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Relaxation dynamics of the mass-selected hydrated Auride ion (Au^-)

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ABSTRACT

By using time resolved photoelectron spectroscopy, decay of optically excited states of hydrated Au^- mass selected in the gas phase was studied. It is suggested that the pump photon can induce injection of an electron from auride chromophore to the water solvent. The cluster with three water molecules ($Au^-(H_2O)_3$) showed a long living excited state with a lifetime of ~19 ± 3 ps, whereas that of $Au^-(H_2O)_2$ is only ~3 ± 1 ps. The fate of an optically excited state of an ionic species can be significantly changed by the number of water (solvent) molecules attached.

1. Introduction

The most important step in photochemical reactions is optical excitation of an electron from an occupied to an unoccupied state of a chromophore by absorption of light. When lifetimes of electrons in optically excited states are long enough, initiation of a photochemical reaction can become competitive to recombination processes of electron–hole pairs [1]. Femtosecond time-resolved photoelectron spectroscopy (fsTRPES) has been widely used for shedding light on the relaxation dynamics and lifetimes of optically excited states [2]. The pump pulse excites an electron, whose relaxation process can be monitored by using a probe pulse with adjusted pump–probe delay in fs time scale. In general, metallic species were found to show very fast relaxation of the optically excited state within several tens of fs via electron–electron scattering mechanisms, whereas semiconductors exhibit much slower relaxation due to their absent density of states at the Fermi level [3].

Relaxation dynamics of small clusters consisting of less than ~20 atoms have been of considerable interest during the past decades. Particularly, mass-selected clusters were used to study size-dependent changes of relaxation dynamics of optically excited states of such small clusters on the atom-by-atom basis. For d-metal clusters, small clusters with less than 10 atoms already showed surprisingly short relaxation times (10–100 fs) which are close to the respective values of bulk metals via electron–electron scattering; since the whole valence d-shell electrons are donated to the cluster valence orbitals, the density of states of such small d-metal clusters is high enough for allowing fast relaxation by electron–electron scattering [4–6]. For sp-metal clusters, in which relaxation of the excited state by electron–electron scattering is not likely, the situation was found to be complex; for some clusters, lifetimes of excited states were very long (ns or ps time scale), whereas for others, efficient energy transfer from excited states to the nuclear motions of clusters allowed fs time scale relaxation dynamics [7,8].

Not only bare metallic clusters but also metal clusters reacting with small molecules such as CO and H_2O have been studied using fsTRPES [9–12]. As a function of the number of molecules attached to a metal cluster, relaxation dynamics were shown to vary significantly. Using fsTRPES we recently showed that for Au_3^-, photodissociation gives rise to the formation of Au and Au_2^- (or Au^- and Au_2) species, and an additional H_2O molecule ($Au_3^-[H_2O]$) accelerated the photodissociation by a factor of 70 [9,13]. On the other hand, when more than two H_2O molecules were attached to this cluster, the photodissociation of Au_3^- was suppressed completely [9]. Here, we studied the relaxation dynamics of Au^- with 2 and 3 water molecules adsorbed in which photodissociation of the chromophore is impossible. This system provides an opportunity to investigate the lifetimes of excited states with different degrees of solvation of the cluster without running into the problem of inducing photodissociation of the solute (Au^-).

2. Experimental

Gold cluster anions are produced in a pulsed arc cluster ion source (PACIS) and mass-selected using a time-of-flight (ToF) mass spectrometer [14]. The experimental set-up is described in detail elsewhere [15]. $Au^-(H_2O)_m$ with $m = 0–4$ are produced by introducing water into the PACIS [9]. A selected bunch of cluster anions is irradiated by two pulses generated in a femtosecond Ti:sapphire laser system. The first pulse (pump pulse) has a photon energy of 3.1 eV and the second pulse (probe pulse) a photon energy of 1.55 eV. The instrumental time resolution is 240 fs and was determined by measuring the cross correlation function of the pump and probe pulses. The kinetic energy of the detached electrons is

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measured using a 'magnetic bottle' type time of flight electron spectrometer [16]. The cluster temperature is estimated to be room temperature, as they spend sufficiently long time in a water cooled extender for thermalization. The pump pulse results in photoexcitation of a certain fraction of the anions in the bunch and the probe pulse detaches electrons from a fraction of the anions in the same bunch. The photon flux of both pulses has to be optimized in order to maximize the number of species hit by a single photon of each pulse, and to minimize the number of species hit by two or more photons from the same pulse.

