure 3) and for the hydrogen-bonded $[M + Ag]^+ + H_2O$ species, and the energy differences converted from hartrees to kilojoules per mole, are provided in Table 2. According to B3LPY/3-21G* calculations, the hydrogen-bonded versions of the complexes of the *n*-alcohols were ~65 kJ/mol higher in energy than those in which both ligands are bound to the metal ion and the length of the hydrogen bond showed a small increase (0.2 Å overall) with increasing length of the hydrocarbon chain, indicating a trend of *decreasing* bond strength. The hydrogen bond to *tert*-butanol was only slightly (0.02 Å) stronger than that to *n*-butanol. Again, we consider the trend in the calculation results to be the important factor, and the theoretical data suggest that, though such an outer sphere interaction between the water molecule and the coordinated alcohol may occur, it is not responsible for the observed trend in hydration rates.

Additional evidence against a conformation involving H_2O bound solely to the alcohol ligand via a hydrogen bond also was provided by an examination of the CID profiles (relative precursor and product ion intensities as a function of collision energy). Relative amplitudes of the rf voltage applied to the end cap electrodes of the ion trap to induce ion activation (proportional to collision energy; data not shown) of 25−30% of 5 V were required, amplitudes consistent with water being covalently bonded to the silver ion rather than hydrogen bonded to the alcohol. Similar activation amplitudes are required to dissociate Ag^+ cationized peptides,[16f,22] and we find that noncovalently bonded or hydrogen-bonded complexes dissociate at significantly lower amplitudes.

We also considered the possibility of a hydrogen-bonded intermediate involving a coordinated water molecule (i.e. H_2O hydrogen bonded to methanol while both are bound to the metal ion) that converts to the lower energy linear arrangement of ligands. If such a hydrogen-bonded intermediate existed and involved the alcohol oxygen lone pair electrons, it would be expected that the amine adducts would exhibit a different trend in hydration tendencies, because the Ag^+ coordinated amine nitrogen lacks a free electron pair. To experimentally test this hypothesis, we investigated the hydration tendency of Ag^+ cationized linear alkylamines (Table 3). The observed trend in hydration reactivities for the amine adducts is similar to that of the alcohol complexes, which does not support the involvement

TABLE 2: Comparison of the Calculated Energies (in kJ/mol) after Geometry Optimization (B3LYP/3-21G*) for the Linear $[M + Ag + H_2O]^+$ (Both Ligands Bound to the Metal Ion) and Hydrogen-Bonded $[M + Ag]^+ + H_2O$ Species[a]

alcohol	$E_{[M+Ag+H_2O]^+}$ (au)	$E_{[M+Ag]^+ + H_2O}$ (au)	ΔE (au)	ΔE (kJ/mol)
methanol	−5367.2327	−5367.2073	0.0254	66.7
ethanol	−5406.3466	−5406.3211	0.0255	66.9
propanol	−5445.4509	−5445.4257	0.0252	66.2
n-butanol	−5484.5515	−5484.5280	0.0235	61.7
tert-butyl alcohol	−5484.5670	−5484.5414	0.0256	67.2

[a] 1 au (hartree) = 2625 kJ/mol.

TABLE 3: Relative Rate Constants for Amine Complexes Obtained through Kinetic Modeling of Temporal Changes in Ion Abundances[a]

	AM + W			AM + M		
alcohol	k_{obs}	k_{ADO}[b]	% eff[c]	k_{obs}	k_{ADO}[b]	% eff[c]
methanol	4.20×10^{-12}	1.75×10^{-9}	0.24	$<3 \times 10^{-12}$	1.47×10^{-9}	<0.2
ethanol	5.50×10^{-11}	1.74×10^{-9}	3.16	6.00×10^{-11}	1.40×10^{-9}	4.29
n-propanol	1.30×10^{-10}	1.73×10^{-9}	7.50	3.00×10^{-10}	1.30×10^{-9}	23.05
n-butanol	3.10×10^{-10}	1.73×10^{-9}	17.94	3.80×10^{-10}	1.30×10^{-9}	29.28
tert-butyl alcohol	1.40×10^{-10}	1.73×10^{-9}	8.10	1.03×10^{-11}	1.30×10^{-9}	0.79

[a] The reactivity of $[RNH_2{-}Ag]^+$ complexes toward addition of water or a second amine ligand increases with the length of RNH_2. A = Ag^+, M = alcohol, W = water. [b] $k_{ADO} = (2\pi q/\mu^{1/2})[\alpha^{1/2} + c\mu_D(2/\pi kT)^{1/2}]$, $c = f(\mu_D, \alpha^{1/2})$ (ref 16). μ = reduced mass, α = polarizability, μ_D = dipole moment, c = the locking constant. [c] % eff = $k_{obs}/k_{ADO} \times 100\%$.

