Ultrafast Hot-Electron Dynamics Observed in Pt_3^- Using Time-Resolved Photoelectron Spectroscopy

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Time-resolved two-photon photoelectron spectra have been measured for free Pt_3^- using femtosecond pulses of 1.5 eV photon energy in a pump-probe configuration. The time-dependent photoelectron distribution reveals a lifetime of optically excited states of less than 70 fs. Such an unexpected fast electron relaxation in Pt_3^- suggests the existence of inelastic electron-electron scattering processes in a triatomic cluster which result in a lifetime similar to those of bulk metals.

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Time-resolved photoelectron spectroscopy on small clusters has recently demonstrated wave packet evolution [1], intramolecular rearrangement [2], and fragmentation dynamics [3,4]. These processes are all related to nuclear motion which can be followed if the excited state is long lived with respect to the vibrational period. Lifetimes within the picosecond (ps) and nanosecond (ns) regimes have been observed in the above experiments. This is consistent with studies on molecular systems, where intramolecular vibrational relaxation and unimolecular dissociation typically is observed on a ps time scale. Intramolecular electronic relaxation could be faster, but so far electronic relaxation processes on a fs time scale have been observed in small molecules only through autoionization of core hole excited states [5,6]. On the other hand, fast electronic relaxation processes were generally held responsible for the failure to record resonant two-photon absorption spectra of metal clusters containing more than a few atoms [7].

Electron relaxation processes have been studied in solids using time-resolved photoelectron spectroscopy, e.g., hot-electron dynamics [8,9] and surface-state dynamics [10–12], as well as spin relaxation [13,14]. Extremely short relaxation times have been found in transition metals. This has been attributed to the high density of states and d-orbital contributions at the Fermi edge of open d-shell metals [15].

In this context the fundamental question arises whether the fast relaxation times are a specific solid state effect or if small transition metal clusters show similar ultrashort inelastic scattering lifetimes. Generally, an increased lifetime is expected for small particles compared to the metallic bulk value, all the more in particles containing less than 100 atoms due to a rather discrete level structure caused by quantum confinement. So far, electron relaxation in small clusters has not been observed in real time.

Here we present data demonstrating that excited electronic states in metal clusters can exhibit ultrashort lifetimes distinctly below 100 fs even if the particle contains only three atoms, as in our case of Pt_3^-. Two-photon photoemission measurements on this transition metal cluster reveal direct evidence for ultrafast inelastic electron scattering processes. These measurements show that the number of electronic states in subnanoparticles can be sufficiently large to provide inelastic electron scattering processes comparable to those in macroscopic metallic systems.

The platinum clusters are produced in a pulsed arc cluster ion source [16] and mass selected in a time-of-flight mass spectrometer. The cluster beam is focused into the source region of a magnetic-bottle-type electron spectrometer, where photoelectrons are detached from a selected cluster anion with femtosecond pulses having 1.5 eV photon energy. Single-shot autocorrelation measurements give a temporal pulse width of 275 fs. Pulse energies of 2 mJ (20 Hz) are used for the detachment of photoelectrons [17]. The power density at the location of the detachment is estimated to be about 10 GW/cm^2. The primary photon beam is split in a ratio of 1:1 and the probe pulse is optically delayed by a movable retroreflector.

Pt_3^- provides an ideal system for two-photon photoemission studies due to an electron binding energy [18] which is somewhat larger than the photon energy at the fundamental wavelength of a Ti:sapphire laser. Hence, the energy dissipation after photoexcitation can be followed in the two-photon photoemission measurement without any complication caused by photoelectrons from direct photodetachment processes. Moreover, fragmentation is avoided because the photon energy of 1.5 eV is less than the dissociation energy of Pt_3 [19]. Furthermore, the conventional photoelectron spectrum of Pt_3^- indicates a high density of valence electronic states. Accordingly, numerous close lying valence states are expected to provide a favorable condition for inelastic electron scattering.