For collecting regular photoelectron spectroscopy (PES) data, a photon energy of 7.9 eV was used. For these experiments, the same method as that of the time resolved study described above was used for the preparation of the mass selected Au $(H_2O)_m$ clusters.

3. Results and discussion

Figure 1 shows photoelectron spectra of Au $(H_2O)_m$ clusters with $m = 0$ 6. In a previous study, Au $(H_2O)_m$ with $m = 0$ 2 were studied using PES [17], and we extended studies of solvated Au up to 6 water molecules attached. For bare Au three peaks centered at 2.31, 3.41, and 4.89 eV, respectively, could be identified. With increasing number of water molecules attached a gradual shift of these peaks of Au to higher binding energies was observed. The fact that there are only rigid shifts of electronic states appearing as a consequence of solvation implies that the chromophore of Au $(H_2O)_m$ clusters is indeed Au , which quite weakly interacts with adsorbed water molecules. As the number of water molecules in a cluster increased from 0 to 2, the width of the peaks in PES increased [17]. For example, the lowest binding energy peak of Au had a full width of the half maximum (FWHM) of 0.15 eV, and this value increased to 0.25 and 0.27 eV as the number of water molecules in a cluster became 1 and 2. For $m > 2$, the FWHM of the first peak of each PES spectrum was 0.27 ± 0.1 eV, i.e., as the number of water molecules in a cluster exceeded 2, no further broadening of the peaks in the PES spectra was found.

As it has been shown previously, the PE spectral shift of the cluster by an additional water molecule can be used for approximately estimating the energy required to remove this additional water molecule from the anionic cluster, i.e. based on the PE spectra in Figure 1, the binding energy of water molecules in the clusters can be roughly estimated [17]. For bare Au , the electron affinity (EA) value is estimated to be 2.31 eV, and VDE of Au (H_2O) is found to be 2.76 eV, and based on these data the binding energy of the first water molecule attached to Au is estimated to be 0.45 eV. Note that the binding energy of H_2O in Au (H_2O) can be estimated based on the following equation.

$$(\text{VDE of Au } (H_2O) \quad \text{EA of Au}) \quad D_o(\text{Au } \ldots H_2O) \quad D_o(\text{Au}\ldots H_2O)^*$$

D_o(Au ...H_2O) and D_o(Au...H_2O)* denote dissociation energies of H_2O...Au in Au (H_2O) and Au(H_2O) at the structure of Au (H_2O), respectively, and D_o(Au...H_2O)* can be regarded as very small and therefore neglected. For more details of the estimation of the binding energy of water molecules in the hydrated Au clusters, readers should refer to Ref. [17]. With increasing number of water molecules, the spectral shift becomes less and less. The binding energy of the sixth water molecule is estimated to be less than 0.32 eV, which is only about 70% of the binding energy of the first water molecule.

Figure 2 displays the PE spectra of Au $(H_2O)_m$ with $m = 1$ to 4, which were obtained using coincident pump and probe pulses with energies of 3.1 eV, and 1.55 eV, respectively, i.e. the pump probe time delay was 0 for obtaining the spectra in Figure 2. The binding energy here was determined to be the difference between the probe photon energy and the kinetic energy of photoelectrons. For Au (H_2O), a peak with a negative binding energy could be seen. The VDE of Au (H_2O) in Figure 1 was found to be 2.79 eV. The binding energy of the peak with the lowest binding energy of Au (H_2O) in Figure 2 is 0.31 eV, which is difference between VDE of Au Au (H_2O) (2.79 eV) and pump photon energy (3.1 eV). Since the same pump photon energy (3.1 eV) was used for coincident pump probe spectra of all clusters in Figure 2, the binding energy of the lowest binding energy peak of each cluster should be higher than that of the VDE of the respective cluster by 3.1 eV. As it will be seen later, these peaks in figures do not necessarily correspond to

