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Real-time observation of ultrafast ionization and fragmentation of mercury clusters

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Abstract. We report on time-resolved multiphoton ionization and fragmentation dynamics of free Hg_n-clusters ($n \leq 110$) with femtosecond laser pulses. Already at laser intensities of 10^{11} W/cm^2 we observe prompt formation of singly, doubly, and triply charged Hg_n clusters. In pump-probe experiments short-time (0–5 ps) oscillatory modulations of the transient Hg_n^+ and Hg_n^{2+} signals are observed which indicate an intermediate state dynamics common to all observed cluster sizes and charge states. Long-time (0–200 ps) transient ionization signals show caged dissociation and recombination chromophore dynamics.

PACS. 33.80.Rv Multiphoton ionization and excitation to highly excited states – 36.40.Qv Stability and fragmentation of clusters

1 Introduction

In recent years clusters and in particular metal clusters have been the fascinating subject of many experimental and theoretical studies. Metal clusters exhibit distinct features ranging from molecular properties seen in small particles to solid state-like behaviour of larger aggregates. A very interesting situation arises in the case of mercury clusters which exhibits a size dependent transition from van der Waals to covalent to metallic bonding. The mercury atom has a $5d^{10}6s^2$ closed electronic shell configuration with an ionization potential of 10.4 eV. Diatomic Hg_2 and small mercury clusters are predominantly van der Waals bound systems as shown by Bréchignac *et al.* [1, 2]. However, the electronic structure changes strongly with increasing cluster size and finally converges towards the bulk electronic structure, where the $6s$ and $6p$ bands overlap, giving mercury its metallic properties.

The investigation of mercury clusters using laser spectroscopy as experimental tool is rather difficult since most of the allowed transitions are in the UV spectral region. The ionization potentials of neutral mercury clusters are reasonably well known [3, 4], while other optical properties, especially the excitation energy of intermediate resonances in the visible and near UV region, are practically unknown. The situation is much better in the case of the charged species as Haberland *et al.* [5, 6] recently reported ionization potentials and absorption spectra.

With the ultrashort duration of our femtosecond laser pulses the time resolution is sufficient for directly measure the real-time dynamics of molecules and clusters for ionization and fragmentation processes. In general, dynamics sensitively depend on the bonding character of the clusters. Therefore, van der Waals, covalent, and metallic mercury clusters should exhibit different short-time behaviour. Here we report studies on the dynamics of multiphoton ionization and fragmentation dynamics of mercury clusters in the femtosecond time domain.

2 Experiment

The experimental set-up consisting of a cluster beam produced by seeded-beam expansion of mercury vapour, amplified femtosecond light pulses and a time-of-flight (TOF) mass spectrometer, has been described in detail elsewhere [7]. In our experiments the cluster ions are extracted perpendicular to the beam with an applied electric field. Using this widely known technique [8, 9] parent ions can be distinguished from fragment ions having initial kinetic energy. In order to generate the femtosecond pulses for our experiments we used two different laser systems. In addition to a colliding-pulse mode-locked (CPM) ring dye laser system we employed a home-built Ti:sapphire laser system generating intense 50–70 fs optical pulses in the wavelength range from 730 nm to 800 nm. Ultrashort laser radiation at other wavelengths is produced by continuum generation. Single pulse experiments were carried out at 255, 310, 510, 620, 750, and 800 nm. For the pump-probe experiments the laser beam was attenuated and split into two equal parts in a Mach-Zehnder set-up with a variable time delay separating the two pulses. The laser intensity was chosen such that neither pump nor probe pulse generated more than 5% of the total ion signal to ensure probing of neutral intermediate states.

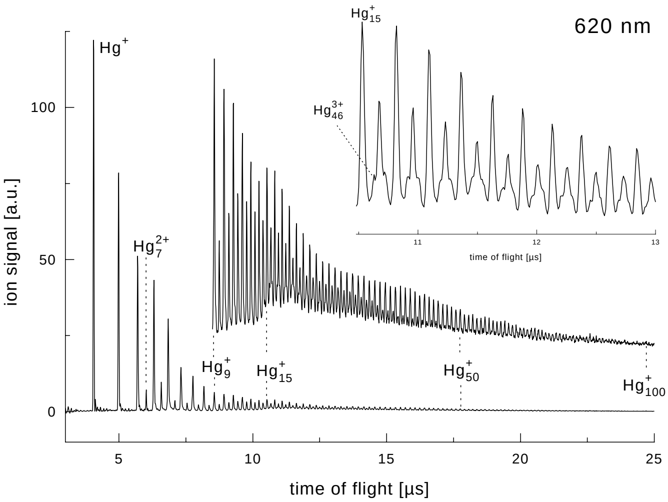

Fig. 1. Time-of-Flight mass spectrum of singly, doubly, and triply charged mercury clusters obtained at 620 nm, 100 fs pulse duration and a laser intensity of 10^{11} W/cm^2.

