

Gas-Phase Studies of Group-11 Cation (Cu^+ , Ag^+ , and Au^+) Reactions with 2-Propanol in a Supersonic Beam-Expansion Source

Ya-Chien Huang, Po-Hua Su, and Chen-Sheng Yeh*

Department of Chemistry, National Cheng Kung University, Tainan, Taiwan 701, R. O. C

(Received August 18, 2000)

The gas-phase reactions of group-11 ions (Cu^+ , Ag^+ , and Au^+) with 2-propanol were investigated using laser vaporization combined with supersonic beam expansion in a time-of-flight mass spectrometer. A number of reaction pathways, including association, dehydrogenation, and dehydration, were observed. Among these metal ions, Au^+ is highly reactive toward 2-propanol. The experimental results are parallel to studies by Wilkins et al. using an FT-ICR mass spectrometer (*J. Am. Chem. Soc.*, **107**, 7316 (1985)). The geometries and binding energies of all complexes M^+-L , where $\text{M}^+ = \text{Cu}^+$, Ag^+ , and Au^+ , $\text{L} =$ 2-propanol, acetone, propene, and H_2O , were estimated using Møller–Plesset perturbation (MP2) and density functional theory (BLYP). The bond strengths of the complex ions involving gold revealed the strongest bonding, due to a relativistic effect. The energetic relationship between the reactants and the products facilitated an interpretation of the observed exit channels. Because of the supersonic beam source employed, larger clusters containing metal ions were generated as well. Because the cluster sizes with solvent molecules were ≥ 2 , the reactivities were apparently limited to Cu^+ and Ag^+ clusters, while the reactive nature changed in Au^+ along with the formation of acetone, lacking in the bare Au^+ reactions. For larger clusters, calculations on $\text{Ag}^+-(2\text{-propanol})_2$ and $\text{Ag}^+-(2\text{-propanol})(\text{acetone})$ complexes using BLYP were performed to obtain their energetics.

Probing the reactions of metal ions with organic substrates in the gas phase without any solvent interference is of particular importance, due to catalytic implications involving bond-activating processes through the metallic centers. There is no doubt that understanding the structures and interacting forces between the metals and molecules will facilitate a complete comprehension of metal ion–molecule reactions. The geometries in metal ion–molecule complexes are strongly dependent on how the metal ions interact with the coordinated molecules. The electrostatic or covalent nature in bonding has been described for a variety of complexes.^{1–6}

For gas-phase metal ion–molecule chemistry, Fourier-transform ion cyclotron resonance⁷ and guided ion-beam⁸ mass spectrometers have provided significant contributions. Both techniques have obtained thermochemical data under thermalized conditions. It should be mentioned that the method used to generate complex ion species might have a significant influence on the final product distributions. Recently, a molecular beam pick-up method as the ion–molecule reaction source was employed to study bare metal ions or molecular cluster ion reactions.^{9–11} Under those circumstances, the association and H-elimination process switch as the cluster sizes change has been observed in alkaline earth metal ion–water clusters.⁹ The alkaline earth metal ion–methanol clusters appeared to have similar behaviors to those in H_2O systems.¹¹ However, Duncan and co-workers have reported that such intracuster reactions with the loss of hydrogen, which leads to $\text{MgOCH}_3^+(\text{CH}_3\text{OH})_{n-1}$, were inhibited in a pulsed beam-expansion source.¹² This was explained in terms of clusters produced at colder temperatures from their source. Therefore, the motivation was to investigate the reactions of group-11 metals

(Cu^+ , Ag^+ , and Au^+) with 2-propanol using a pulsed-beam expansion source.

Staley et al.¹³ and Wilkins et al.¹⁴ studied Cu^+ , Ag^+ , and Au^+ with a series of alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, isobutanol, and 2-methyl-2-propanol) using an FT-ICR mass spectrometer. The intriguing findings were that Cu^+ , Ag^+ , and Au^+ exhibited distinct reactivities toward these alcohols. A diversity of processes, such as dehydrogenation or dehydration, occurred in association with metal insertion into the C–O or C–H bond. Wilkins proposed oxidative addition via α C–H bond insertion to proceed dehydrogenations, as opposed to an O–H insertion mechanism, as suggested by Staley.^{13,14} In the Fe^+ , Cr^+ , and Mo^+ reactions with alcohols, Gross thought that the high O–H bond energy did not favor metal-ion insertion based on a thermodynamic consideration.¹⁵ Au^+ displayed the highest reactivity, while Ag^+ produced fewer reaction products. According to Wilkins's results with Ag^+ , Ag^+-ROH condensations were always the predominant products, except for the 2-propanol and 2-methyl-2-propanol reactions.¹⁴ Moreover, we also noted that the most extensive products were observed in those reactions of Au^+ with 2-propanol and 1-butanol.¹⁴ Thus, 2-propanol was chosen as a target molecule.

In this study, we attempted to investigate whether a beam-expansion source, analogous to Duncan's design,¹² can produce similar reactions to those of Wilkins et al.¹⁴ In addition, ab initio and density functional theory (DFT) methods were employed to study the structures and binding energies of the relevant M^+-L reaction products, where $\text{M}^+ = \text{Cu}^+$, Ag^+ , and Au^+ , $\text{L} =$ 2-propanol, acetone, propene (C_3H_6), and H_2O . The relative energies between the reactants and the products can

then be attained so as to examine the thermodynamic stability. Since a supersonic molecular beam was used in our experiments, the reactions of larger metal ion–molecule clusters were also studied. Further, theoretical calculations were conducted on the larger cluster ions, $\text{Ag}^+-(2\text{-propanol})_2$ and $\text{Ag}^+-(2\text{-propanol})(\text{acetone})$, to facilitate interpreting the experimental observations.

Experimental

A description of the apparatus used for this experiment was previously given.^{16,17} A laser-vaporization technique combined with a supersonic molecular beam was employed to induce metal ion–molecule reactions. A copper (99.999%) or silver (99.9%) rod was suspended in a cutaway holder, a rod holder without a growth channel to produce primarily cation complexes containing one and two ligands, attached to a Jordan pulsed valve, whereas gold foil (99.9%) was wrapped around an Al rod for producing Au ions. The metal rods were irradiated using a 532 nm wavelength of the second-harmonic output of a Nd:YAG laser (QuantaL Brilliant) operated at 10 Hz with 1–2 mJ/pulse. The vaporization laser beam was focused 1.5 cm ahead of the metal rods. Helium carrier gas with a back pressure of 6 atm seeded with 2-propanol vapor was expanded supersonically and intersected with metal ions at the vaporized region. HPLC-grade 2-propanol was used in these experiments. $\text{CH}_3\text{CH}(\text{OD})\text{CH}_3$ (ACROS, 98+%) and $\text{CH}_3\text{CD}(\text{OH})\text{CH}_3$ (Aldrich, 98%) were used to clarify the reaction mechanisms. These deuterated samples were loaded into a liquid reservoir, where the buffer gas carried the 2-propanol vapor into a pulsed valve, and conducted inside a glovebox filled with nitrogen gas.

The ion products were expanded and skimmed (1 mm diameter) into a reflectron time-of-flight mass spectrometer. The positive ions were extracted by applying pulsed voltages to two metal plates, i.e. repeller and extraction plates, and traveled along a field-free tube. They were then reflected using a double-stage reflector and detected using a dual microchannel plate detector.

Theoretical Computations

The calculations were carried out using second-order Møller–Plesset perturbation theory (MP2) and the BLYP density functional theory. The double-zeta valence basis sets and the effective core potentials (ECPs) of Hay and Wadt were used for Cu, Ag, and Au atoms.¹⁸ In order to prevent an imbalance in the basis set between the metals and ligands, the split-valence double-zeta 6-31G basis was restricted for our calculation choice to the ligands. Three basis sets, i.e. 6-31G, 6-31G(d), and 6-31G(d,p), were selected to optimize the H_2O and $\text{M}^+-\text{H}_2\text{O}$ complexes, where $\text{M}^+ = \text{Cu}^+, \text{Ag}^+, \text{and Au}^+$. The relativistic effects were included in the Hay–Wadt ECPs of Ag and Au. We also added the f polarization functions to increase the flexibility of the ECP basis. The f exponents are 3.525 for Cu, 1.611 for Ag, and 1.050 for Au.¹⁹ Once the basis set was chosen, the ligand and metal cation–ligand complex geometries were obtained at the MP2 and BLYP theory levels with 6-31G(d,p) plus ECP on metals. The harmonic vibrational frequencies were computed at the MP2 and BLYP levels to clarify whether the minima were genuine, and to calculate the zero-point energy. For metal ion–(2-propanol) complexes, the zero-point energies were calculated at the BLYP/6-31G(d,p). Natural charge populations were studied on the complexes at the MP2 level using a natural bond orbital (NBO) analysis. The calculations were performed using a Gaussian 98 software package.²⁰

Results and Discussion

Reactions of Bare Metal Ions with 2-Propanol. Prior to seeding 2-propanol vapor, *pure* He gas was used to inspect the ion products from our ion source. Figure 1 shows that only Cu^+ , Ag^+ , and Au^+ atomic signals appeared, and that no other impurities, i.e. metal clusters and oxides, were detected. The Cu^+ and Ag^+ mass spectra show doublet patterns for the isotopes for each element. Copper has two isotopes, 63 (69.1%) and 65 (30.9%), and silver possesses 107 (51.8%) and 109 (48.2%) with nearly equivalent abundances.

