

Optical absorption of isolated silver cluster-tryptophan: A joint experimental and theoretical study

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Received 30 August 2006

Published online 24 May 2007 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2007

Abstract. We present a joint experimental and theoretical gas phase study of photoabsorption and photofragmentation of silver cluster-biomolecule complexes. We demonstrate on the example of $[\text{Trp.Ag}_3]^+$ that binding of the metal cluster to a biomolecule leads to a significant enhancement of the photoabsorption in comparison with $[\text{Trp.H}]^+$ and $[\text{Trp.Ag}]^+$. This enhancement arises due to the coupling between the excitations in the metallic subunit with charge transfer excitations between silver cluster and tryptophan. Our experimental studies show that silver clusters up to eleven atoms can be bound to tryptophan and we present first results on the photofragmentation of the Trp.Ag_{11}^+ complex cation, in which properties of cluster subunit remain preserved.

PACS. 31.15.Qg Molecular dynamics and other numerical methods – 31.15.Ar Ab initio calculations

1 Introduction

The development of metal nanoparticle-biomolecule hybrid systems and their application in the generation of ordered structures in solution or at surfaces is a promising route for development of new specific biosensors and nanoscale architectures with desired structural, electronic and optical properties [1]. The applications of nanoparticles as biosensors are based on a remarkable enhancement of photoabsorption and emission processes which occurs near a metal surface or a metal nanoparticle [2]. These effects are generally interpreted as resulting from a local amplification of the electromagnetic field of the biomolecule due to coupling with the metal surface plasmon. The application of this phenomenon enables fluorescence labeling, imaging and Raman scattering of single molecules [3–5].

The understanding of nanoparticle-biomolecule hybrid systems at the molecular level is challenging. Indeed, it involves an investigation of the coupling between excitations of metallic particles and biomolecules. In this context, the gas-phase approach is valuable since it allows the experimental and theoretical studies of well-defined systems without external interactions (solvent or substrate). However, the optical properties of gas-phase nanoparticle-biomolecule hybrids still remain scarcely investigated.

Here we present a joint gas-phase experimental and theoretical study of the optical properties of silver cluster-tryptophan complexes. We demonstrate an order of magnitude enhancement of the optical absorption in $[\text{Trp.Ag}_3]^+$ compared to $[\text{Trp.H}]^+$, $[\text{Trp.Ag}]^+$. Furthermore, we show that silver tryptophan complexes with up to eleven silver atoms can be produced experimentally and we present first results on their photofragmentation.

2 Experimental and computational

Experiments were performed using a commercial quadrupole ion trap (QIT) from Thermofinnigan (LCQ Duo with MSⁿ option) coupled with an off-axis electrospray source. The ion trap has been modified in order to couple it with a VIS/UV tunable OPO laser. This coupling allows photodissociation spectroscopy studies on trapped biomolecular ions [6, 7].

Mixing an amino-acid or a peptide solution with a metal salt is a very common way to form metal cationized ions. We recently managed to produce silver cluster-tryptophan complex ions [8]. The electrolyte solution was prepared by mixing (1:1) a solution of silver nitrate salt (500 μM in pure water) and a solution of tryptophan (100 μM in $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ 1:1 (v/v)). 3% of acetic acid was added to the final solution. As already published, tryptophan-silver complexes with different stoichiometries