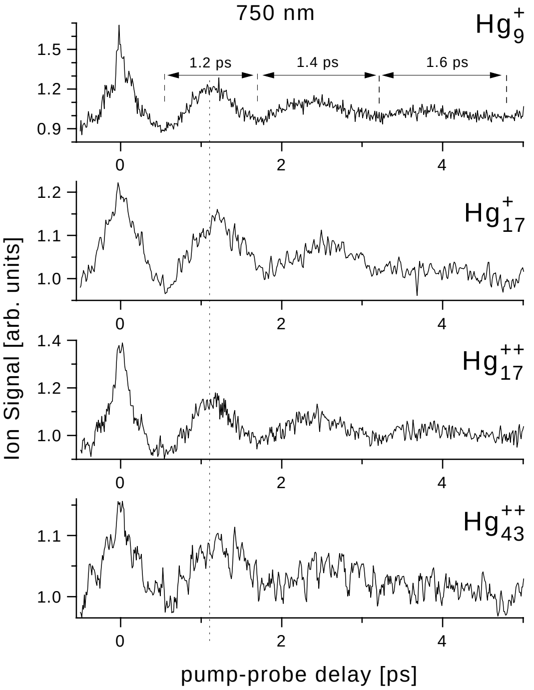

Fig. 2. Pump-Probe spectra of selected singly and doubly charged mercury clusters with similar oscillatory short-time dynamics indicating a common intermediate state.

3 Results

Figure 1 shows a time-of-flight (TOF) mass spectrum with a typical mercury cluster size distribution. In addition to singly charged clusters we observe doubly charged clusters Hg_n^{2+} and starting at Hg_{46}^{3+} even triply charged clusters. The smallest doubly charged cluster observed with $\lambda = 400$ nm is Hg_3^{2+}. Depending on laser wavelength and expansion conditions the signal of the doubly charged clusters for a given n exceeds that of the singly charged species by up to a factor of five. The intensity ratio between singly and doubly charged clusters of a given size does not change when the laser intensity is lowered by an order of magnitude, although the total ion signal decreases. The situation is very similar for all the wavelengths employed. By applying lower extraction fields in the interaction region and comparing the measured ion mass peak widths in the TOF spectra with the resolution of the spectrometer we find that the peaks of the smaller cluster ions Hg^+ to Hg_4^+ are all broadened due to their initial kinetic energy. From this we conclude that most of the observed signal for these small ions originates from fragmentation of larger ionic clusters. This is supported by the results of the pump-probe experiments discussed below. For higher laser intensities ($\geq 10^{12}$W/cm^2) fragmentation increases strongly and at intensities of $\approx 10^{13}$W/cm^2 total destruction of the clusters into single atoms, singly and multiply charged, due to Coulomb explosion is observed [10].

Immediately following the excitation of a neutral excited state the ionization dynamics of all investigated clusters (Hg^+–Hg_{110}^+ and Hg_7^{2+}–Hg_{110}^{2+}) exhibit a strongly damped oscillation (see Fig. 2). Surprisingly, this oscillation is observed for all laser wavelengths in the visible and near UV spectral region, e.g. for 800 nm, 750 nm, 620 nm, 510 nm, and 310 nm, but not for 400 nm. Note that the oscillation is also not periodic. A Fourier analysis gives a group of frequencies in the range of 20–40 cm^{-1}. The mean frequency of this nonperiodic oscillation depends on cluster size and charge state as Fig. 2 shows, and drops from a value of 26 cm^{-1} for Hg_{10}^+ to 22 cm^{-1} for Hg_{60}^+. Since all cluster sizes and charge states exhibit this oscillatory behavior, we preliminary assign the dynamics to a dimer or trimer chromophore which is embedded within all the clusters.

On a longer time scale ($t = 5$–200 ps) the ionization dynamics exhibit a more complex behavior. For small cluster sizes with $n = 1 - 4$ we observe a signal increase with a time constant τ ranging from 5 to 10 ps and a double exponential decrease with $\tau_1 = 20$ to 50 ps and $\tau_2 > 200$ ps as shown in Fig. 3. Note, that even the ionization signal of the Hg-atom – as in the case of the "short-time" dynamics – shows such a time dependence. Due to the atomic nature of Hg and due to the decay time scale of tens of picoseconds atomic processes can be excluded to cause the observed dynamics of the Hg-atom. Thus the detected Hg^+-ions have to be fragments of larger cluster ions. They reflect the dynamics of neutral excited states within the parent clusters. This conclusion is supported by an experiment where the expansion conditions of the molecular beam have been such that only Hg, Hg_2, Hg_3, and Hg_4 are contained in the beam. Under these conditions all observed dynamics except the coherence peak at $\Delta t = 0$ vanish.