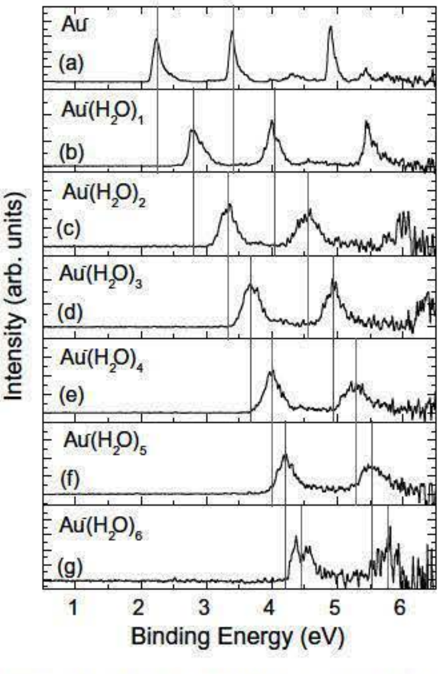

Figure 1. Photoelectron spectra of solvated auride ions with 0 to 6 water molecules. Center of each peak is denoted with vertical line.

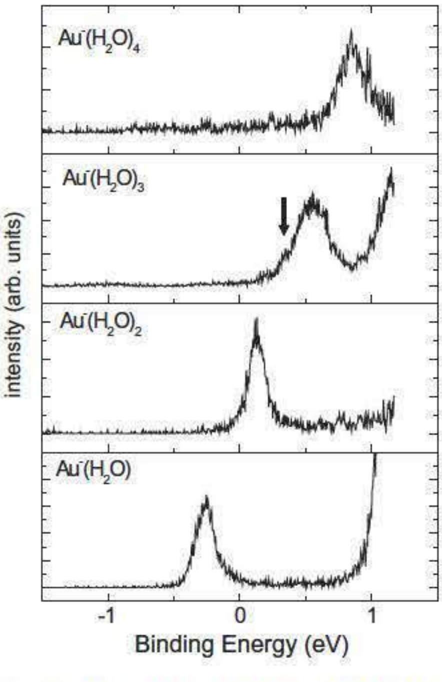

Figure 2. Pump–probe spectra of solvated auride ions with 1 to 4 water molecules at zero time delay.

resonant excitations, thus non resonant excitations cannot be excluded.

In Figure 2, it is notable that the peak of PE spectrum of Au (H$_2$O)$_3$ is significantly broader than those of other clusters with smaller or larger numbers of water molecules in a cluster. Particularly, a peak centered at 0.57 eV and a shoulder at 0.37 eV (marked with an arrow) can be seen in the photoelectron spectrum of Au (H$_2$O)$_3$ using pump and probe with 0 delay. As it will be shown later, there are two different components here, which are resonant and non resonant excitations, respectively.

In order to shed light on the relaxation dynamics of the optically excited states of hydrated audride, fsTRPES of Au (H$_2$O)$_m$ with n = 1 4 were recorded. For m = 1 and 4, the peaks shown in Figure 2 at zero delay spectra rapidly disappeared with increasing pump probe delay; the intensity of these peaks can only be seen within the pump probe delay range of 250 to 250 fs (data not shown). One can suggest that non resonant excitation by pump photon took place for m = 1 and 4. Only for Au (H$_2$O)$_m$ with m = 2 and 3, excited states survived for significantly longer times of pump probe delay compared to our upper limit of the time resolution. Therefore, it is suggested that only these clusters show resonant excitation using our pump photon energy (3.1 eV, Figures 3 and 4).