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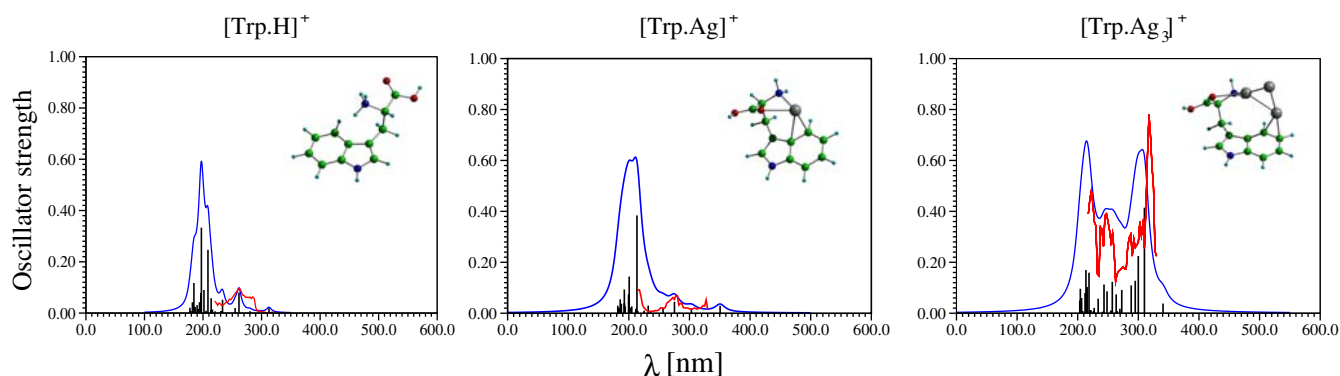


Fig. 1. (Color online) Comparison between the experimental photofragmentation spectra (red line) and calculated absorption spectra (blue line and black sticks) absorption spectra for: (a) $[\text{Trp.H}]^+$, (b) $[\text{Trp.Ag}]^+$ and (c) $[\text{Trp.Ag}_3]^+$.

of the general form $n; m$ (where n is the number of tryptophans and m the number of silver atoms) were observed in the mass spectra [8].

Parallel to the experimental studies, the structural properties and stationary absorption spectra of $[\text{Trp.H}]^+$, $[\text{Trp.Ag}]^+$ and $[\text{Trp.Ag}_3]^+$ were determined using density functional theory (DFT) with the hybrid functional B3LYP [9,10]. For Trp, the 6-311G** atomic orbital (AO) basis set augmented by diffuse functions for appropriate description of excited states was employed. All ground state optimizations were performed employing a 19-electron relativistic effective core potential (19el-RECP) from the Stuttgart group for silver [11]. The absorption spectra were calculated using our 11el-RECP with the corresponding AO basis set which has been developed for an accurate description of excited states of silver clusters [12–14]. The extensive search for the structures of $[\text{Trp.Ag}_3]^+$ was performed by the simulated annealing procedure coupled with molecular dynamics simulations in the framework of the semiempirical AM1 method. The structures found were subsequently reoptimized using the DFT method. Similar study of complexes formed by tryptophan and larger silver clusters is in progress.

3 Results and discussion

Comparison of the photoabsorption cross-section, observed by means of photofragmentation measurements of $[\text{Trp.H}]^+$, $[\text{Trp.Ag}]^+$ and $[\text{Trp.Ag}_3]^+$ together with theoretical absorption spectra obtained by time-dependent density functional theory (TDDFT) is shown in Figure 1. All three complexes exhibit a strong absorption in the region around 200 nm which can be attributed to the well-known $\pi-\pi^*$ transitions within the indole subunit of tryptophan. In addition to that, both $[\text{Trp.H}]^+$, $[\text{Trp.Ag}]^+$ exhibit weak charge transfer excitations at 290 and 330 nm, respectively [7]. As shown by the theoretical analysis, these correspond to the charge transfer from the indole subunit to the NH_3^+ and Ag^+ subunits. A dramatically different situation arises in the case of $[\text{Trp.Ag}_3]^+$ complex. Here, a very strong absorption occurs around 320 nm which can be attributed mainly to the excitations within

the Ag_3^+ subunit but also contains a charge transfer contribution. Furthermore, the absorption in the range between 230 and 290 nm is also significantly enhanced due to the coupling between the excitations involving the indole and Ag_3^+ subunits. Analysis of the optical properties of the $[\text{Trp.Ag}_3]^+$ is presented elsewhere [15]. We wish to point out that even in these small systems similar effects occur as in large nanoparticle-biomolecule complexes. This demonstrates that joint gas-phase theoretical studies on such model systems can provide a significant insight into the optical properties which are important for potential applications. Therefore, in the following we show that the complexes between larger silver clusters and tryptophan can be also produced experimentally. This is particularly important, since it allows to investigate the size and structure dependence of the optical properties of these hybrid systems.