TABLE 4: Comparison of Rate Constants Obtained through Kinetic Modeling of Experimental Data (k_{obs}) and Theoretical Capture Rate Constants (k_{ADO}) Based upon Average-Dipole-Orientation Theory[a]

	AM + M => AM2		AM + W => AMW		AMW + M => AM2 + W		AMW => AM + W
amine	k_1	k_1'	k_2	k_2'	k_3	k_3'	k_{-2}
methyl	1×10^{-11}	2.8×10^{-5}	5.1×10^{-12}	1.4×10^{-4}	6.4×10^{-10}	1.8×10^{-3}	$<1 \times 10^{-5}$
ethyl	9.6×10^{-11}	2.7×10^{-4}	3.7×10^{-11}	1.0×10^{-3}	3.3×10^{-10}	9.2×10^{-4}	5.0×10^{-4}
n-propyl	2.1×10^{-10}	5.9×10^{-4}	1.2×10^{-10}	3.4×10^{-3}	3.3×10^{-10}	9.2×10^{-4}	5.5×10^{-4}
n-butyl	2.9×10^{-10}	8.1×10^{-4}	2.1×10^{-10}	5.9×10^{-3}	3.5×10^{-10}	9.8×10^{-4}	2.5×10^{-4}

[a] The reaction efficiency (percentage of k_{ADO} actually observed) increases with the length of ROH and decreases with branching. A = Ag^+, R = amine 1, W = water, k = (molecules AM/cm^3)$^{-1}$ (molecules AMW/cm^3)$^{-1}$ s^{-1}, k' = (molecules AM/cm^3)$^{-1}$ s^{-1}.

of hydrogen bonding involving the alcohol oxygen lone pair in product or intermediate stabilization. Ab initio calculations failed to produce local minima for the energies of the $[M + Ag + H_2O]^+$ species when structures involving hydrogen bonding were postulated. Calculations initiated with a hydrogen-bonding interaction instead produced final conformations very similar to those shown in Figure 3, with the ligands separated and bound on opposite sides of the metal ion.

Reaction rates for the formation of ion/molecule complexes through gas-phase collisions are, in part, dependent upon the masses of the species involved, ionic charge, molecular polarizability, and molecular dipole moment. This dependency has been quantified by the average dipole orientation (ADO) theory,[17] which has been used qualitatively and quantitatively to predict capture rate constants for ion/molecule reactions occurring in the gas phase. The capture rate constant provides the maximum value for the reaction rate constant. The actual rate constant will also depend on the ability of the complex to distribute or transfer excess energy once the molecule is captured, to stabilize the product formed by the initial collision. Calculated capture rate constants for the formation of $[2M + Ag]^+$ and $[M + Ag + H_2O]^+$ are shown in Table 4. The variation in hydration tendencies predicted by ADO theory is small, and the predicted trend, which for the hydration reactions is solely dependent upon the change in mass of the parent complex, is opposite to that observed experimentally. The trend in reaction efficiency (the percent of the ADO capture constant actually observed) shows an increase with the increasing size of the alcohol alkyl group. Because ADO theory accounts for neither distribution of excess energy from reactive collisions nor the electronic influence of the first ligating alcohol on the silver ion's ability to attract and bond to a second ligand, the change in percent efficiency for the hydration of the $[M + Ag]^+$ complexes may be qualitatively interpreted as a measure of the contribution of these factors to the hydration behavior of these complexes.

The influence of the existence of more degrees of freedom within the larger alcohol ligands, which could distribute excess energy from reactive collisions within the molecule and assist in stabilizing the formation of a bond between the Ag^+ ion and the water molecule, cannot be ruled out as a factor contributing to the observed trend in hydration tendencies. However, significant variations occur in the rate constants obtained for the hydration of the *n*-butanol complex with Ag^+ compared to a *tert*-butyl alcohol version. The reactivity toward hydration of the latter complex is much reduced in comparison to that of the former, which suggests that stabilization by distribution of excess energy from reactive collisions is not the only factor responsible for the observed trends in hydration tendencies.