Under the same experimental conditions, e.g. vaporization power and backing pressure, as shown in Fig. 1, ion–molecule reactions took place whenever 2-propanol was employed in the He gas. Figure 2a shows that several reaction products were observed in the low-mass region (< 150 amu). The Cu^+ reactions with 2-propanol primarily yielded $\text{Cu}^+-\text{H}_2\text{O}$, $\text{Cu}^+-\text{C}_3\text{H}_6$, and $\text{Cu}^+-\text{CH}_3\text{COCH}_3$, as well as the $\text{Cu}^+-\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ association channel. In addition to complexation, a peak along with a Cu^+ signal was weakly generated and assigned as $\text{C}_3\text{H}_7\text{O}^+$. Taking the assumption of Wilkins, $\text{C}_3\text{H}_7\text{O}^+$ is referred to $\text{CH}_3\text{C}^+(\text{OH})\text{CH}_3$. Acetone (mass 58) is two mass units less than 2-propanol (mass 60). Hence, a triplet band located at the mass 120 region is ascribed to both the $\text{Cu}^+-\text{ace-}$

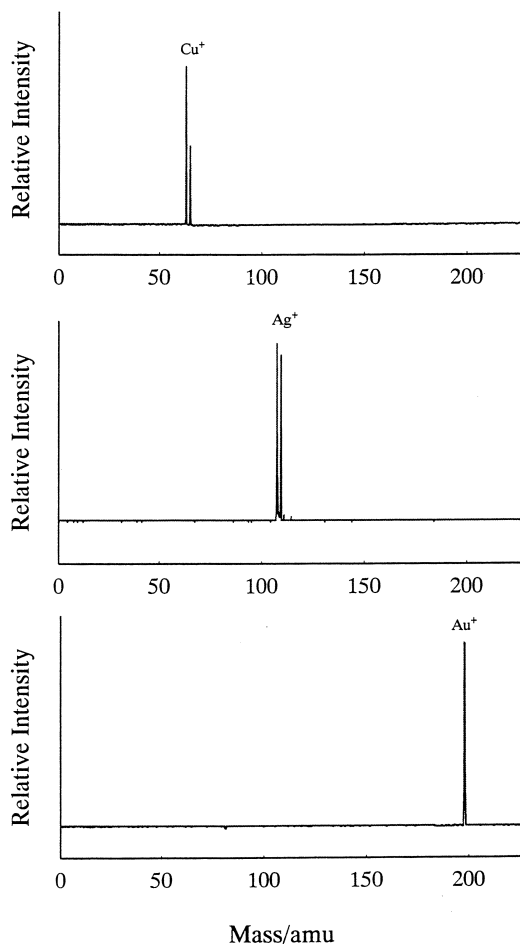


Fig. 1. Mass spectra corresponding to Cu^+ , Ag^+ , and Au^+ atomic signals.

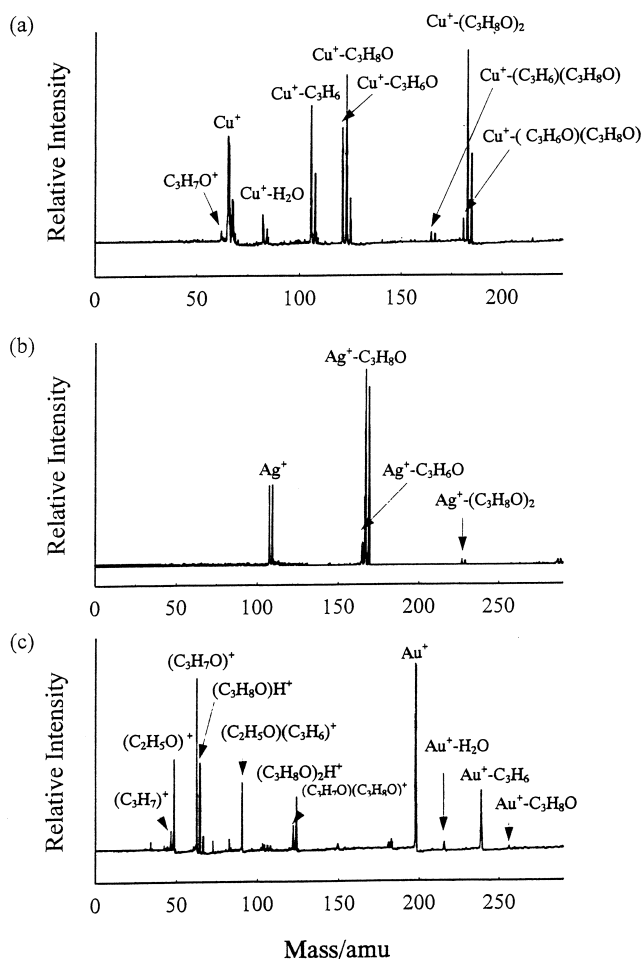


Fig. 2. Mass spectra for the reactions of 2-propanol with (a) Cu^+ , (b) Ag^+ , and (c) Au^+ .

tone and $\text{Cu}^+-(2\text{-propanol})$ complexes and the middle peak, with a mass of 123, consisting of $^{63}\text{Cu}^+-(2\text{-propanol})$ and $^{65}\text{Cu}^+-\text{acetone}$, two components. With regard to $\text{Cu}^+-\text{C}_3\text{H}_6$, a photodissociation action was conducted to facilitate the identification of C_3H_6 by means of their fragments. The photodissociation laser beam crossed the ion beam at the turning point of the reflector in the RTOF mass spectrometer. The fragment and parent ions were analyzed using their flight times. Figure 3 shows the resulting fragments as Cu^+ together with a charge-transfer channel, C_3H_6^+ . Power-dependence measurements using 355 nm revealed a two-photon process for C_3H_6^+ formation. A parallel experiment was performed by seeding pure propene gas into the He carrier gas to form the $\text{Cu}^+-\text{C}_3\text{H}_6$ complex. Identical consequences (same fragments as shown in Fig. 3 and a two-photon absorption at 355 nm) were obtained from photodissociation under the same experimental conditions. This implies that the C_3H_6 species is propene, although the other isomeric structures cannot be completely excluded. The C_3H_6^+ observation via photodissociation indicates that an intact propene is bound to Cu^+ . On the basis of Wilkins' results, the product distributions were 4% for $\text{C}_3\text{H}_7\text{O}^+$, 9% for $\text{Cu}^+-\text{H}_2\text{O}$, 21% for $\text{Cu}^+-\text{C}_3\text{H}_6$, 21% for $\text{Cu}^+-\text{CH}_3\text{COCH}_3$, and 45% for $\text{Cu}^+-\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$.¹⁴ It should be noted that the

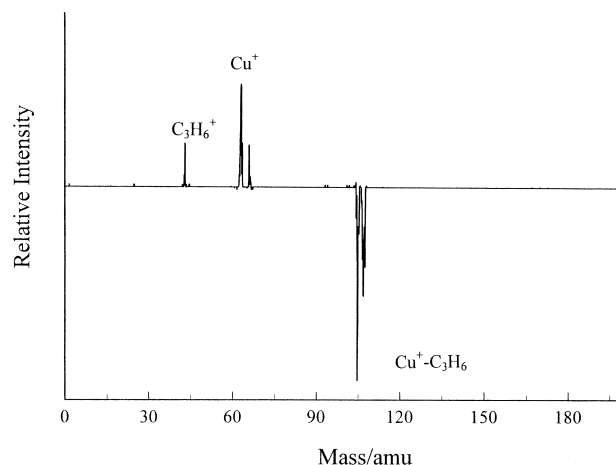


Fig. 3. Photodissociation mass spectrum of $\text{Cu}^+-\text{C}_3\text{H}_6$ at 355 nm with laser intensity of 1.4 mJ/pulse. The depletion signal represents the parent ions with two copper isotopes and is accumulated based on a data acquisition cycle; photodissociation laser on subtracted from laser off.

intensities of our resulting ions can be varied to some extent by appropriately tuning the experimental parameters, e.g. the timing between the vaporization laser and the extraction voltages. In order to investigate any possible internal temperature effect, He cooling gas was replaced by Ar with a larger polarization. The resulting products from Ar were the same as those from He. Our product channels are in good agreement with Wilkins: the formation of H_2O and C_3H_6 complexes via dehydration, the generation of acetone complexes via dehydrogenation, and the production of $\text{CH}_3\text{C}^+(\text{OH})\text{CH}_3$ accompanied by CuH . Figure 2a also displays larger solvent clusters containing two molecules. As can be seen, copper ions still persist with dehydrogenation and dehydration process reactivities, whereas the reaction products diminished significantly in magnitude. We discuss this issue later in the text.