Starting with the Hg_5^+-cluster ion the dynamics on a longer time scale change with increasing cluster size and finally reaches the time dependence shown in Fig. 4. For short delay times a fast decrease ($\tau_1 \approx 5$–10 ps) of the ion signal is seen which is followed by an increase with time constants of $\tau_2 \approx 20$–60 ps to a level of 50 to 75% of the original signals around $\Delta t = 0$. Eventually, for long delay times the ionization signal decreases with a time constant

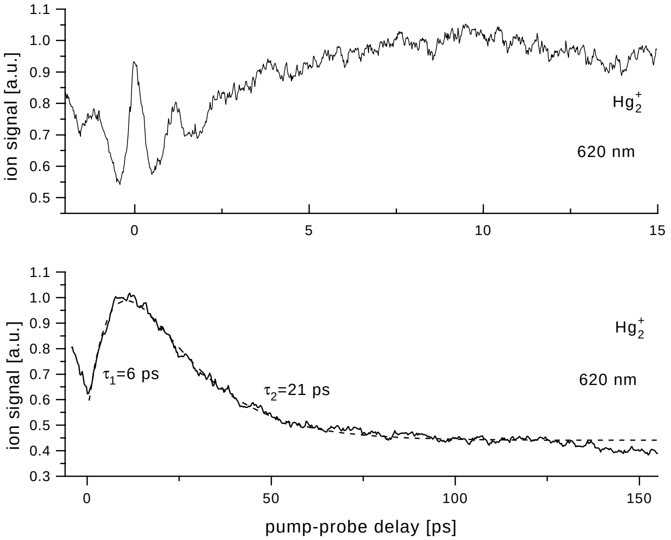

Fig. 3. Time dependence of the Hg_2^+ ion signal on longer time scales. Note that due to lower resolution the coherence peak at $\Delta t = 0$ and the oscillatory structure seen in the upper panel are smeared out in the lower pannel.

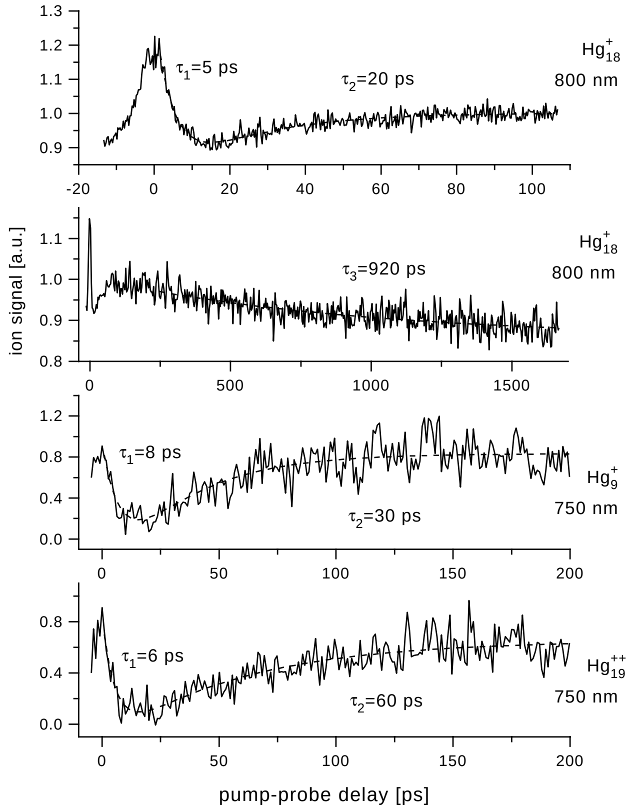

Fig. 4. Fast scan pump-probe spectra of different mercury cluster ions. The dynamics shown here can be explained invoking a model of caged chromophore dissociation and recombination.

of $\tau_3 = 500\,\mathrm{ps} - 1\,\mathrm{ns}$. The time constants τ_1, τ_2, and τ_3 strongly depend on the intensity of pump and probe pulses as shown in Fig. 5.