In the experiment the complexes of the silver clusters and tryptophan with up to 11 silver atoms have been observed and isolated. Here we concentrate only on the largest observed species $[\text{Trp-2H+Ag}_{11}]^+$. The isolation spectrum for $[\text{Trp-2H+Ag}_{11}]^+$ together with the comparison between experimental and calculated isotopic distribution is presented in Figure 2. The isotopic distribution shows that the $[\text{Trp-2H+Ag}_{11}]^+$ is a dominant product, but the ratios between the odd and even peaks and the right part of the distribution indicate that other complexes with similar masses might also be present to a smaller extent. The collision induced dissociation (CID) spectrum for the $[\text{Trp-2H+Ag}_{11}]^+$ is shown in Figure 3a. The main fragmentation channel leads to the dissociation of the complex and to the formation of Ag_{11}^+ indicating that the cluster is bound to tryptophan as an intact unit. This has been confirmed theoretically. Our preliminary theoretical results indicate that the structure of Ag_{11}^+ subunit in $[\text{Trp-2H+Ag}_{11}]^+$ is closely related to the one of the free cluster which corresponds to trigonal prism with all five faces capped by silver atoms reported previously [16].

The photodissociation experiments were performed at 220, 260, 290, 310 and 330 nm. The corresponding photodissociation spectra are presented in Figures 3b–3d. Generally, a strong photodissociation is observed leading to the tryptophan loss and leaving the pure Ag_{11}^+

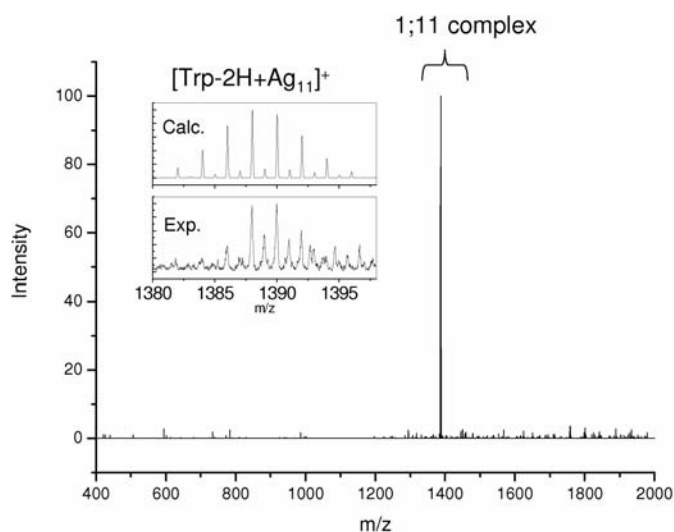


Fig. 2. Isolation spectrum of the 1;11 complex. The insert compares the experimental and calculated isotopic distribution for the $[\text{Trp-2H+Ag}_{11}]^+$.

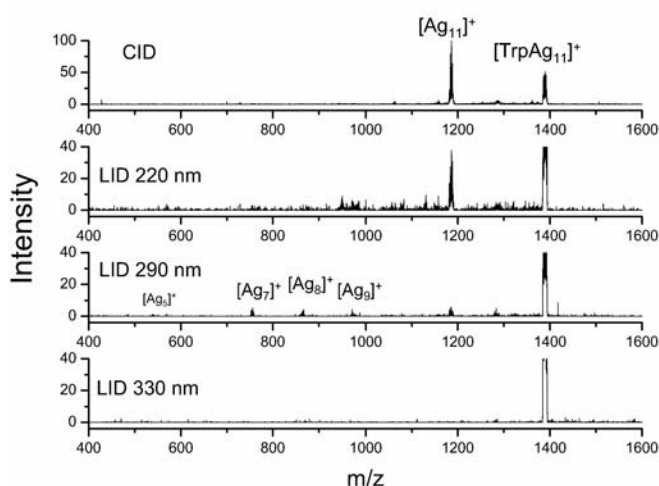


Fig. 3. Dissociation spectra of the (1;11) complex. (a) CID spectrum. The complex is isolated with a width of 10 Da, and activated at 20% of collision energy during 30 ms. (b), (c) and (d) Photodissociation spectra measured at 220, 290, and 330 nm during 500 ms of laser irradiation (10 laser shots).