The possibility of covalent bond formation involving hybridized atomic orbitals on silver has been offered to explain both the preferred geometries and the preferred coordination numbers of silver(I) complexes. Ab initio modeling of silver complexes has supported the involvement of Ag^+ in covalent interactions with ligands in the gas phase.[23] It has been suggested that hybridization involving the unoccupied 5s orbital and the occupied $3d_{z^2}$ orbital of the silver ion could produce an orbital capable of further hybridization with the silver $5p_z$ orbital, resulting in a pair of atomic orbitals through which two ligands could coordinate to silver to produce the preferred linear structure.[20] Formation of a covalent bond to such a hybridized orbital would decrease electron density on the opposite side of the silver ion, facilitating the entrance of a second ligand. This effect would be expected to increase with increasing bond strength of the first ligand. The existence of sd-hybridization has also been employed by Armentrout to account for trends in the bond strengths of a second ligand to complexes of first and second row transition elements[24] and most recently for Ag(I).[21] These sd-hybridized orbitals would redistribute electron density in the metal s-orbital to a location perpendicular to the metal−ligand axis, thus enhancing the bond strength of the second ligand. The energy required for hybridization is provided by the bonding energy of the first ligand. Stronger bonding of the first ligand thus assists the hybridization. It has been shown that the strength of the first ligand/Ag^+ interaction is generally consistent with the expectations of HSAB theory for a variety of ligands and that the bond strength between the alcohol ligand and the Ag^+ ion increases from methanol to ethanol.[25] If this trend in the relationship of bond strength to the Lewis base character of the alcohol extends to the larger alcohols, formation of a covalent bond to a hybridized atomic orbital on Ag^+ could produce a trend in hydration consistent with our observations of the alcohol adducts.

Energies for the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital, and the positions of these orbitals about molecules as determined by ab initio calculations have been useful for explaining the spectroscopic and electrochemical behavior of metal-containing molecules and supramolecular assemblies.[26] Our ab initio calculations for the highest occupied molecular orbital (HOMO) of $[M + Ag + H_2O]^+$ species show that an increase in the size of the alcohol's alkyl group is accompanied by increased delocalization of electron density from the water molecule and silver ion into the alcohol alkyl group (Figure 4). The highest energy bonding interaction between the water molecule and the silver ion occurs well below the HOMO and appears to involve a π-type interaction between both of the lone electron pairs of the oxygen atom of the H_2O molecule and a hybridized d orbital of the silver ion (Figure 5). Additional σ-type bonding interactions between the water molecule and silver ion occur at lower energies. The molecular orbitals between the HOMO and the orbitals in which the bonding interactions with the water molecule occur are delocalized over the silver ion, alcohol oxygen, and one or more atoms of the alcohol alkyl group. The delocalization increases as the length of the alcohol alkyl group increases and decreases with the extent of branching of the alcohol. A similar pattern in redistribution of electron density is observed in the ab initio modeling of the amine adducts of Ag^+. Because these orbitals are predominately either antibonding or nonbonding with respect to the water molecule, such a redistribution of electron density away from the Ag^+ ion toward the alcohol alkyl group would stabilize the interaction between the silver ion and water molecule, consistent with our observations of hydration trends.

Conclusion

We have investigated the tendency for complexes composed of Ag^+ and a single small alcohol to undergo reactions in the gas phase to make hydrated and bis-alcohol complexes. The hydration tendencies of the complexes demonstrate that the chemistry of these species in the gas phase is not governed simply by Pearson's scale of HSAB behavior.[19] Siu, Hopkinson, and co-workers[27] have already questioned the relevancy of the HSAB model to gas-phase complexes containing Ag^+ and have suggested that the model can only be applied when delocalization of metal ion charge due to a large number of coordinating ligands occurs.