The mass spectrum in Fig. 2b illustrates that the $\text{Ag}^+-\text{acetone}$ complex was the only detectable product in addition to the simple $\text{Ag}^+-(2\text{-propanol})$ association in the reactions of Ag^+ with 2-propanol. The experimental conditions focused mainly on the generation of Ag^+ coordinated with one molecule adduct, as shown in Fig. 2b. From the reaction outcomes, Ag^+ has been shown to be much less reactive toward 2-propanol compared with Cu^+ . We found the $\text{Ag}^+-(2\text{-propanol})$ complex to have a dominant abundance over that of the $\text{Ag}^+-\text{acetone}$ channel. This fact is invariant to the experimental conditions, which is contrary to Wilkins' observations, where the product distributions were 84% and 16% for $\text{Ag}^+-\text{acetone}$ and $\text{Ag}^+-(2\text{-propanol})$, respectively.¹⁴

If the ion-molecule chemistry shifted to gold, Au^+ induces manifold products involving a number of dissociative attachment reactions with 2-propanol, as depicted in Fig. 2c. Besides the channels yielded from the dehydration process, a strong peak regarded as $\text{CH}_3\text{C}^+(\text{OH})\text{CH}_3$ ($\text{C}_3\text{H}_7\text{O}^+$) accompanied by AuH and an appropriate intensity of $\text{CH}_3\text{C}^+\text{H}(\text{OH})$ ($\text{C}_2\text{H}_5\text{O}^+$) with the formation of AuCH_3 appeared. Wilkins reported the largest production (39%) in $\text{CH}_3\text{C}^+(\text{OH})\text{CH}_3$ and a 19% distribution in $\text{C}_2\text{H}_5\text{O}^+$.¹⁴ We also observed a very small

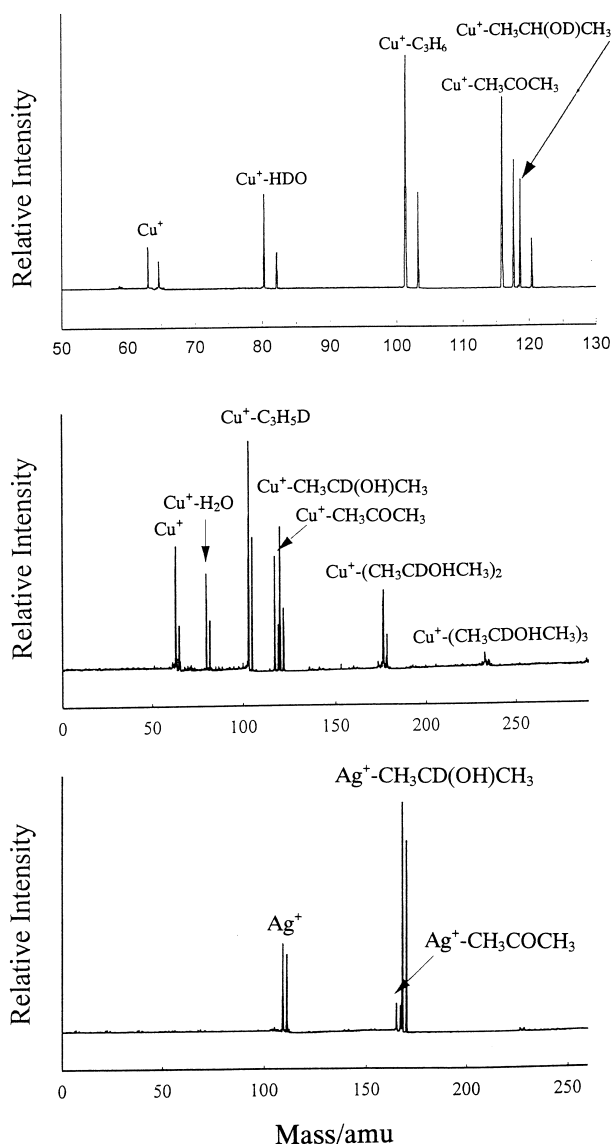
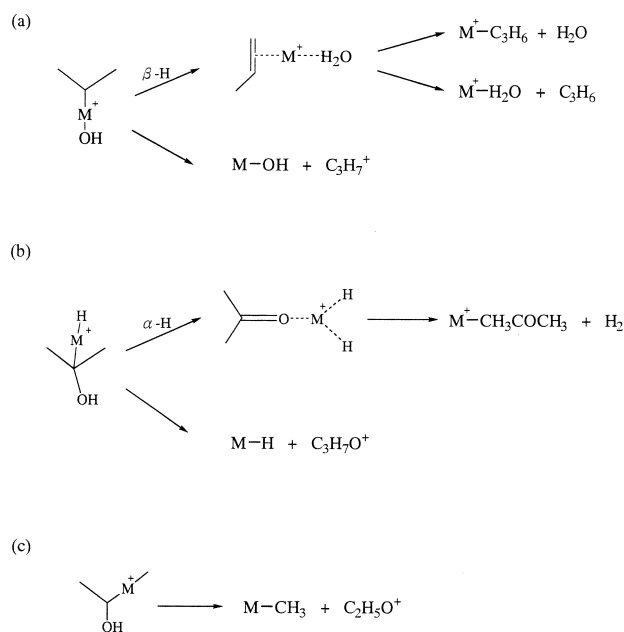


Fig. 4. Mass spectra for the reactions of deuterium-substituted $\text{CH}_3\text{CH}(\text{OD})\text{CH}_3$ with (a) Cu^+ and $\text{CH}_3\text{CD}(\text{OH})\text{CH}_3$ with (b) Cu^+ and (c) Ag^+ .

amount of $\text{Au}^+-(2\text{-propanol})$, while no $\text{Au}^+ \text{--} \text{acetone}$ could be identified. Both 2-propanol and acetone complexes had production yields $\leq 1\%$ in Wilkins' studies.¹⁴ It was quite surprising that there was such a small amount of $\text{Au}^+-(2\text{-propanol})$ condensation, which was expected to be readily synthesized under the beam conditions in our experiments. In Fig. 2c, some Au^+ free clusters, e.g. $(\text{C}_2\text{H}_5\text{O})(\text{C}_3\text{H}_6)^+$, $(\text{C}_3\text{H}_7\text{O})(\text{C}_3\text{H}_8\text{--O})^+$, were generated from our source.

Basically, our results are consistent with a previous investigation by Wilkins and co-workers. Cu^+ , Ag^+ , and Au^+ primarily undergo dehydration, dehydrogenation, and/or hydride abstraction pathways, depending on their reactivities. These dissociative attachment reactions were proposed to result from metal-ion insertion into the C–O, or C–H bond.^{14,15} The thermodynamic factor governs the final products produced.^{14,15}

Deuterated reagents, $\text{CH}_3\text{CH}(\text{OD})\text{CH}_3$ and $\text{CH}_3\text{CD}(\text{OH})\text{CH}_3$, were conducted to identify the above-mentioned inser-



Scheme 1.

tion mechanisms. Figure 4 displays the reactions of Cu^+ with $\text{CH}_3\text{CH}(\text{OD})\text{CH}_3$ and $\text{CH}_3\text{CD}(\text{OH})\text{CH}_3$ and of Ag^+ with $\text{CH}_3\text{CD}(\text{OH})\text{CH}_3$. Based on a careful examination, a quartet pattern was observed in the location of the $\text{M}^+ \text{--} \text{CH}_3\text{CD}(\text{OH})\text{CH}_3$ mass regions. They were assigned as $\text{M}^+ \text{--} \text{CH}_3\text{COCH}_3$ and $\text{M}^+ \text{--} \text{CH}_3\text{CD}(\text{OH})\text{CH}_3$ adducts including two isotopes in metals for each complex. As expected, dehydration with competitive expulsion of H_2O or C_3H_6 appears to be the oxidative addition of metal ions into the C–O bond, followed by β -hydrogen migration with a subsequent elimination of water or propene. For the dehydrogenation pathway, this process proceeds through metal-ion insertion into either the α C–H or O–H bond. Subsequently, an α -hydride shift is followed by reductive elimination to retain acetone, forming $\text{M}^+ \text{--} \text{acetone}$. Unfortunately, our deuterated experiments were not able to distinguish whether the C–H or O–H bond is involved in the metal-ion oxidative addition. However, this is most likely to occur on the lesser binding energy of C–H, as proposed by Wilkins¹⁴ and Gross.¹⁵ The binding energies of α C–H and O–H are 381.2²¹ and 438.9 kJ mol^{–1},²² respectively. The primary reaction routes are depicted in Scheme 1. In addition to the dehydration mechanism, Scheme 1a suggests how the hydroxide abstraction takes place in gold cation reactions, in spite of its low production yield. Wilkins reported a 4% C_3H_7^+ formation value.¹⁴ In contrast to hydroxide abstraction, hydride abstraction, forming AuH in Scheme 1b, occurs readily. For hydride abstraction, copper ions do not show much reaction with 2-propanol and Ag^+ is totally inert, as can be seen in Fig. 2. Scheme 1c illustrates the metal ion insertion into the C–C bond for the formation of $\text{C}_2\text{H}_5\text{O}^+$ in Au^+ reactions.

