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MALDI TOF and theoretical investigation of silver clusters obtained by gamma irradiation

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ABSTRACT

The aim of this study is to evaluate the size and stability of radiolytically produced silver clusters. The clusters obtained by the gamma irradiation of a mixture of a silver salt and polyvinyl alcohol (PVA) were studied both theoretically and by mass spectrometry. MALDI TOF mass spectrometry of the Ag_n clusters showed the presence of clusters containing between 5 and 29 atoms. Both the theoretical and experimental results of this paper show that the most stable clusters are small clusters with an odd number of atoms. The stability of these clusters is correlated with the cluster's electronic configuration.

1. Introduction

Clusters can be classified as a new type of material because clusters have properties that are fundamentally different from both those of discrete molecules and the relevant bulk solid. The term "cluster" is defined as an aggregate of a countable number of particles, such as atoms or molecules. The study of small metal clusters has contributed extensively to the understanding of size-dependent and many-body character of nanoscale physics and chemistry. Important examples of size-dependent characteristics have been observed in the measurement and theoretical calculation of metal cluster melting [1,2], the transition of a cluster's structure from planar to three-dimensional [3,4], and the reactivity of gold-cluster nanocatalysts [5,6]. Resonant absorption frequencies have recently been measured for gas phase Ag_n^+ clusters using photodepletion [7] and for Ag_n clusters in rare-gas matrices [8]. Both studies show maxima in the resonance absorption frequencies that are associated with closed-shell clusters.

Spectral analysis of both positive and negative ion silver clusters indicates that the intensity of peaks associated with clusters containing an odd number of atoms is larger than the intensity of peaks associated with clusters containing an even number of atoms. This phenomenon may be explained by simple electron counting. Clusters containing an odd number of atoms have an even number of valence electrons, which results in spin pairing. Therefore, these clusters have enhanced stability compared to those clusters with an even number of atoms [9–12]. The mass spectra of silver clusters also contain peaks for specific "magic numbers" [13], where a steep decrease in ion intensity is observed after the corresponding peak. An explanation of this observation is based on the Jellium model [9–14] in which the stability of the cluster is determined by the energy levels of the valence electrons bound in the cluster. At the magic numbers, the number of atoms in the cluster corresponds to the number of electrons necessary for shell closing to occur in the electron shell model when charge is taken into consideration [9–12]. For example, Ag_3^+ and Ag_9^+, which respectively have 2 and 8 valence electrons, appear as magic numbers. These clusters correspond to the closing of the first and second shell in the electron shell model.

Among the most fundamental properties of a cluster are the energies required to ionize the neutral cluster either by the addition or loss of an electron. As observed for silver clusters in the literature [15], the addition of an electron is defined as the electron affinity (EA), and the loss of an electron is defined as the ionization energy (IE). The odd–even pattern discussed above for the ion intensities in the mass spectra of silver clusters also manifests itself for the EAs and IEs for Ag_n clusters. Ag_n clusters with odd numbers of atoms are easier to ionize through both the addition of an

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electron or the removal of an electron, as these clusters have both relatively high electron affinities and relatively low ionization energies. It should be stressed that the matrix used must have a lower IE or higher EA than the cluster. Some matrices that may be successfully used for detecting silver clusters by the MALDI TOF technique have the required properties.

In this study, we investigate the structure and the stability in the gas phase of Ag_n silver clusters formed by gamma irradiation using MALDI TOF(matrix assisted laser desorption/ionization, time-of-flight), MALDI TOFTOF and theoretical *ab initio* calculations. The stability of Ag_{11} clusters was studied with the aid of the MALDI TOFTOF, a tandem mass spectrometry method. In MALDI TOFTOF, the collision induced dissociation (CID) technique is coupled with TOF, which enables MSMS(tandem mass spectrometry) analysis. In the mass spectra for clusters of a characteristic size, the Ag isotopic abundance in nature is observed [16].

2. Material and methods

The formation of silver clusters using two different synthetic procedures were investigated previously [17]. Two mixtures of 5 ml of distilled water, 1 ml of PVA (0.05 g/ml) and 144 mg of $AgNO_3$ were prepared using ultrasound. These mixtures were aerated for 30 min under Ar or N_2O in order to remove oxygen and were exposed to gamma-irradiation (^{60}Co radiation facility) under ambient conditions. The irradiation was performed at a dose rate of 10 kGy/h until an absorbed dose of 55 kGy was reached. This dose is required for complete reduction of the Ag^+ ions in the solution. Oxidized species were not detected in the analyses of the mass spectra. The intensity of the investigated cluster's peaks was larger for the sample prepared under N_2O when using the same laser intensity.

2.1. Mass spectrometry analysis

Positive and negative ion MALDI TOF mass spectra were acquired using a MALDI TOF (AB Applied Biosystems, Voyager-DE PRO, Framingham, USA). MALDI TOFTOF analyses were performed using a 4700 Proteomics Analyzer (Applied Biosystems).