Figure 1 shows two photoelectron spectra of Pt_3^- taken with pulses from two different lasers. Spectrum (a) shows a single-photon photoelectron spectrum of Pt_3^- recorded with a ns laser at a photon energy of 3.0 eV [20]. The sharp double peak at the beginning of the spectrum results from emission from the highest occupied molecular orbitals of Pt_3^- [18]. In C_{2v} geometry, which represents the most stable isomer of Pt_3, the highest occupied orbitals

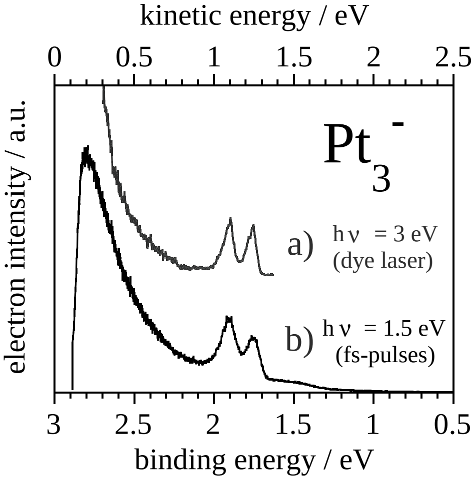

FIG. 1. (*a*) Single-photon photoelectron spectrum of Pt$_3^-$ taken with dye-laser pulses of 3.0 eV photon energy [20]. (*b*) Two-photon photoelectron spectrum of Pt$_3^-$ taken with fs-laser pulses of 1.5 eV photon energy. Photoelectrons from three-photon processes are visible below 1.7 eV. Note the overall similarity of the one-photon and two-photon photoelectron spectra.

are composed from the 6s and 5d atomic orbitals resulting in a leading configuration $(a_1)^2(b_1)^1(a_1)^0$ [21]. The anion is discussed to be triangular as well [18]. The photoelectron peak at lowest binding energy determines the electron affinity of Pt$_3$ (1.7 eV). The rising slope on the high binding energy side of the spectrum in Fig. 1(*a*) originates partially from thermionic emission [20]. Spectrum 1(*b*) shows a photodetachment spectrum taken with a single fs-laser pulse and a photon energy of 1.5 eV. Since the photon energy is chosen smaller than the electron affinity, at least two photons are necessary to detach an electron from Pt$_3^-$. In this case the detachment probability is equal to the product of the excitation probabilities of the intermediate as well as the final state. The two-photon emission spectrum looks very similar to the ns spectrum. The small broadening of the fs spectrum with respect to Fig. 1(*a*) is attributed to the lifetime broadening and experimental resolution. Since direct two-photon photoemisson processes are many orders of magnitude less probable than resonant processes, the electron signal is attributed to resonantly excited intermediate electronic states. Thus the overall similarity of the photoemission spectra in Fig. 1 indicates a smooth density of intermediate unoccupied electronic states in Pt$_3^-$.

Varying the delay between pump and probe pulses the dynamics of the photoexcited intermediate state can be probed in real time. Figure 2 shows delay spectra in which the probe pulse has been delayed up to 500 ps with respect to the pump pulse. The intensity at binding energies larger than 0.25 eV results from two-photon photoemission. At energies below 0.25 eV weak three- and more-photon processes are observed. The spectra represent the result of detachment from photoexcited Pt$_3^{-*}$ ($h\nu_{\text{pump}} = 1.5$ eV). The photoelectron signal is displayed on a binding energy

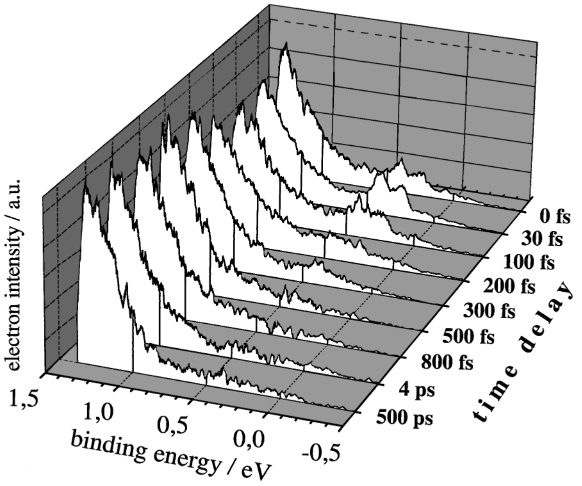

FIG. 2. Time-resolved photoelectron spectra of Pt$_3^-$ as a function of the time delay between pump and probe pulses ($h\nu_{\text{pump}} = h\nu_{\text{probe}} = 1.5$ eV). The varying photoelectron intensity in the two-photon photoemission spectra provides evidence for a fast electron relaxation process. The double peak structure at the top of the spectrum vanishes within 300 fs. Each delay spectrum is obtained by subtracting the intensity of the pump-only and probe-only spectra from the combined pump-probe spectrum. Thus, any contributions from two-photon emission of either the pump-only or probe-only pulses have been eliminated. In order to ensure a proper normalization for the subtraction, pump-only and probe-only spectra were measured individually for each delay. Systematic errors due to stability fluctuations of the laser pulses and the cluster beam on a long-term scale were minimized by recording alternately each of the spectra for 5 min only. The total accumulation time of each delay spectrum was about 2 h. The spectra are normalized to the total intensity.