For m = 2, the pump probe signal showed a single peak centered at the binding energy of only 0.1 eV, when the pump probe delay was shorter than 100 fs. When a longer pump probe delay was used, an additional state centered at 0.3 eV appeared (denoted with arrow in the figure) whereas reduction of the intensity of the peak at 0.1 eV took place at the same time. When the pump probe delay became longer than 1.3 ps, a gradual decrease in the intensity of both pump probe peaks could be found. Since we could observe non resonant excitation for m = 1 and 4 under the same conditions as those of TRPES experiment for m = 2, non resonant excitation should also be seen for m = 2. It is likely that the broad peak centered at 0.1 eV corresponds to the overlap of non resonant and resonant excitation, whereas that at 0.3 eV corresponds to purely resonant excitation. The peak at 0.1 eV does not fully disappear with increasing pump probe delay and therefore, this peak cannot be assigned solely non resonant excitation.

Previous studies on I (H$_2$O)$_m$ clusters using TRPES found that the pump photon can excite an electron from the I chromophore to the surrounding water molecules, which is weakly bound with binding energies of several hundred meV [18]. The electron injected from the anionic chromophore to the surrounding water molecules should temporarily occupy an electronic state of water, which is weakly bound by the dipole moment of water molecules. The binding energies of the excited states assigned to the charge transfer to solvent (CTTS) in I (H$_2$O)$_m$ are close to those of the pump probe signals of Au (H$_2$O)$_2$. Therefore, it is reasonable to suggest that we have also CTTS in the Au (H$_2$O)$_2$ induced by the pump photon. In Figure 3b, the integrated intensity of the

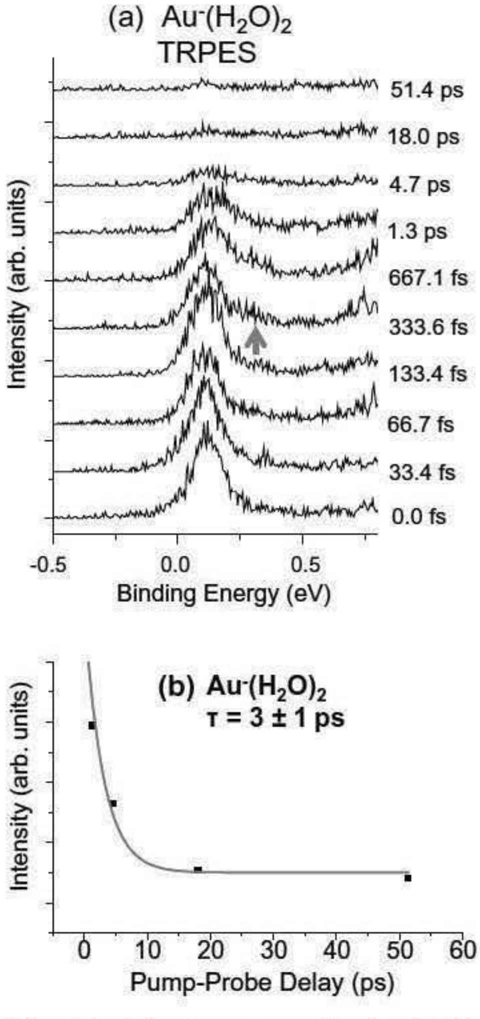

Figure 3. (a) Time-resolved photoelectron spectra for solvated auride ions with 2 water molecules. (b) Decay of the optically excited states of solvated auride ions with 2 water molecules is summarized.