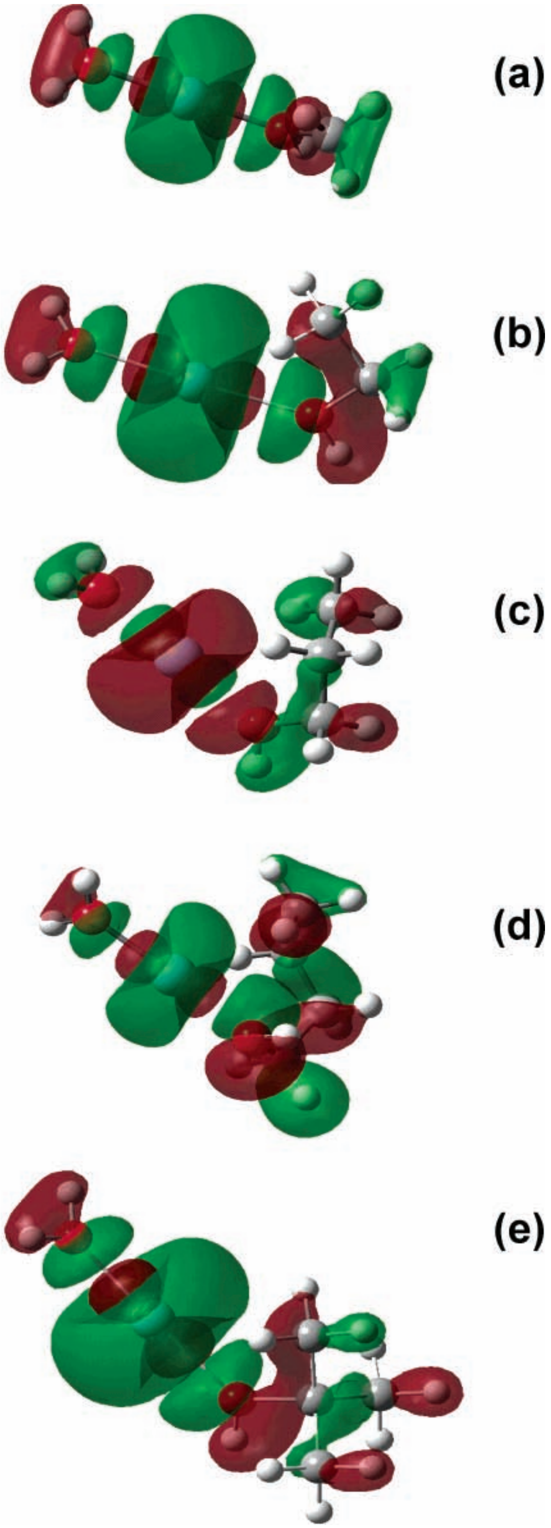

Figure 4. HOMO geometry of hydrated *n*-alcohol/Ag^+ complexes, $[M + Ag + H_2O]^+$ with M = (a) MeOH, (b) EtOH, (c) *n*-PrOH, (d) *n*-BuOH, and (e) *tert*-BuOH, as determined using ab initio calculations (DFT, B3LYP/3-21G*). The geometry suggests that the electron density on the alcohol alkyl group increases with C-chain length and decreases with branching.

Rate constants for hydration obtained using ADO theory are consistent in magnitude with the rate constants obtained by kinetic modeling, but they do not follow the trend observed experimentally. Stabilization of the hydrated complexes through distribution of excess energy from reactive collisions among the degrees of freedom of the alcohol alkyl group is generally