The thermodynamic factor is always one of the considerations in ion–molecule reactions. With the aid of the theoretical approach, the energetic relationship between reactants and products can be estimated to facilitate the interpretation of the $\text{M}^+ \text{--} \text{L}$ complexes observed, where $\text{M}^+ = \text{Cu}^+$, Ag^+ , and Au^+ , $\text{L} = 2\text{-propanol}$ ($\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$), acetone (CH_3COCH_3),

Table 1. Binding Energies (D_0 in kJ mol^{-1}) of Complexes of Cu^+ , Ag^+ , and Au^+ with H_2O and CH_3COCH_3 as a Function of Methods and Basis Sets and Comparison with the Literature Values

		$\text{Cu}^+-\text{H}_2\text{O}$	$\text{Ag}^+-\text{H}_2\text{O}$	$\text{Au}^+-\text{H}_2\text{O}$	$\text{Ag}^+-\text{CH}_3\text{COCH}_3$
MP2	6-31G	199.6	143.1	183.7	
	6-31G(d)	169.5	118.4	158.2	
	6-31G(d,p)	167.4	116.3	156.5	126.8
BLYP	6-31G	230.1	152.7	217.1	
	6-31G(d)	198.7	126.8	191.2	
	6-31G(d,p)	199.6	126.8	191.6	145.2
Exptl		146.4 ^{a)} 160.7 $\pm$ 7.5 ^{b)}	139.3 ^{e)} 121.8 ^{f)}		159.8 $\pm$ 18.8 ⁱ⁾
	Theory	162.3 ^{c)} 149.0 ^{d)}	123.0 ^{g)}	150.2 ^{h)}	160.7 ^{g)}

a) Taken from reference 23. b) Taken from reference 24. c) Taken from reference 25. d) Taken from reference 26. e) Taken from reference 27. f) Taken from reference 28. g) Taken from reference 5. h) Taken from reference 2. i) Taken from reference 29.

Table 2. Binding Energies (D_0 , kcal mol^{-1}) of Cu^+ , Ag^+ , and Au^+ Complexes Using 6-31G(d,p)

	Cu^+				Ag^+				Au^+			
	2-Pro-panol ^{a)}	Ace-tone ^{b)}	C_3H_6	H_2O	2-Pro-panol ^{a)}	Ace-tone ^{b)}	C_3H_6	H_2O	2-Pro-panol ^{a)}	Ace-tone ^{b)}	C_3H_6	H_2O
MP2	193.3	190.0	169.0	167.4	134.7	126.8	106.7	116.3	200.8	198.3	253.6	156.5
BLYP	233.9	243.1	232.2	199.6	145.2	145.2	123.4	126.8	241.0	256.9	300.0	191.6

a) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$. b) CH_3COCH_3 .

propene (C_3H_6), and H_2O . Upon these metal ion–ligand species, H_2O with the retention of Cu^+ , Ag^+ , and Au^+ and $\text{Ag}^+-\text{CH}_3\text{COCH}_3$ are the only examples where the experimental and/or the theoretical values in the binding energy are available.^{23–29} In order to select an appropriate level to describe the above complexes, we performed calculations by varying the ligand basis sets, i.e. 6-31G, 6-31G(d), and 6-31G(d,p), on the smallest $\text{M}^+-\text{H}_2\text{O}$ adducts.

As shown in Table 1, the convergence of the binding energies is attained at the 6-31G(d,p) basis for both the MP2 and BLYP methods. The value estimated by MP2 using 6-31G(d,p) on $\text{Cu}^+-\text{H}_2\text{O}$ is within the margin of error of the measurements by Armentrout et al.²⁴ and is 5.1 kJ mol^{-1} , slightly more than the Bauschlicher et al. value.²⁵ However, it is greater than the experimental value of Michl²³ and the theoretical calculation from Ohanessian²⁶ by approximately of 18 kJ mol^{-1} . In contrast, BLYP resulted in excessive energy in binding, and a C_s symmetry was attained at BLYP/6-31G(d,p) level. Previous studies^{25,26} all exhibited a C_{2v} symmetry for $\text{Cu}^+-\text{H}_2\text{O}$ as the same structure, calculated by the MP2 method. Hence, the high binding energy and incorrect estimated symmetry make BLYP/6-31G(d,p) useless in describing the $\text{Cu}^+-\text{H}_2\text{O}$ system. With respect to the interaction of Ag^+ with H_2O , the BLYP method presented good agreement with early reports in both theoretical and experimental measurements.^{5,27,28} On the other side, the binding energy was slightly underestimated by MP2. If we move on to examine $\text{Ag}^+-\text{CH}_3\text{COCH}_3$ using the 6-31G(d,p) basis, the BLYP prediction resides within the limits of the experimental values²⁹ and 15.5

kJ mol^{-1} less strongly bound than the energy calculated by Ma.⁵ Compared with BLYP, the MP2 performance is less accurate in predicting the bond energy for the Ag^+ –ligand complexes. For the $\text{Au}^+-\text{H}_2\text{O}$ system, a previous value of 150.2 kJ mol^{-1} by Schwarz and co-workers using the CCSD(T) level of theory is the only available data.² It turns out that the MP2 approach gives an estimation which is only 6.3 kJ mol^{-1} larger than the Schwarz's result.

In addition to σ -donor molecules, such as H_2O , CH_3COCH_3 , and $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, in our studies, a π -bonded ligand, e.g. C_3H_6 , was generated and coordinated with Cu^+ and Au^+ as well. The unsaturated C_3H_6 molecule is a candidate to simultaneously act as a σ -donor and a π -acceptor. That is, the interaction with metal ions involves metal ion $\leftarrow \text{C}_3\text{H}_6$ electron donation and metal ion $\rightarrow \text{C}_3\text{H}_6$ π -back donation. In a survey of previous studies in C_3H_6 (propene) complexing with Cu^+ , Ag^+ , and Au^+ , Schröder et al. semiquantitatively predicted $\text{Au}^+-\text{C}_3\text{H}_6$ with a binding energy of 292.9 ± 29.3 kJ mol^{-1} .³⁰ The computations resulting from MP2 and BLYP using 6-31G(d,p) produce 253.6 and 300.0 kJ mol^{-1} for $\text{Au}^+-\text{C}_3\text{H}_6$, respectively. Lacking accurate experimental data, it is essentially difficult to make a $D_0(\text{Au}^+-\text{C}_3\text{H}_6)$ comparison between MP2 and BLYP. Koch et al. investigated C_2H_4 complexes containing Cu^+ , Ag^+ , and Au^+ with binding energies computed as 189.9, 137.7, and 260.7 kJ mol^{-1} , respectively.⁴ In consideration of the inductive effect, a methyl group replacing a hydrogen atom on propene would favor electron transfer from the ligand to the metal ions, subsequently increasing the binding energy by the coordination of propene to M^+ . The issue per-

Table 3. Natural Population Analysis of M^+-L Complexes

			$M^+ = Cu^+$	$M^+ = Ag^+$	$M^+ = Au^+$
L = $CH_3CH(OH)CH_3$	Charge of M		0.94	0.97	0.84
	Populations ^{a)}	s	0.09	0.03	0.25
L = CH_3COCH_3	Charge of M		0.93	0.97	0.84
	Populations ^{a)}	s	0.11	0.03	0.28
L = C_3H_6	Charge of M		0.92	0.95	0.79
	Populations ^{a)}	s	0.15	0.07	0.45
L = H_2O	Charge of M		0.96	0.98	0.92
	Populations ^{a)}	s	0.07	0.02	0.15

a) Populations refer to 4s, 5s, and 6s for Cu^+ , Ag^+ , and Au^+ , respectively.

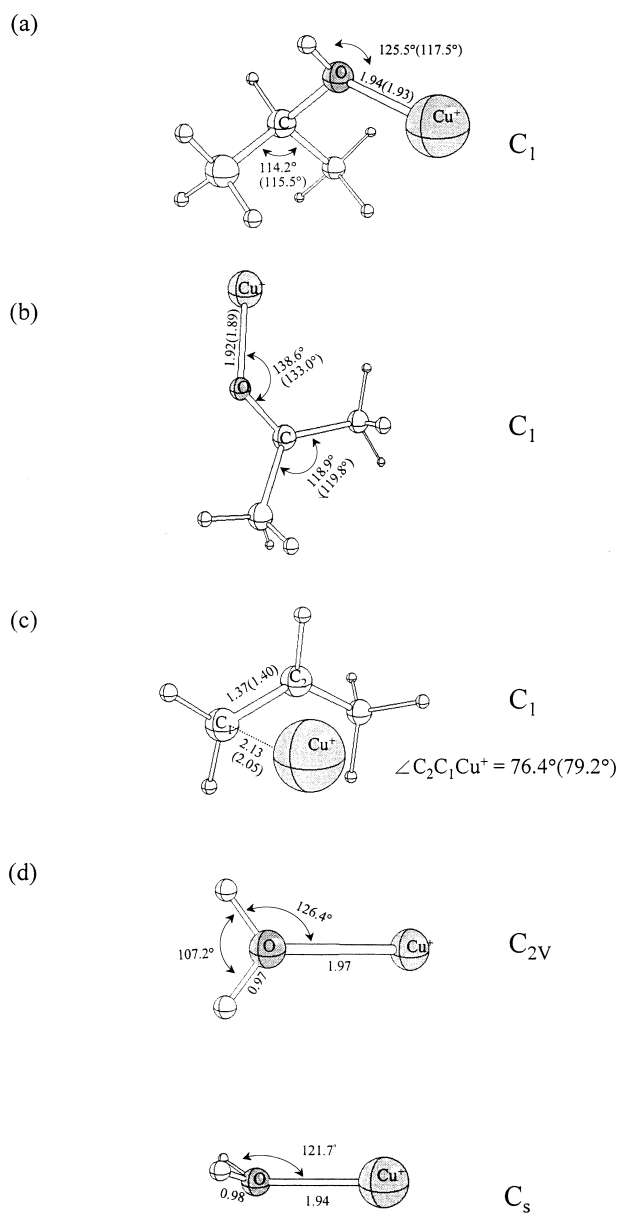


Fig. 5. Optimized structures for (a) $Cu^+-CH_3CH(OH)CH_3$, (b) $Cu^+-CH_3COCH_3$, (c) $Cu^+-C_3H_6$, and (d) Cu^+-H_2O at MP2/6-31G(d,p) and BLYP/6-31G(d,p) (in parenthesis). Selected bond lengths in Å and angles in degree.