scale of Pt$_3^{-*}$[$E_{\text{bin}}(\text{Pt}_3^{-*}) = h\nu_{\text{probe}}$-$E_{\text{kin}}$]. The spectrum at zero delay corresponds to the fs spectrum in Fig. 1(*b*). The remaining curves in Fig. 2 have been obtained by delaying the probe pulse from 30 fs to 500 ps. A fast dynamics of the intermediate excited states is evident from the varying photoelectron intensity. A decrease of the double peak intensity is clearly seen for an increasing delay of the probe pulse whereas the intensity at higher binding energies increases. At small delay times intensity is shifted to higher binding energies which is accompanied by an asymmetric broadening of the double peak on the high energy flank. Within 300 fs the intensity of the double peak drops significantly. Its intensity has almost vanished within the ps time regime. Additionally, an overall decrease of the emission intensity between 0.5 and 1 eV can be recognized. The nonvanishing intensity above 1 eV binding energy at time delays >1 ps proves resonant excitation while in the case of two-photon photoemission without the existence of real intermediate states the intensity should drop to zero. Moreover, a relative intensity shift should not occur.

The intensity of the double peak measured relative to the total emission signal as a function of the delay time is shown in Fig. 3. Fluctuations of the cluster and laser

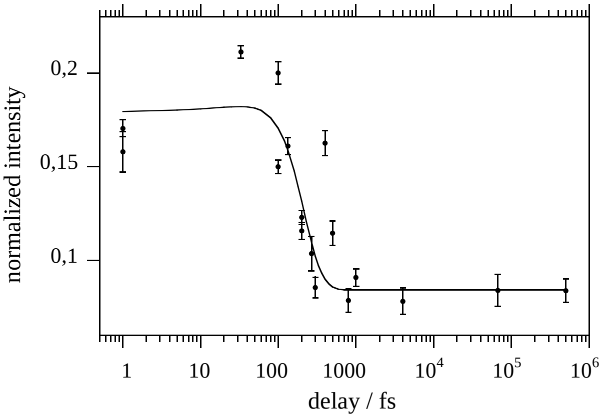

FIG. 3. Intensity variation of the double peak intensity at 0.3 eV (Fig. 2) relative to the total electron signal as a function of the delay (dots). A least square fit (line) following a first order rate equation delivers an inelastic electron relaxation time of <70 fs.

intensities are not considered in the statistical error bars. For delays up to 100 fs the ratio reaches a maximum of more than 0.2. This ratio decreases continuously to below 0.1 between 100 and 900 fs and, thereafter, stays constant up to the maximum delay of 500 ps. The remaining offset is due to autodetachment (after absorption of pump and probe photon) and photodetachment processes out of the excited cluster anions. Also, additional higher-order photoemission processes contribute to the offset. The line in Fig. 3 shows a fit based on the population dynamics of the intermediate photoexcited states. In case of the highest excited electronic states a first order rate equation model describes the transient population $N(t)$ of the intermediate states by $dN(t)/dt = A(t) - \beta N(t)$ [15]. $A(t)$ is the population rate of the intermediate states which is proportional to the temporal envelope of the pump pulse. The depletion of the anions in the electronic ground state during the laser pulse is assumed to be negligible. β is the inverse relaxation time. The photoelectron intensity $P(\tau)$ of the initially populated transient states is measured by the second pulse (probe) at a certain delay τ. Considering the temporal intensity distribution of the probe pulse $[I(t) = I_0 \operatorname{sech}^2(t)]$, the double peak intensity versus the delay τ is given by $P(\tau) = c_1 + c_2 \int_{-\infty}^{+\infty} I(t - \tau) N(t)\, dt$. We note that the pump and probe pulses were polarized perpendicular to each other which justifies the above model assuming noninterfering pump and probe pulses. c_1 and c_2 are fit parameters to match the offset and the amplitude of the data. c_1 has been fit to the data points at a delay larger than 1 ps. Taking into account the width of the pump and probe pulses (~275 fs) the lifetime $1/\beta$ of the photoexcited states is derived to be less than 70 fs. This short relaxation time observed in Pt_3^- indicates a fast decay of the primarily excited states through inelastic electron-electron scattering. On the femtosecond scale an energy flow into the vibrational system plays a minor role. The free cluster represents an isolated system in which the energy of the primary excitation is redistributed among a manifold of states within the heated electron system. Fast relaxation via electron-electron scattering is favored by a high density of states located within the Franck-Condon region [$r_{\mathrm{Pt-Pt}}(\mathrm{Pt}_3)$] 2.9 Å [19]]. The absorbed photon excites many close lying states which overlap energetically due to lifetime broadening. In a decay cascade the energy of the primary single electron excitation is distributed into a many electron excited state. Photodetachment from such multielectron excited states delivers photoelectrons with a lower kinetic energy than detachment from the primarily excited states. This is the reason for the accumulation of intensity at the high binding energy side of the photoelectron spectra in Fig. 2. The normalization to the total intensity is justified by the fact that the excited Pt_3^- particle can release the excess energy only by electron emission (radiative cooling is not expected on this time scale). This is in sharp contrast to solids where the energy dissipates into the bulk. Moreover, even after the energy has been transferred into the vibrational system of the isolated Pt_3^- cluster there still exists a relatively high probability for redistribution into an electron excitation due to the spatial localization of the system and the limited vibrational degrees of freedom in a triatomic cluster.