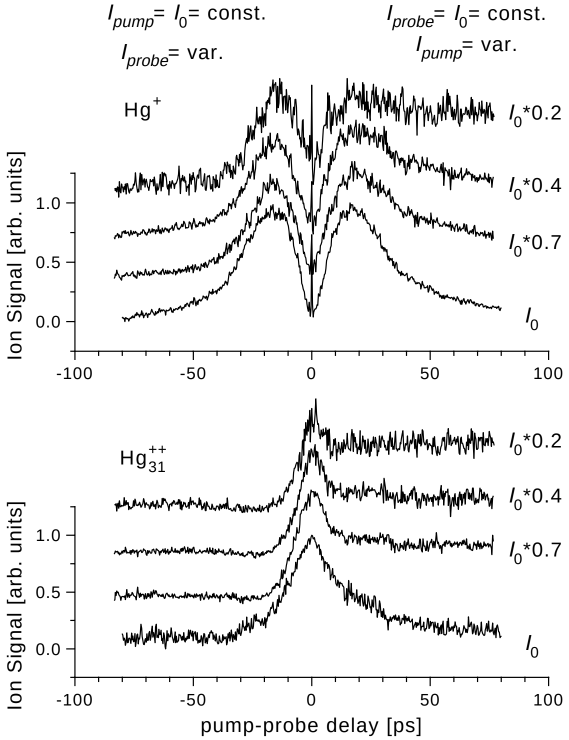

Fig. 5. Dependence of the transient ionization spectra of Hg^+ and Hg_{31}^{2+} on the applied laser intensity ($I_0 = 10^{11}\ \mathrm{W/cm}^2$). For pump pulses with low intensity a recovery of the signal for long time delays can barely be seen while for more intense pump pulses this changes to almost a single exponential decay.

4 Discussion

We observe that the relative intensity of singly and doubly charged clusters of a given mass do not change with laser intensity varying by a factor of ten. From this we conclude, that the doubly charged clusters are not formed with singly charged cluster ions as intermediates. In such a two-step process the first step would transfer the cluster from the electronic ground state to the continuum of the singly charged ion and in the second step a second electron would be removed leaving the cluster in the doubly charged ionic state. In that case the signal of the doubly charged species would drop faster than that of the singly charged when lowering the laser intensity and it would vanish at a higher threshold intensity. But that is clearly not the case. Our results show some differences to the findings of Broyer *et al.* [11]. In their analysis of the Hg_n-cluster ionization by electron impact they suggest a model of sequential ionization, where first an electron is excited to the continuum and then a second electron is released by impact afterwards. However, on the basis of our time-resolved measurements shown in Fig. 2, we can exclude such a two-step process. The observed dynamics have to occur in a *neutral* intermediate state, i.e. *prior* to the ionization by the probe laser in our experiments. In a two-step process via a singly charged cluster the transient signal of the doubly charged cluster ion of the same mass should exhibit the same dynamics as seen in the singly charged cluster. But this is not the case since for instance the observed dynamics for Hg_{17}^{+} and for Hg_{17}^{2+} are clearly different (see Fig. 2).

The oscillatory transient ionization signal seen for short delay times and common to all measured cluster sizes and charge states leads us to the conclusion that a "chromophore" system plays an important role in the excitation of the neutral clusters. Evidence for such a chromophore structure has also been found for the rare gas clusters which are van der Waals bound systems similar to the small Hg-clusters [12]. Calculations based on our data performed by Bennemann and coworkers [13] support such a chromophore model. According to their calculations the ionic cluster has a covalent bound dimer chromophore to which the remaining atoms of the cluster are bound by strong polarization forces. When exciting a van der Waals cluster by an ultrashort laser pulse to an ionic configuration a breathing oscillation of the cluster with a frequency in the range of 20–50 cm^{-1} is predicted. This breathing mode is caused by a contraction of the cluster after an increase of the binding energy due to the polarization forces and could explain the oscillatory behaviour seen in our ionization transients. This argument applies also for neutral clusters in high Rydberg states which could be the relevant neutral intermediate states in our pump-probe experiments. However, the calculations in [13] are only valid for the van der Waals bound Hg_n-clusters or when exciting to the twofold ionic continuum in the case of a covalently bound species.

Bréchignac and coworkers [2] locate the transition from van der Waals to covalent bonding around $n \approx 12$. The question in which size range the transition to metallic bonding occurs is still open. Rademann *et al.* [3] suggest $n \approx 70$ because the ionization potential has reached the bulk value for these cluster sizes. Haberland *et al.* [5] proposed a value of about $n \approx 200$ on the basis of their photoionization experiments on mass-selected positively charged clusters. Very recently a value of $n \approx 400 \pm 30$ has been reported by Busani *et al.* [14] on the basis of a detailed study of photoelectron spectra of mass-selected negatively charged mercury clusters.