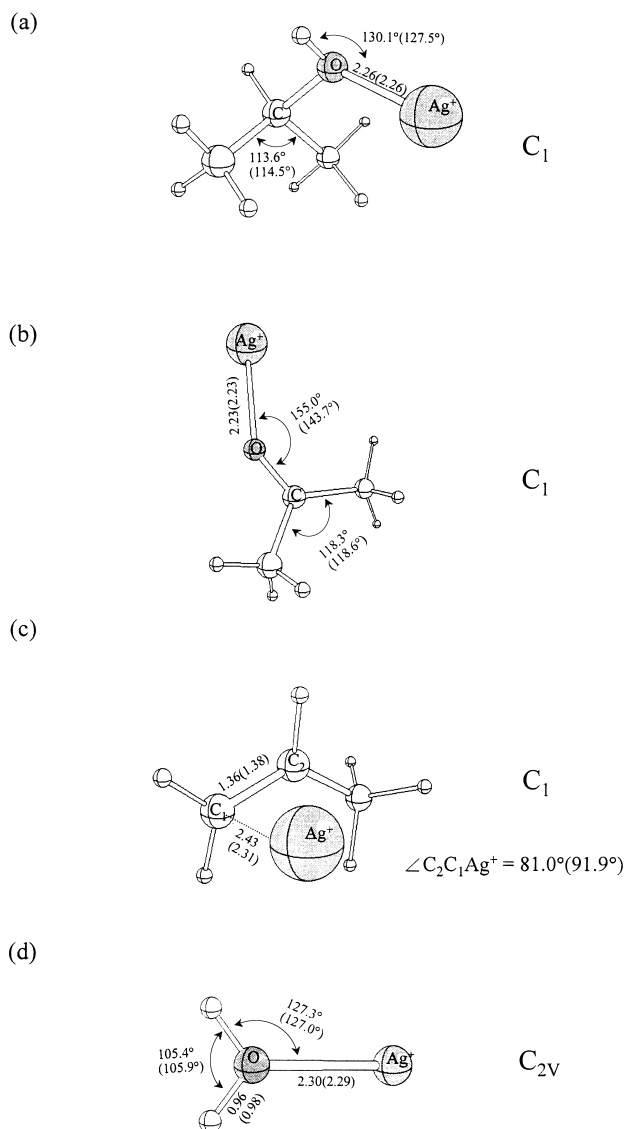


Fig. 6. Optimized structures for (a) $Ag^+-CH_3CH(OH)CH_3$, (b) $Ag^+-CH_3COCH_3$, (c) $Ag^+-C_3H_6$, and (d) Ag^+-H_2O at MP2/6-31G(d,p) and BLYP/6-31G(d,p) (in parenthesis). Selected bond lengths in Å and angle in degree.

taining to electron donation will be discussed immediately. It is, then, expected that the bond strength is $Au^+-C_3H_6 > Au^+-$

C_2H_4 .

Our computational analysis seems to direct the use of MP2/6-31G(d,p) in estimating the binding energies of the σ -donor molecules complexing with Cu^+ and Au^+ , whereas BLYP/6-31G(d,p) is more reliable for the π -bonded C_3H_6 complexes. Interestingly, coordination with Ag^+ appears to involve a simplified use of BLYP/6-31G(d,p) with various ligands. Our procedure has revealed the complexity of choosing one uniform level of theory to analyze the transition-metal complexes. In conclusion, we employed 6-31G(d,p) in both the MP2 and BLYP methods to model the target complexes. Qualitatively, they are sufficient to describe the interactions between metal ions and molecules, the geometries of the complexes and the relative energetics between the reactants and products.

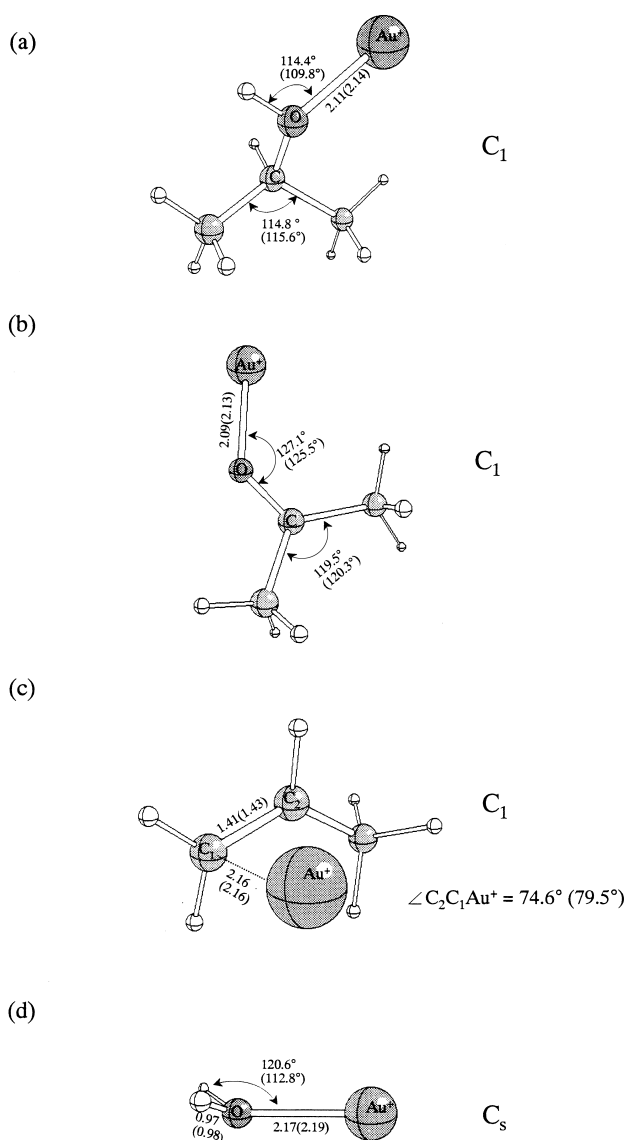


Fig. 7. Optimized structures for (a) $Au^+-CH_3CH(OH)CH_3$, (b) $Au^+-CH_3COCH_3$, (c) $Au^+-C_3H_6$, and (d) Au^+-H_2O at MP2/6-31G(d,p) and BLYP/6-31G(d,p) (in parenthesis). Selected bond lengths in Å and angles in degree.

The binding energies of Cu^+ , Ag^+ , and Au^+ with a series of ligands are listed in Table 2. It was found that BLYP has evaluated larger binding energies compared with the MP2 calculations. With the same ligands, the trends of cation stabilization by coordination are in the order $Ag^+ < Cu^+ < Au^+$. Cu^+-H_2O was computed to be slightly larger than Au^+-H_2O in binding energy at either MP2 or BLYP. An increase in D_o upon coordination with Au^+ has been interpreted in terms of relativistic effects.⁴ Relativity causes a significant contraction of the Au^+ (s^0d^{10}) valence 6s orbital, while this effect is minor for Cu^+ and Ag^+ . Consequently, the electrophilic character of the 6s orbital is enhanced, which results in a significant electron transfer from the ligand to Au^+ . Thus, this procedure increases the covalent bonding between Au^+ and the ligands. Table 3 gives results of the natural population analysis of metal cation–ligand complexes. As expected, the 6s populations of Au^+ are distinctly promoted, suggesting a marked ligand $\rightarrow M^+$ σ -donation. For Cu^+ and Ag^+ complexes, the Cu^+ –ligand adducts exhibit more effective electron transfer. With respect to the valence d orbital populations, a survey of each valence d orbital is doubly occupied with population > 1.96 for Cu^+ and Ag^+ , while a lowering of the population, on the average, to 1.9 for the highest filled d orbitals of Au^+ in the respective complex is observed. This indicates a negligible $M^+ \rightarrow$ ligand ($M^+ = Cu^+$ and Ag^+) back donation, though only a small contribution involved the Au^+ electron donation. With regard to the group-11 metal cations interplaying with ligands, it is clear that this interaction is predominantly an electrostatic force, as can be seen from the metal charges listed in Table 3; nevertheless, the participation of covalency arising mainly from ligand $\rightarrow M^+$ electron donation is important in Au^+ –ligand bonding.

The relativistic effect also affects the complex geometries, such as the bond lengths and bond angles. Figures 5–7 depict the structural features. Regarding the $M^+-C_3H_6$ complexes, Bauschlicher and co-workers studied two different four-membered rings involving the formation of M^+-C bonds responsible for $M^+-C_3H_6$, where $M^+ = Sc^+$, Y^+ , and La^+ .³¹ Those two four-membered rings include one allyl-like structure with one hydrogen bound to the metal and the other with a hydrogen attached to the $C_3H_6^+$ central carbon. On the basis of our photodissociation, resulting in an intact C_3H_6 , we have attempted to exclude the allyl-like structure. That with a hydrogen bound to the central carbon was chosen as a model, as well as the configurations shown in Figs. 5–7. It appears that the former structures are approximately 62.8 kJ mol^{-1} less stable in energy than the geometries given in Figs. 5–7.