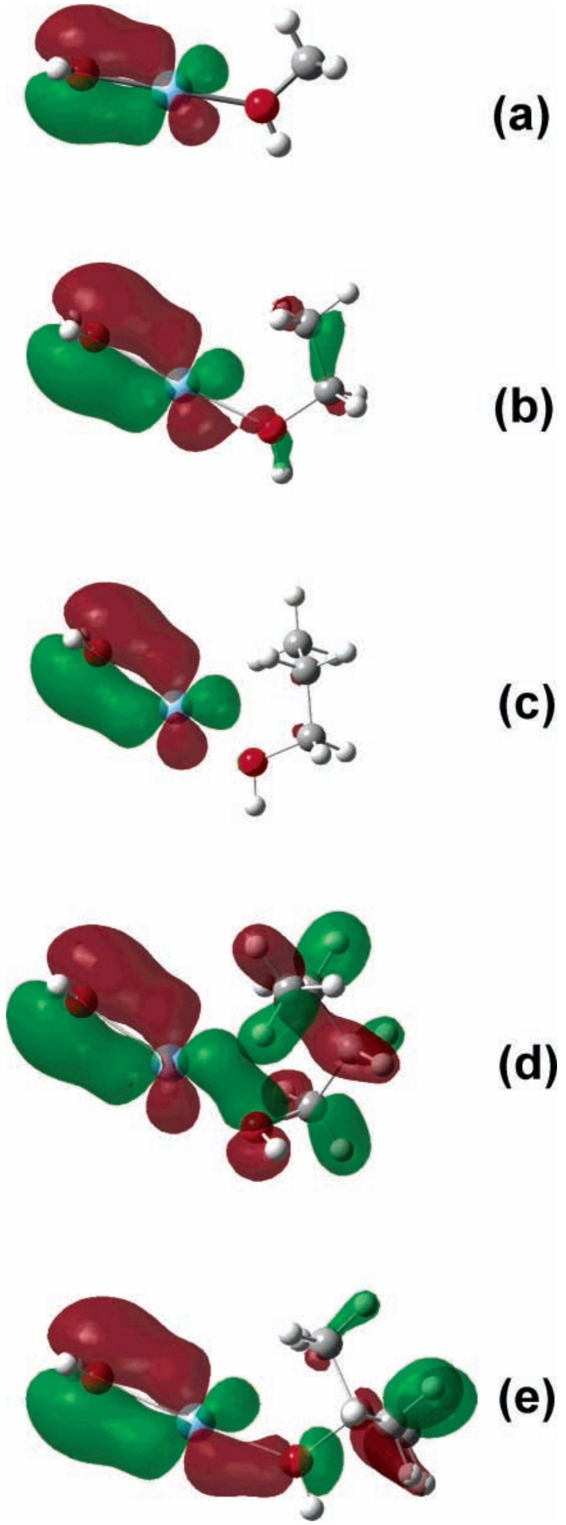

Figure 5. Geometries of the highest energy H_2O bonding orbitals as determined using ab initio calculations (DFT, B3LYP/3-21G*) for hydrated Ag^+ complexes with (a) methanol, (b) ethanol, (c) *n*-propanol, (d) *n*-butanol, and (e) *tert*-butyl alcohol. The orientation of the orbitals suggests a π-type interaction between H_2O and the hybridized metal *d*-orbital.

consistent with the observed trends but fails to explain the change in hydration tendencies with the extent of branching in the alcohol ligand. Bonding of the alcohol ligand may promote a redistribution of electron density on the silver ion through atomic orbital hybridization to facilitate hydration. In this respect, the association reactivity observed is reminiscent of the trends in gas-phase acidity of alcohols first reported by Blair and co-workers.[28] In part, the influence of an alkyl group on the acidity of gas-phase alcohols has been attributed to increasing polarizability with chain length, and partial delocalization of charge. In the present study, molecular orbitals obtained through ab initio calculations show that electron density in interactions between the alcohol ligand and the Ag^+ ion may be delocalized into the alcohol alkyl group, with the extent of delocalization being dependent upon the length of the alkyl group in a manner consistent with observed hydration trends. These results suggest that electronic effects involving the alkyl group of the alcohol ligand play a significant role in the formation and stabilization of the hydrated complex.

Acknowledgment. M.V.S. acknowledges the support for this work by the National Science Foundation (CAREER-0239800), a First Award from the Kansas Technology Enterprise Corporation/NSF Kansas EPSCoR program, the U.S. Department of Energy through the INEEL Institute and Wichita State University. D.H. acknowledges support of the Wichita State University Research Sites for Educators in Chemistry program sponsored by the National Science Foundation.

References and Notes

(1) Sunner, J.; Kishizawa, K.; Kebarle, P. *J. Phys. Chem*. **1981**, *85*, 1814.

(2) (a) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem*. **1980**, *52*, 1641. (b) Peake, D. A.; Gross, M. L. *Anal. Chem*. **1985**, *57*, 115.

(3) (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc*. **1981**, *103*, 784. (b) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6624. (c) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (d) Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1986**, *108*, 1806. (e) Sunderlin, L. S.; Armentrout, P. B. *J. Phys. Chem.* **1988**, *92*, 1209. (f) Sunderlin, L. S.; Armentrout, P. B. *Int. J. Mass Spectrom. Ion Processes* **1989**, *94*, 149. (g) Armentrout, P. B. In *Selective Hydrocarbon Activation: Principles and Progress*; Davies, J. A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1990; p 467.