Our observation of a similar oscillatory structure in the ionization signal of large singly charged clusters may be due to fragmentation of even larger doubly charged clusters in agreement with Bennemann's result [13]. A Fourier analysis shows that clusters with the same e/m ratio, for instance the clusters Hg_{21}^{+} and Hg_{42}^{2+}, exhibit the same frequency in the short-time oscillatory signal [15]. This indicates that predominantly a symmetric fragmentation process occurs at least for larger clusters ($n \geq 15 - 20$).

The reason why we observe a very similar ionization dynamics no matter what wavelength we use for excitation (except 400 nm) is due to the existence and excitation of a chromophore. Energetically close to the ground state of the chromophore dimer ion are the neutral Rydberg states. Assuming that these Rydberg states are the neutral intermediate states in our pump-probe experiments, the observed dynamics and wavelength independence would be due to the almost identical potential curves.

With all the wavelengths applied in our pump-probe experiments we can excite Rydberg states in the energy range of about 6.5 eV to 8 eV by absorption of four or five photons. Wavelengths for which this Rydberg excitation is not possible do not show these oscillations. For instance with 400 nm only excited states below 6.2 eV or above 9.3 eV are accessible. Note that we observe a significant reduction of the doubly charged cluster ion signal for all wavelengths (800 nm, 400 nm, 255 nm) where the total excitation energy is above the dimer ionization potential of 9.2 eV. This is because with those wavelengths a direct ionization from the ground state of the neutral cluster can occur.

As is shown in Fig. 4 the mercury cluster ionization signal for large pump-probe delay times decreases and finally increases again resembling very much the dissociation and recombination dynamics of molecules encaged in clusters [16–18]. The experiments of Lineberger and coworkers [16, 17] and Zewail and coworkers [18] both show dissociation and strongly damped oscillations at early times and a late signal increase due to recombination of the fragments. Both groups interpret their results invoking a "cage effect" where a (dimer) chromophore dissociates and eventually recombines due to collisions with the surrounding atoms or molecules. A very similar interpretation of our transients require a localized excitation of a (dimer-) chromophore within the Hg_n-clusters. The oscillatory structure in our transient ion signal could be due to vibration of the chromophore itself or an oscillation of the chromophore against the cluster forming a solvent shell. Due to collisions with the surrounding cluster atoms the dissociating chromophore fragments loose energy and finally some of them recombine after a time of some 10 to 100 ps. The motion within the cluster should critically depend upon how much energy the chromophore looses per collision.

In the spectra shown in Fig. 5 the recovery of the ion signal for delay times > 20 ps can barely be seen for low pump pulse intensities. For more intense pump pulses the transient ion signal changes to almost a single exponential decay. This again can be interpreted within the caged chromophore model. If the energy deposited by the pump pulse into the cluster is low, the cluster is able to stabilize after ejection of several small fragments. Recombination of the chromophore can take place. For higher deposited energies stabilization is no longer possible and the cluster brakes apart.

Within the framework of both models, the breathing mode and the caged chromophore dissociation, the ejection of a single charged mercury atom is unlikely from an energy point of view. Therefore the observation of ionized atomic fragments reflecting the dynamics of larger neutral clusters is somewhat in contradiction to a localized chromophore excitation and charge localization on a dimer or trimer in the center of the cluster assumed in both models. In the case of two or more charges being localized at opposite positions at the cluster surface, ejection of singly charged atoms would be more probable. In combination with the above mentioned symmetric fragmentation a localized excitation of two (or more) separate chromophore structures is not unlikely. A more detailed discussion of the models presented here is beyond the scope of this paper and will be given in a forthcoming publication [19].

5 Summary

We have reported results of experiments with femtosecond laser pulses to study the ultrafast dynamics of neutral mercury clusters in single pulse and in pump-probe experiments. We observed prompt formation of singly, doubly, and triply charged clusters for rather low laser intensities ($10^{11}\,\mathrm{W/cm^2}$). The obtained size distributions of ionic clusters are very similar and do not depend upon the applied wavelengths ranging from the UV to the IR spectral region (255–800 nm). Pump-probe experiments revealed an intermediate state "short-time" dynamics independent of cluster size and charge state. We believe this is due to a "chromophore" which is common to all observed clusters. "Long-time" transient ionization signals for all Hg_n-clusters ($5 \leq n \leq 110$) show a fast (5–8 ps) decay, a slow (20–80 ps) recovery of the ionization signal and another very slow (> 200 ps) decay which may indicate a caged dissociation and recombination of the Hg_2^* chromophore. However, we cannot exclude contributions from a fragmentation of very large clusters beyond the transmission region of our spectrometer.

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