Optimization at MP2 and BLYP clearly display that the M^+ –ligand bond distance decreases in the order $Ag^+ > Au^+ > Cu^+$ in complexation of the same ligand. A purely electrostatic interaction would have the bond-to-ligand distance increased from Cu^+ to Au^+ . In an inspection of 2-propanol complexes, $\angle HOM^+$ follows the order $Ag^+ > Cu^+ > Au^+$. Such decreased bond angles represent metal ions bound toward a lone pair of electrons of an oxygen atom, which lies on the molecular plane. The other lone pair is perpendicular to the molecular plane in 2-propanol. An analogous phenomenon was observed at $\angle M^+OC$ for acetone complexes, where one oxygen lone pair lies on the molecular plane perpendicular to the acetone dipole moment. The deviation from C_{2v} symmetry, as the C_s

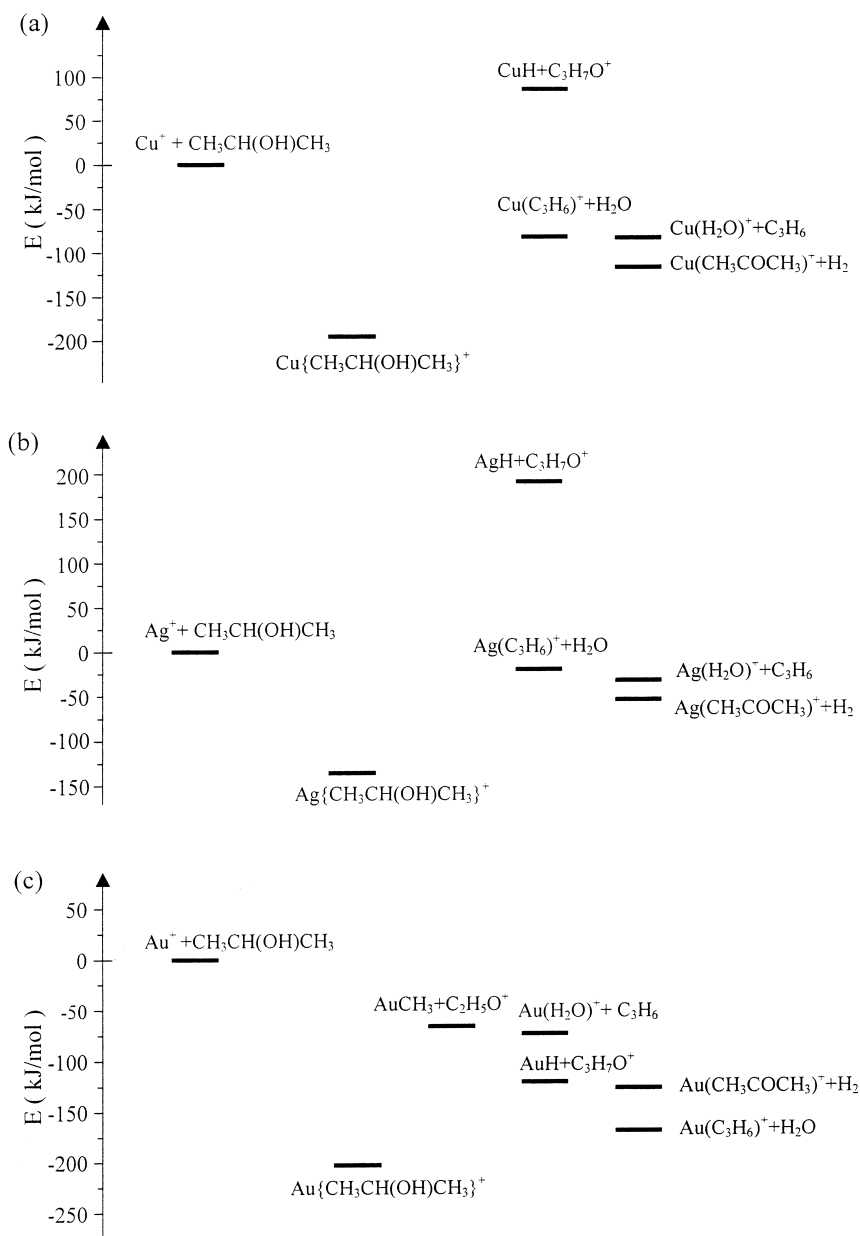


Fig. 8. Schematic energy profile calculated at MP2/6-31G(d,p) for the product channels in the reactions of (a) $\text{Cu}^+ + \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, (b) $\text{Ag}^+ + \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, and (c) $\text{Au}^+ + \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$. E is relative energy.

structure in $\text{Au}^+ - \text{H}_2\text{O}$, demonstrates the covalent contribution in the $\text{Au}^+ - \text{H}_2\text{O}$ moiety with Au^+ pointing toward one of the lone pairs. The dominant interactions are ion-dipole forces resulting in a C_{2v} symmetry for both the $\text{Cu}^+ - \text{H}_2\text{O}$ and $\text{Ag}^+ - \text{H}_2\text{O}$ complexes. A nonplanar C_s structure for $\text{Au}^+ - \text{H}_2\text{O}$ was computed by Schwarz et al.²

In addition to the observation of marked covalency in the interactions of the σ -donor ligands with Au^+ , a drastically enhanced binding energy appears in the π -bonded $\text{Au}^+ - \text{C}_3\text{H}_6$ system, as shown in Table 2. The smaller difference in the ionization potential between the gold cation and the ligands would promote such an electron-transfer process. Both IP values are 9.73 and 9.22 eV for C_3H_6 and Au, respectively.²¹ The small energy gap, i.e. $\Delta\text{IP} = 0.51$ eV, suggests the preference of electron donation from C_3H_6 to Au^+ , as evident in Table 3.

The electron-transfer behavior reflected its effect on the $\text{C}=\text{C}$ bond length. Figures 5–7 illustrate that the $\text{C}=\text{C}$ bond lengthens in the order as $\text{Ag}^+ < \text{Cu}^+ < \text{Au}^+$, ranging from 1.36 Å to 1.41 Å (MP2) or 1.38 Å to 1.43 Å (BLYP).

Following the bonding configurations in those metal ion–molecule complexes, the energetic information on the complex ions provides a guide to interpret the dehydration, dehydrogenation, and association pathways. Figures 8 and 9 depict the energy changes of the metal complexes from the reactants, if one takes into account the MP 2 and BLYP calculations, respectively. Both MP2 and BLYP reveal consistent trends in describing the Cu^+ and Ag^+ stabilization by coordination, even though, the relative quantitative energies from both methods are poorly matched. As can be seen in Figs. 8a–b and 9a–b, the reaction paths in dissociative attachment and direct con-

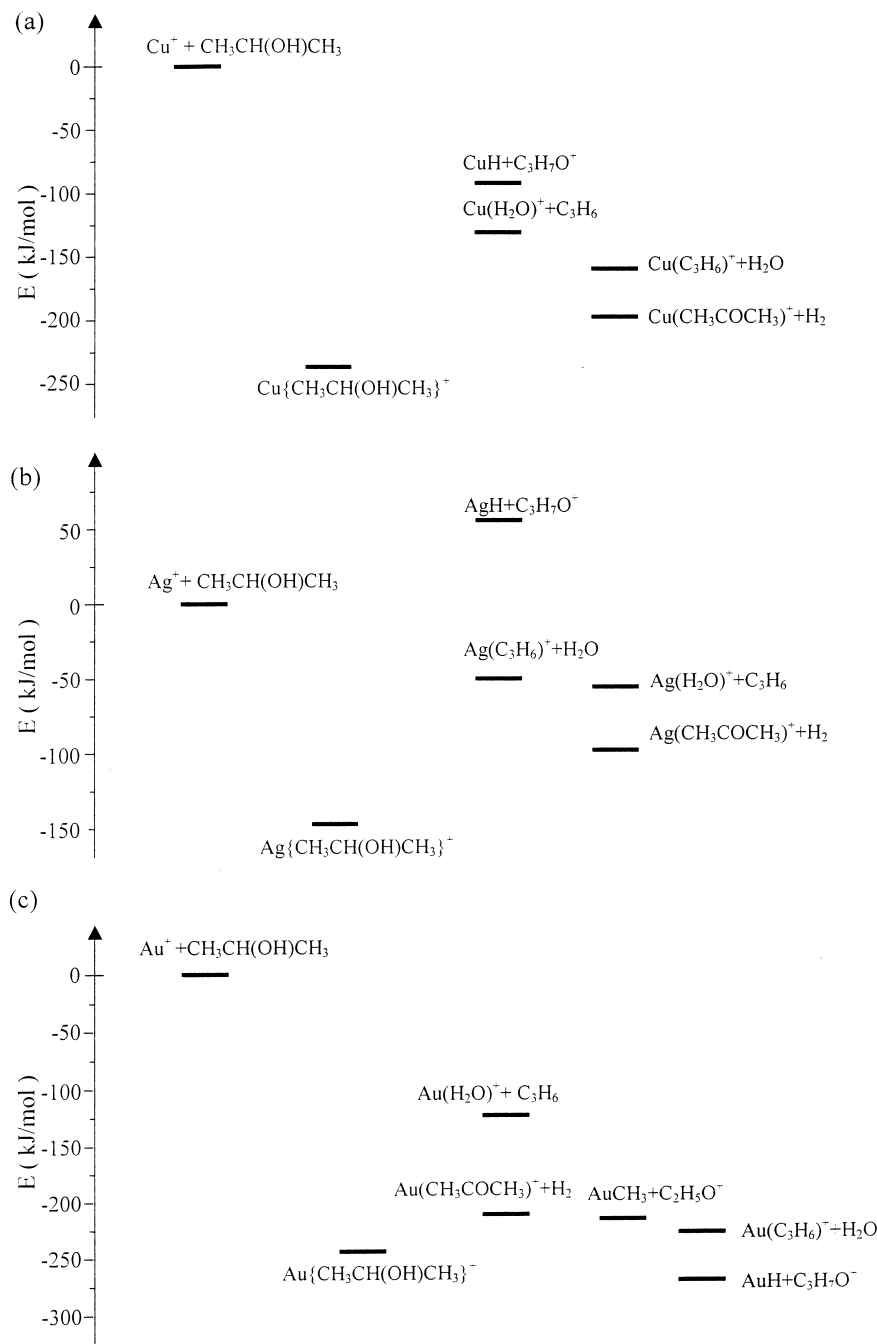


Fig. 9. Schematic energy profile calculated at BLYP/6-31G(d,p) for the product channels in the reactions of (a) $\text{Cu}^+ + \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, (b) $\text{Ag}^+ + \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, and (c) $\text{Au}^+ + \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$. E is relative energy.