(4) (a) Nicoll, J. B.; Dearden, D. V. *Int. J. Mass Spectrom*. **2001**, *204* (1−3), 171. (b) Kempen, E. C.; Brodbelt, J. S. *Anal. Chem*. **2000**, *72* (21), 5411. (c) Blair, S. M.; Brodbelt, J. S.; Marchand, A. P.; Chong, H.-S.; Alihodzic, S. *J. Am. Soc. Mass Spectrom*. **2000**, *11* (10), 884. (d) Kempen, E. C.; Brodbelt, J. S.; Bartsch, R. A.; Jang, Y.; Kim, J. S. *Anal. Chem*. **1999**, *71* (24), 5493. (e) Blair, S. M.; Brodbelt, J. S.; Madhusudhan Reddy, G.; Marchand, A. P. *J. Mass Spectrom*. **1998**, *33* (8), 721. (f) Wu, H.-F.; Brodbelt, J. S. *J. Am. Chem. Soc*. **1994**, *116* (14), 6418. (g) More, M. B.; Ray, D.; Armentrout, P. B. *J. Am. Chem. Soc*. **1999**, *121* (2), 417. (h) More, M. B.; Ray, D.; Armentrout, P. B. *J. Phys. Chem. A* **1997**, *101* (23), 4254. (i) Bartoszek, M.; Graubaum, J.; Wendland, D.; Dambowski, R. *Eur. Mass Spectom*. **1999**, *5* (2), 81. (j) Colton, R.; Mitchell, S.; Traeger, J. C. *Inorg. Chim. Acta* **1995**, *231* (1−2), 87.

(5) (a) Alvarez, E. J.; Vartanian, V. H.; Brodbelt, J. S. *J. Am. Soc. Mass Spectrom*. **1997**, *8* (6), 620. (b) Chu, I.-H.; Zhang, H.; Dearden, D. V. *J. Am. Chem. Soc*. **1993**, *115* (13), 5736.

(6) (a) Ralph, S. F.; Sheil, M. M.; Scrivener, E.; Derrick, P. J. *Eur. Mass Spectrom*. **1997**, *3* (3), 229. (b) Ralph, S. F.; Iannitti, P.; Kanitz, R.; Sheil, M. M. *Eur. Mass Spectrom*. **1996**, *2* (2/3), 173. (c) Chen, Q.; Cannell, K.; Nicoll, J.; Dearden, D. V. *J. Am. Chem. Soc*. **1996**, *118* (27), 6335.

(7) (a) Blanda, M. T.; Farmer, D. B.; Brodbelt, J. S.; Goolsby, B. J. *J. Am. Chem. Soc*. **2000**, *122* (7), 1486. (b) Goolsby, B. J.; Brodbelt, J. S.; Adou, E.; Blanda, M. *Int. J. Mass Spectrom*. **1999**, *193* (2/3), 197. (c) Zhou, J.; Kawanishi, Y.; Zhang, Y.; Yuan, H.; Huang, Z. *Chem. Lett*. **1999**, *4*, 345. (d) Wong, P. S. H.; Yu, X.; Dearden, D. V. *Inorg. Chim. Acta* **1996**, *246* (1−2), 259.

(8) (a) Gatlin, C. L.; Turećek, F. *J. Mass Spectrom.* **2000**, *35*, 172. (b) Gatlin, C. L.; Turećek, F.; Vaisor, T. *J. Mass Spectrom.* **1995**, *30*, 1605. (c) Gatlin, C. L.; Vaiser, T.; Turećek, F. *J. Am. Chem. Soc*. **1995**, *117*, 3637. (d) Saraswathi, M.; Miller, J. M. *Rapid Commun. Mass Spectrom*. **1996**, *10*, 1706. (e) Yalcin, T.; Wang, J.; Wen, D.; Harrison, A. G. *J. Am. Soc. Mass Spectrom*. **1997**, *8*, 749. (f) Wen, D.; Yalcin, T.; Harrison, A. G. *Rapid Commun. Mass Spectrom*. **1995**, *9*, 1155. (g) Hoppilliard, Y.; Rogalewicz, F.; Ohanessian, G. *Int. J. Mass Spectrom*. **2001**, *204* (1−3), 267. (h) Rogalewicz, F.; Hoppilliard, Y.; Ohanessian, G. *Int. J. Mass Spectrom.* **2001,** *206* (1−2), 45. (i) Lee, Q. P.; Amster, I. J. *J. Am. Soc. Mass Spectrom*. **1996**, *7*, 722. (j) Zhang, D.; Tao, W. A.; Cooks, R. G. *Int. J. Mass Spectrom*. **2001**, *204* (1−3), 159. (k) Tao, W. A.; Zhang, D.; Cooks,