2.2. Preparation of MALDI matrix

A saturated solution of the matrix α-cyano-4-hydroxycinnamic acid (CHCA) was prepared by dissolving the compound in 50% acetonitrile with the addition of 0.1% trifluoroacetic acid. The solution was vortexed thoroughly and was sonicated in a water bath for several minutes at room temperature. The 2,5-dihydroxybenzoic acid (DHB) matrix was prepared by dissolving the matrix in 50% acetonitrile with the addition of 0.3% trifluoroacetic acid [18]. The CHCA and DHB solutions were used for the preparation of samples for MALDI TOF analysis. All employed chemicals were obtained from Sigma–Aldrich (St. Louis, WI, USA).

MALDI TOF mass spectral analysis of the samples was performed in a linear and reflectron mode with delayed extraction. Mass spectra were calibrated using the standard calibration mix2 in the mass range of 170–4000 Da. MALDI TOFTOF experiments were carried out using N_2 gas for the study of fragmentation through metastable decomposition. The selection of the precursor ion also involved the selection of precursor fragments resulting from post-source decay between the ion source and the time-ion-selector. Typically, the precursor ion or $(M + Na)^+$ was selected in a window (±5 Da) that was centered on the first isotope. It was verified that only the chosen precursor was selected in this window. To achieve the best statistics, averages of mass spectra for over 100 different spots on the target, with each spot including 100 laser shots, were calculated. The laser fluence was adjusted to produce an unsaturated signal for the selected ion precursor. An aliquot of each sample solution containing the internal standard was combined in a 1:1 ratio with either the CHCA or DHB matrix and was mixed thoroughly. Aliquots (0.5 μL) of the mixtures were spotted on a 100 spots sample plate and were air-dried. Ions were obtained by laser desorption using a 200 Hz frequency N_2 pulse laser operating at 337 nm.

Samples were mixed in ratios of 1:10 v/v ratio. A concentration of 10 mg/ml of CHCA was obtained by diluting the CHCA in a 1:1 acetonitrile:water solution. After dilution, 0.5 μL aliquots of the sample were placed on a MALDI plate. Samples were subsequently air-dried and analyzed. Data Explorer version 4.9 was used for the analysis of the recorded spectra. Ions of the CHCA matrix were used for internal calibration, on the basis of the theoretically calculated masses of CHCA monomers, dimers and trimers, respectively, at *m/z* values of 190.05 (molecular formula $C_{10}H_7NO_3$), 379.09 (molecular formula $C_{20}H_{14}N_2O_6$) and 568.14 (molecular formula $C_{30}H_{21}N_3O_9$). The mass spectrum of the matrix was recorded in order to eliminate the signals generated by the matrix itself. For negative ions, a DHB matrix, which has the characteristic mass of 154.12 [19], was used. The applied laser intensity was between 10 and 30% of the maximum available laser power.

CHCA matrix was used for positive and negative ions, DHB matrix was used only for negative ions.

2.3. MALDI TOFTOF MSMS measurements

Each sample was measured by using the MSMS 1 kV positive mode in the 4000 Series Explorer Version 3.0 software. The precursor mass was the molecular mass of the selected clusters, and the mass window was −1.00 Da and +5.00 Da of the precursor mass. Molecular ions were extracted from the ion source after a 460 ns delay. The suppressor for the metastable ion was turned off. The accelerating voltage at the ion source was +8.0 kV, and the grid voltage was +6.85 kV. The collision cell was at +7.0 kV. Fragment ions were extracted from the collision cell after a 27.3 ms delay. The accelerating voltage from the collision cell was +15.0 kV. The sampling bin size was 0.5 ns with an input bandwidth of 500 MHz and a vertical full scale of 200 mV. The reflectron detector voltage was +2.1 kV. The pressure inside the collision cell was adjusted with atmospheric gas to the level of 10^{-6} Torr before the initiation of the measurement. Each spectrum was automatically acquired by accumulating the results of 5000 shots with random edge-biased positioning of each laser shot. By using the Data Explorer Version 4.6 software, the resulting mass spectrum was internally calibrated with the most abundant isotopic peaks of the precursor ion and a known fragment ion. A Mass Spec Calculator Professional version 4.09 demo program was used to assist in the identification of the fragment ions.

3. Results and discussion

The formation mechanism of silver clusters was explained in and our previous paper [17]. Silver clusters were produced from $AgClO_4$ by gamma irradiation [20]. Clusters were stabilized by sodium polyphosphate and analyzed by optical spectroscopy. However, our research was mass spectrometric characterization of obtained clusters.

Samples produced by the gamma-irradiation of a mixture of PVA and $AgNO_3$ were analyzed by mass spectrometry. The results indicated that positive Ag cluster ions were formed in the presence of a CHCA matrix in both working modes and that the resolution was greater when the measurement was performed in a reflectron