condensation are, indeed, exothermic. This explains, at least, the formation of 2-propanol, acetone, H_2O , and propene complexes with Cu^+ and the generation of 2-propanol and acetone complexes containing Ag^+ . However, the absence of $\text{Ag}^+ - \text{H}_2\text{O}$ and $\text{Ag}^+ - \text{C}_3\text{H}_6$ in these experiments cannot be simply explained by the thermodynamic picture. An additional potential-energy surface calculation is helpful to present a distinct explanation. Experimentally, the hydride abstraction produced a neutral metal hydride and $\text{C}_3\text{H}_7\text{O}^+$ in the Cu^+ and Au^+ reactions with 2-propanol. Hence, the products relative to the reactants in energies were also calculated for both Cu^+ and Ag^+ re-

actions. These computations lead to the formation of CuH and $\text{C}_3\text{H}_7\text{O}^+$ located above the reactants at MP2, but below the dissociation limit of $\text{Cu}^+ - (2\text{-propanol})$ at BLYP. However, AgH and $\text{C}_3\text{H}_7\text{O}^+$ appear to be endothermic channels for both methods. An inspection of the calculated binding energies of CuH (MP2: 203.3 kJ mol $^{-1}$, BLYP: 269.9 kJ mol $^{-1}$) and AgH (MP2: 162.8 kJ mol $^{-1}$, BLYP: 220.9 kJ mol $^{-1}$), BLYP results give a good agreement with the experimental reports (CuH : 278.2 kJ mol $^{-1}$, AgH : 215.5 ± 7.9 kJ mol $^{-1}$).²¹ In consideration of the binding energies of the π -bonded C_3H_6 complexes mentioned earlier, BLYP seems to present a better de-

scription of the covalent nature bonding under the level of the method employed here. Qualitatively, the exit channels, i.e. metal hydride and $\text{C}_3\text{H}_7\text{O}^+$, have the highest energies among these products. We observed $\text{C}_3\text{H}_7\text{O}^+$ weakly in Cu^+ reactions with no sign of hydride abstraction for Ag^+ in these experiments.

In the case of Au^+ , the sequence of the energy products is quite different from the MP2 and BLYP performance. The greatest deviation appears in the $\text{Au}^+-(2\text{-propanol})$ moiety from the BLYP results, which do not give rise to the lowest surface energy for the condensation process. The association complex is expected to be produced without the existence of a barrier and to have the minimum energy in the entire reaction pathway. If we take account of the little yield of $\text{Au}^+-(2\text{-propanol})$ in our supersonic source, it shows that Au^+ has manifested an intriguing behavior in the reactions. As stated earlier, Au^+ appears to be highly reactive toward 2-propanol with the involvement of a number of oxidative-addition and reductive-elimination mechanisms, leading to the generation of $\text{Au}^+-\text{H}_2\text{O}$, $\text{Au}^+-\text{C}_3\text{H}_6$, AuH , $\text{C}_3\text{H}_7\text{O}^+$, $\text{Au}-\text{CH}_3$, and $\text{C}_2\text{H}_5\text{O}^+$. On the basis of Figs. 8c and 9c, these processes are accessible for the reactions of Au^+ with 2-propanol under thermal conditions. However, it is still not known whether there is no appearance of the dehydrogenation product $\text{Au}^+-\text{acetone}$ in the experiments. For example, the loss of H_2 is supposed to be a more thermodynamically favored route than the loss of C_3H_6 , followed by the formation of $\text{Au}^+-\text{H}_2\text{O}$. Therefore, kinetic control may, again, play a crucial role. Finally, concerning $D_0(\text{AuH})$, the prediction ($290.8 \text{ kJ mol}^{-1}$) of BLYP is in concert with the experimental value ($292.5 \pm 7.9 \text{ kJ mol}^{-1}$)²¹, while it is 42.7 kJ mol^{-1} less strongly bound from a MP2 evaluation.

In this study, laser ablation was introduced to generate metal ions. It is known that laser-ablated metal ions can be formed in electronically excited states and readily access the endothermic pathways relative to the ground-state reactions. Although we cannot exclude the excited-state ions involved in the reactions, the reaction products are consistent with the results from Wilkins et al.,¹⁴ using an FTICR mass spectrometer. In particular, we also have seen no production of $\text{Ag}^+-\text{C}_3\text{H}_6$, $\text{Ag}^+-\text{H}_2\text{O}$ and $\text{Au}^+-\text{CH}_3\text{COCH}_3$ channels from our source. Otherwise, such chemical specificity would likely be washed out in the excited-state reactions. The same inference can be drawn concerning the reactions of $\text{Ag}^+-(2\text{-propanol})_n$ clusters, as shown later. It is possible that the observed ion-molecule reactions were mainly from the ground-state reactivity.

Metal Ion-(2-Propanol) Clusters Reactions. As mentioned earlier concerning the reactions of Cu^+ with 2-propanol, the product intensities diminished rapidly once the solvent molecules increased. Similarly, both Ag^+ and Au^+ revealed reactivity change when the second solvent started to coordinate with the metal centers. Figure 10a displays that there was no formation of Cu^+ complexes containing $\text{C}_3\text{H}_6\text{O}$, C_3H_6 , and H_2O with cluster sizes ≥ 3 in the reactions of Cu^+ with 2-propanol. Figure 10b shows an example in $\text{Ag}^+-(2\text{-propanol})_n$ clusters. Clusters of up to eight 2-propanol molecules were produced. At $n = 1$, it is clear that the dehydrogenation channel $\text{Ag}^+-\text{acetone}$ is alone with the $\text{Ag}^+-(2\text{-propanol})$. Based on a careful examination, however, we observed no reaction product with a cluster size ≥ 2 , except for the association ad-

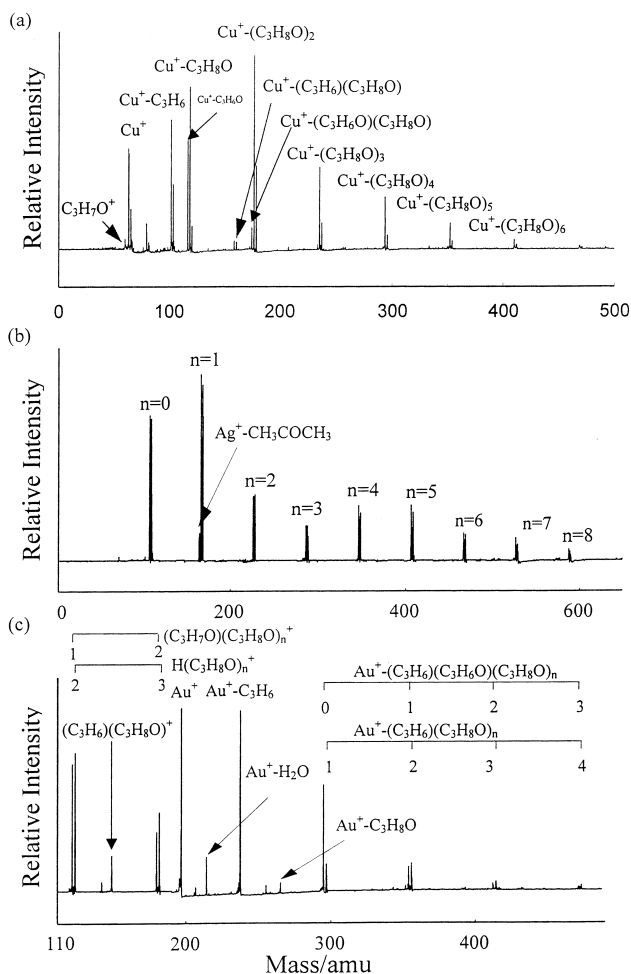


Fig. 10. Mass spectra of the larger clusters containing (a) Cu^+ , (b) Ag^+ with $\text{Ag}^+-\{\text{CH}_3\text{CH}(\text{OH})\text{CH}_3\}_n$ as the dominant products, and (c) Au^+ .

ducts. Different from Cu^+ and Ag^+ , Au^+ changes the reactivity drastically with the formation of acetone channels, as shown in Figure 10c. In the reactions of bare Au^+ with 2-propanol, no $\text{Au}^+-\text{acetone}$ complex was observed. Here, acetone was readily produced for the cluster size $n \geq 2$. No $\text{Au}^+-(2\text{-propanol})_n$ association products were generated. The condensation mechanism is difficult due to the extremely high activity of Au^+ . It should be noted that the cluster-ion reactions can be classified into the following mechanisms: (1) subsequent cluster growth after a bare metal ion-molecule reaction, (2) a cluster ion-molecule reaction following cluster formation, and (3) an intracuster metastable reaction.³² According to the results given in Figure 10, reaction path (1) may be excluded. It is expected to show all cluster sizes containing H_2O and C_3H_6 ligands if process (1) proceeds. Either reaction (2) or (3) can contribute to the reaction products observed in our experiments. However, the nature of both processes has a substantial difference. For instance, although the changes in the metal reactivities, as evident in Figure 10, are related to the solvation effect for reaction (2), it is explained by the cage effect if reaction (3) occurs. At this stage, we are unable to distinguish both processes in our experimental configuration.