R. G.; Nikolaev, E. N. *J. Am. Chem. Soc*. **2000**, *122*, 1059. (l) Lee, V. W.-M.; Li, H.; Lau, T.-C.; Guevremont, R.; Siu, K. W. *J. Am. Soc. Mass Spectrom*. **1998**, *9*, 760.

(9) (a) Teesch, L.; Adams, J. *Top. Mass Spectrom*. **1994**, 39. (b) Teesch, L. M.; Adams, J. *J. Am. Chem. Soc.* **1990**, *112* (11), 4110. (c) Gross, M. L. *Acc. Chem. Res*. **1994**, *27*, 361 and references therein. (d) Hu, P.; Gross, M. L. *J. Am. Chem. Soc*. **1993**, *115*, 8821. (e) Nemirovskiy, O. V.; Gross, M. L. *J. Am. Soc. Mass Spectrom*. **2000**, *11* (9), 770. (f) Mallis. L. M.; Russell, D. H. *Anal. Chem.* **1986**, *58*, 1076. (g) Bluhm, B. K.; Shields, S. J.; Bayse, C. A.; Hall, M. B.; Russell, D. H. *Int. J. Mass Spectrom*. **2001**, *204* (1−3), 32. (h) Loo, J. A. *Int. J. Mass Spectrom*. **2001**, *204* (1−3), 113.

(10) (a) Gaucher, S. P.; Leary, J. A. *Anal. Chem.* **1998**, *70* (14), 3009. (b) Gausher, S. P.; Leary, J. A. *Int. J. Mass Spectrom.* **2000**, *197*, 139. (c) Konig, S.; Leary, J. A. *J. Am. Soc. Mass Spectrom.* **1998**, *9* (11), 1125.

(11) (a) Vachet, R. W.; Hartman, J. R.; Callahan, J. H. *J. Mass Spectrom*. **1998**, *33* (12), 1209. (b) Hartman, J. R.; Vachet, R. W.; Callahan, J. H. *Inorg. Chim. Acta* **2000**, *297* (1−2), 79. (c) Vachet, R. W.; Callahan, J. H. *J. Mass Spectrom*. **2000**, *35* (3), 311. (d) Vachet, R. W.; Hartman, J. A. R.; Gartner, J. W.; Callahan, J. H. *Int. J. Mass Spectrom*. **2001**, *204*, 101.

(12) Combariza, M. Y.; Vachet, R. W. J. *Am. Soc. Mass Spectrom*. **2002**, *13* (7), 813.

(13) Wu, H.-F.; Brodbelt, J. S. *Inorg. Chem*. **1995**, *34*, 615.

(14) (a) Scott, J. R.; Groenewold, G. S.; Gianotto, A. K.; Benson, M. T.; Wright, J. B. *J. Phys. Chem. A* **2000**, *104*, 7079. (b) Groenewold, G. S.; Scott, J. R.; Gianotto, A. K.; Hodges, B. D. M.; Kessinger, G. F.; Benson, M. T. *J. Phys. Chem. A* **2001**, *105*, 9681−9688. (c) Groenewold, G. S.; Hodges, B. D. M.; Scott, J. R.; Gianotto, A. K.; Appelhans, A. D.; Kessinger, G. F.; Wright, J. B. *J. Phys. Chem. A* **2001**, *105*, 4059.

(15) (a) Perera, B. A.; Ince, M. P.; Talaty, E. R.; Van Stipdonk, M. J. *Rapid Commun. Mass Spectrom*. **2001**, *15*, 615. (b) Perera, B. A.; Gallardo, A. L.; Barr, J. M.; Tekarli, S. M.; Anbalagan, V.; Talaty, E. R.; Van Stipdonk, M. J. *J. Mass Spectrom*. **2002**, *37*, 401. (c) Talaty, E. R.; Perera, B. A.; Gallardo, A. L.; Barr, J. M.; Van Stipdonk, M. J. *J. Phys. Chem. A* **2001**, *105*, 8059.