cluster. It is particularly interesting to note that excitation at 290 nm, produces smaller cluster fragments (Ag_9^+ , Ag_8^+ , Ag_7^+ and Ag_5^+). These fragments arise during 500 ms of irradiation as a consequence of a particularly strong absorption of small bare silver clusters at 290 nm. In contrast, at 330 nm no photodissociation is observed.

In Figure 4 we present the total fragmentation yield of $[\text{Trp-2H+Ag}_{11}]^+$ as a function of the wavelength. The total fragmentation yield is defined as $\sigma = \ln(\text{parent} + \Sigma \text{frag}/\text{parent})/\phi$ where ϕ represents the laser fluence, *parent* is the intensity of the $[\text{Trp-2H+Ag}_{11}]^+$ complex peak and Σfrag is the summed intensity of the observed bare silver cluster peaks. A broad absorption is observed in

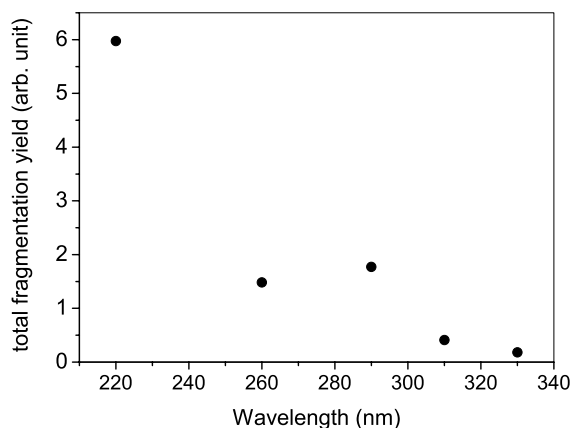


Fig. 4. Total fragmentation yield of the $[\text{Trp-2H+Ag}_{11}]^+$ as a function of the laser wavelength.

the interval from 220 to 290 nm. In contrast, above 310 nm no fragmentation has been observed. Our preliminary theoretical study indicates that the strong interaction among excitations within Ag_{11}^+ and tryptophan subunits occurs, leading to intense transitions spread over the large energy interval. Moreover, the intense transitions originating from isolated Ag_{11}^+ located around 260 and 290 nm can be also identified in $[\text{Trp-2H+Ag}_{11}]^+$. This is a common feature found also for other silver-tryptophan complexes, although intensities are influenced by size and the structure of the cluster.

4 Conclusion

We have demonstrated experimentally and theoretically that the enhancement of photoabsorption by binding of a small metal clusters to tryptophan can be achieved. For example, the absorption in $[\text{Trp.Ag}_3]^+$ is enhanced by an order of magnitude with respect to $[\text{Trp.Ag}]^+$ and $[\text{Trp.H}]^+$. Comparison of experimental and theoretical results allowed us to reveal the electronic mechanism responsible for the strong photoabsorption of this hybrid system. This provides a general basis for understanding the optical properties of large hybrid systems beyond the local field amplification macroscopic description. By changing the size of silver clusters, we expect that further increase in photoabsorption and tuning of wavelengths can be achieved. We have also demonstrated experimentally that the formation of complexes between larger silver cluster and tryptophan can be achieved. Our first results show the wavelength dependence of the photofragmentation in $[\text{Trp-2H+Ag}_{11}]^+$ complex. This will enable in the future to investigate the size dependence of optical properties of silver-cluster-tryptophan complexes.

This work was supported by the Deutsche Forschungsgemeinschaft SFB 450, the CNRS and the Humboldt foundation.

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