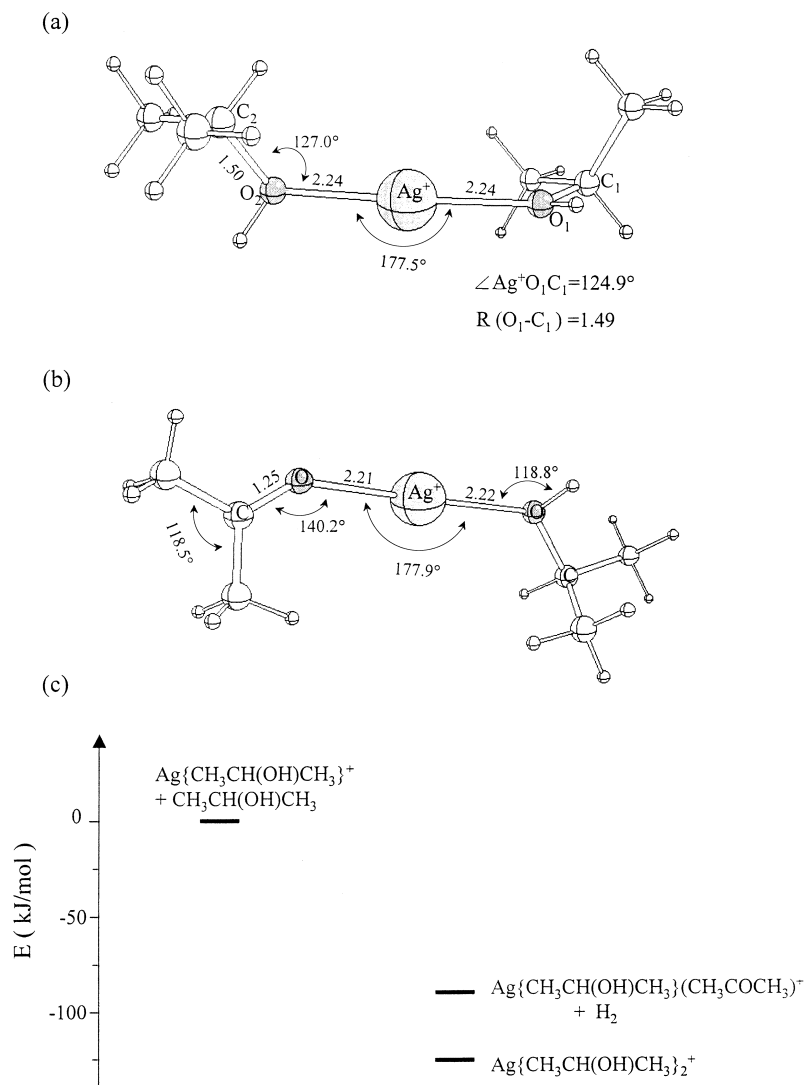


Fig. 11. Optimized structures for (a) $\text{Ag}^+-(\text{CH}_3\text{CH}(\text{OH})\text{CH}_3)_2$ and (b) $\text{Ag}^+-(\text{CH}_3\text{CH}(\text{OH})\text{CH}_3)(\text{CH}_3\text{COCH}_3)$ at BLYP/6-31G(d,p). (c) The energy profile calculated at BLYP/6-31G(d,p) for the product channels in the reactions of $\text{Ag}^+-(\text{CH}_3\text{CH}(\text{OH})\text{CH}_3)_2 + \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$. Selected bond lengths in $\text{\AA}$ and angles in degree. E = relative energy.

For larger clusters with $n \geq 2$, theoretical calculations chosen on $\text{Ag}^+-(2\text{-propanol})_2$ and $\text{Ag}^+-(2\text{-propanol})(\text{acetone})$, assuming a dehydrogenation process, were performed. Based on a previous analysis, BLYP/6-31G(d,p) was used to model these clusters. The geometries were fully optimized. Figure 11a and b depict the optimization configurations corresponding to $\text{Ag}^+-(2\text{-propanol})_2$ and $\text{Ag}^+-(2\text{-propanol})(\text{acetone})$, respectively. The $\text{O}-\text{Ag}^+-\text{O}$ reveals nearly 180° as a linear structure. Bauschlicher and co-workers have computed a linear $\text{Cu}^+-(\text{H}_2\text{O})_2$, resulting from sd hybridization on metal to reduce the electron density along the metal-ligand bonding axis.²⁵ With respect to $\text{Ag}^+-(2\text{-propanol})_2$, two $\angle\text{COH}$ arrangements are in a staggered configuration. The calculated binding energy (D_0) with respect to Ag^+ and two 2-propanol molecules is $266.9 \text{ kJ mol}^{-1}$. Although the Ag^+-O bond distances are very similar in $\text{Ag}^+-(2\text{-propanol})$ and $\text{Ag}^+-(2\text{-propanol})_2$, the binding energy of the second $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ ligand coordinated to Ag^+ is less by 20.9 kJ mol^{-1} than the first ligand coordination energy. For $\text{Ag}^+-(2\text{-propanol})(\text{acetone})$ species, the binding energy is

found to be $268.6 \text{ kJ mol}^{-1}$. As can be seen in Figure 11c, both $\text{Ag}^+-(2\text{-propanol})_2$ condensation and $\text{Ag}^+-(2\text{-propanol})(\text{acetone})$ dehydration are the thermodynamically favored paths, yet the condensation channel, i.e. $\text{Ag}^+-(2\text{-propanol})_2$, has lower energy. This is consistent with an experimental observation, as shown in Figure 10b. However, the energetics between the reactants and the products are unable to resolve what driving force forms acetone readily once the solvent molecules increase in Au^+ . This remains an open question.

Summary

1. The reactions of group-11 cations (Cu^+ , Ag^+ , and Au^+) with 2-propanol have been investigated by a technique using laser vaporization combined with a supersonic beam expansion. Metal ions underwent several types of mechanisms with the involvement of C-O, C-H and/or C-C insertion. The observed reaction products were parallel to the results by Wilkins *et al.* using an FT-ICR mass spectrometer. Compared with Cu^+ and Ag^+ , the enriched chemistry reveals the high reactivity

ty of the Au^+ center. In contrast with the dominant association channels produced in both Cu^+ and Ag^+ , the $\text{Au}^+-(2\text{-propanol})$ complex was yielded weakly under supersonic expansion circumstances.

2. MP2 and DFT methods were carried out on all complexes. The BLYP level of theory evaluated stronger binding energies than the MP2 calculations. We found that it is difficult to use one uniform level of theory to model complexes consisting of σ -donor and π -bonded ligands. Calculations at higher levels using better basis sets in both metals and ligands would lead to a more precise description of the binding energies. Qualitatively, both methods predicted similar trends in the binding energies and the interactions of the metal ions with ligands. Due to the relativistic effect, Au^+ exhibits the strongest interaction with a series of ligands. Most of the reaction products generated can be interpreted in terms of the thermodynamic stability based on the energetic relation between the reactants and the products. The absence of $\text{Ag}^+-\text{H}_2\text{O}$, $\text{Ag}^+-\text{C}_3\text{H}_6$ and $\text{Au}^+-\text{acetone}$, however, is likely in association with the kinetic factor.

3. In addition to M^+ -ligand adducts, larger cluster ions, $\text{M}^+(\text{ligand})_n$, were investigated as well. These reactions were apparently confined to Cu^+ and Ag^+ with cluster sizes ≥ 2 , while the reactivity changed, leading to the formation of acetone, which was absent in the reactions of bare Au^+ with 2-propanol, appeared in $\text{Au}^+(\text{solvent})_n$ with $n \geq 2$. $\text{Ag}^+-(2\text{-propanol})_2$ and $\text{Ag}^+-(2\text{-propanol})(\text{acetone})$ clusters were chosen for theoretical computations using BLYP/6-31G(d,p). It is evident that the $\text{Ag}^+-(2\text{-propanol})_2$ channel has a lower energy than that of $\text{Ag}^+-(2\text{-propanol})(\text{acetone})$.

This research was supported by the National Science Council of the Republic of China. We appreciate helpful discussions with Dr. Ching-Han Hu concerning the theoretical calculations and grateful for his permission to use his computer facilities. Generous allocations of computational time at the National Center for High-Performance Computing of the National Science Council are also acknowledged.

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