(16) (a) Lee, V. W.-M.; Li, H.; Lau, T.-C.; Siu, K. W. M. *J. Am. Chem. Soc*. **1998**, *120*, 7302. (b) Chu, I. K.; Gou, X.; Lau, T.-C.; Siu, K. W. M. *Anal. Chem*. **1999**, *71*, 2364. (c) Chu, I. K.; Shoeib, T.; Guo, X.; Rodriquez, C. F.; Lau, T.-C.; Hopkinson, A. C.; Siu, K. W. M. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 163. (d) Tang, X.; Ens, W.; Standing K. G.; Westmore, J. B. *Anal. Chem*. **1988**, *60*, 1791. (e) Barr, J. M.; Van Stipdonk, M. J. *Rapid Commun. Mass Spectrom*. **2002**, *16*, 566. (f) Anbalagan, V.; Perera, B. A.; Silva, A. T. M.; Gallardo, A. L.; Barber, M.; Barr, J. M.; Terkarli, S. M.; Talaty, E. R.; Van Stipdonk, M. J. *J. Mass Spectrom*. **2002**, *37*, 910.

(17) (a) Su, T.; Bowers, M. T. *Int. J. Mass Sprectrom. Ion Processes* **1973**, *12*, 347. (b) Su, T.; Bowers, M. T. *Int. J. Mass Sprectrom. Ion Processes* **1975**, *17*, 211.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E., Jr.; Burant, J. C.; Sapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Benucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Makick, D. K.; Rabuck, A. D.; Taghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Kieth, T.; Al-Laham, M. A.; Nanayakkary, C. Y.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.5; Gaussian Inc.: Pittsburgh, PA, 1998.

(19) (a) Pearson, R. G. *Inorg. Chem*., **1988**, *27*, 734. (b) Pearson, R. G. *J. Org. Chem*. **1989**, *54*, 1423.

(20) Cotton, A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley and Sons: New York, 1988; p 941.

(21) Koizumi, H.; Larsen, M.; Armentrout, P. B. *J. Phys. Chem. A* **2003**, *107*, 2829.

(22) Anbalagan, V.; Patel, J. N.; Niyakorn, G.; Van Stipdonk, M. J. *Rapid Commun. Mass Spectrom*., in press.

(23) Ma, N. L. *Chem. Phys. Lett.* **1998**, *297*, 230.

(24) Rodgers, M. T.; Armentrout, P. B. *Mass Spectrom. Rev.* **2000**, *19*, 215.

(25) (a) Deng, H.; Kebarle, P. *J. Am. Chem. Soc*. **1998**, *120*, 2925. (b) El Aribi, H.; Shoeib, T.; Ling, Y.; Rodriques, C.; Hopkinson, A.; Sui, K. *J. Phys. Chem. A* **2002**, *106* (12), 2908−14.

(26) (a) D'Souza, F. D.; Zandler, M. E.; Smith, P. M.; Deviprasad, G. R.; Klykov, A.; Fujitsuka, M.; Ito, O. *J. Phys. Chem. A* **2002**, *106*, 649. (b) D'Souza, F.; Deviprasad, G. R.; Zandler, M. E.; Hoang, V. T.; Klykov, A.; Van Stipdonk, M. J.; Perera, A.; El-Khouly, M. E.; Fujitsuka, M.; Ito, O. *J. Phys. Chem. A* **2002**, *106*, 3243. (c) Cotton, F. A.; Gruhn, N. E.; Gu, J.; Huang, P.; Lichtenberger, D. L.; Murillo, C. A.; Van Dorn, L. O.; Wilkinson, C. C. *Science* **2002**, *298*, 1971.

(27) Shoeib, T.; Gorelsky, S. I.; Lever, A. B. P.; Siu, K. W. M.; Hopkinson, A. C. *Inorg. Chim. Acta* **2001**, *315* (2), 236.

(28) (a) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc*. **1968**, *90*, 6561. (b) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc*. **1970**, *92*, 5986. (c) Blair, L. K.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc*. **1973**, *95*, 1057.