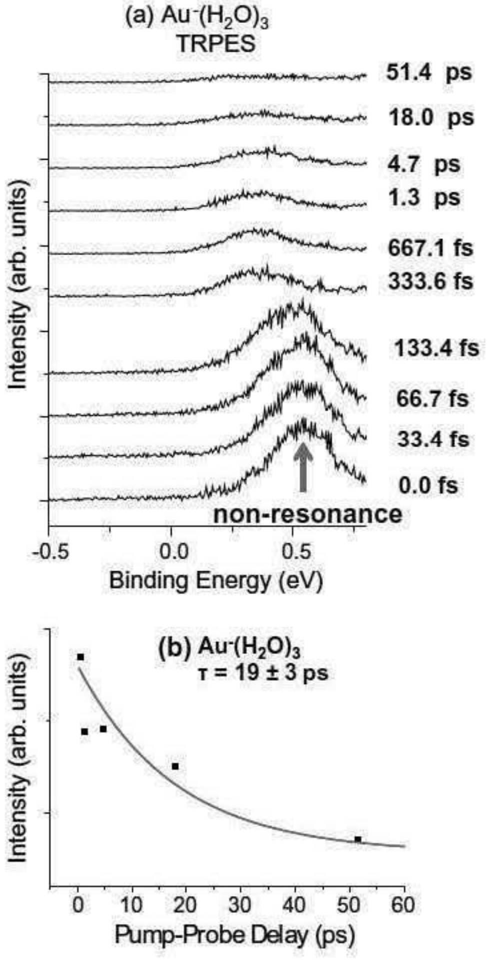

Figure 4. (a) Time-resolved photoelectron spectra for solvated auride ions with 3 water molecules. (b) Decay of the optically excited states of solvated auride ions with 3 water molecules is summarized.

pump probe signal of Au $(H_2O)_2$ in the pump probe delay range above 200 fs was fitted as a function of pump probe delay by exponential relaxations. The lifetime of the slow relaxation of Au $(H_2O)_2$ is estimated to be ~3 ± 1 ps. The fact that we observed a peak of excited state centered at 0.1 eV for shorter pump probe delay and an additional peak at 0.3 eV at longer ones is also in agreement with previous results of I $(H_2O)_m$. Here, the initial drop in the binding energy of the excited state was attributed to the repulsive interaction between solvent and detached electrons induced by the rapid geometric rearrangement of water molecules in the cluster just after photoexcitation by pump pulse [18,19].

In the case of Au $(H_2O)_3$, a major peak overlapped with a shoulder at lower binding energy appeared in the zero delay spectrum and the peak centered at 0.57 eV disappeared rapidly as a function of pump probe delay, whereas that at 0.37 eV relaxed more slowly. Here again, the peak centered at 0.37 eV can be attributed to the CTTS from auride to water solvent. The rapidly disappearing peak at binding energy of 0.57 eV of Figures 2 and 4 can be attributed to the non resonant excitation, as we have also observed for $m = 1$ and 4. The decay curve of Figure 4b shows that the lifetime of the excited state at 0.37 eV is ~19 ± 3 ps, which is significantly longer than that for two water molecules. It was previously suggested that the additional electron can be more stabilized by an increasing number of water molecules in a cluster, which can ultimately result in a longer lifetime of the electron temporarily residing in water, in line with our results [18].

We observed resonant excitation only when two or three water molecules were attached to the auride ion. In water solvents an electron should be bound by a binding energy of several hundreds meV and the excited states corresponding to such weakly bound electrons appear at these binding energies. By using a fixed pump energy (3.1 eV) such states can only be reached in the case of clusters with a suitable ground state electronic structure. There should be an electronic state with binding energy comparable to the sum of 3.1 eV plus the binding energy of weakly bound electron at water (~several hundreds meV).

A long living optically excited state can result in photochemistry, since only electrons at excited state with sufficiently long lifetime can participate in chemical reactions, in which transfer of optically excited electrons of the chromophore needs to be initiated. For example, TiO_2 photocatalysts can start chemical reactions by electron transfer from the TiO_2 conduction band to OH groups formed during water splitting [1]. Here, we show that lifetime of excited electrons at solvated anion can be considerably changed by altering the number of solvents attached to the ion.

4. Conclusion

Using fsTRPES, the decay of optically excited states of solvated Au mass selected in the gas phase using ToF mass spectrometry was studied. Relaxation time was found to be very sensitive to the number of water molecules in a cluster: the cluster with three water molecules (Au $(H_2O)_3$) showed a long living excited state with a lifetime of 19 ± 3 ps, whereas auride with two water molecules attached showed a lifetime of 3 ± 1 ps for the optically excited state. We show that the lifetime of the optically excited state of an ionic species can be changed by the number of water molecules attached, implying that photochemistry initiated by such species can be strongly dependent on the degree of solvation.

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