The <70 fs relaxation time in free Pt_3^- can be attributed solely to electron relaxation. Measurements on free nanoparticles provide the principal advantage that the data are not influenced by energy dissipation into the bulk. Since we have used an excitation energy below the electron affinity of Pt_3, the intermediate photoexcited states are energetically inhibited to decay into the continuum. Therefore, the decay process in Pt_3^- at 1.5 eV is not influenced by autodetachment processes. Such states are known to possess extremely short lifetimes of a few femtoseconds due to a large phase space available in the continuum. Thus the observed relaxation should be solely determined by the density of the occupied and unoccupied states of Pt_3^-. Furthermore, the relaxation at an excitation energy of 1.5 eV is not related to plasmon excitations [22,23] as these are not expected for small Pt clusters at the excitation energies used here.

The redistribution of intensity from low to high binding energies in Fig. 2 indicates electron scattering processes in Pt_3^- which are similar to those in solid metals. Here the primarily excited electron scatters with electrons below the Fermi level by simultaneous excitation of secondary electrons into unoccupied states above the Fermi edge. The lifetimes of excited states below the vacuum level depend on the density of states around the Fermi level, which determines the phase space volume of the scattering processes. The larger the phase space the shorter the lifetimes. This has been confirmed for solid transition metals by two-photon photoemission. In particular, an extremely high density of states exists in metals with an open d-shell, e.g., Ta [15]. Ag and Cu, on the other hand, have relaxation times which are substantially larger. Similarly, two-photon photoion measurements on large nanoparticles (70 nm in size containing about 10^7 atoms) have demonstrated average inelastic scattering lifetimes of optically excited states below 10 and 20 fs for Pd and Au, respectively [24]. In analogy to the dependence of the inelastic scattering lifetimes on the density of states in solids and large nanoparticles we postulate a high number of electronic states in Pt_3^- which causes the ultrafast relaxation in this transition metal cluster in contrast to noble and alkali metal clusters.

Fast electron relaxation has not been observed in time-resolved photoelectron spectra of, e.g., Au_3^- [4], Na_2 [1], and $I_2(Ar)_{20}^-$ [3]. Instead, pump-probe photoelectron spectra have revealed unimolecular dissociation and wave packet evolution. Vibrational dynamics has also been observed in Ag_3^- using femtosecond time-resolved photoion measurements [25]. In contrast to Pt_3^-, the above metal clusters possess a closed shell electronic structure. The number of electronic states is therefore considerably reduced which is evident from the conventional photoelectron spectra. This discrete level structure strongly lowers the probability of electron-electron scattering in noble metal and alkali clusters in contrast to open-shell transition metal clusters.

The suggestion of a dense electron level structure in Pt_3^- is supported by recent relativistic configuration interaction calculations on small Pt_n clusters. Including spin orbit interaction the lowest nine electronic states in Pt_3 have been calculated within an energy range of 0.3 eV [21]. Also the integrated density of occupied states at the Fermi energy of solid platinum (1.9 states/eV · atom [26]) is comparable to that of Pt_3.

In summary, time-resolved two-photon photoelectron spectra reveal ultrafast hot-electron relaxation dynamics of optically excited states in free Pt_3^-. Using an excitation energy of 1.5 eV an inelastic scattering lifetime of less than 70 fs has been deduced from the photoelectron intensity variation at the top of the valence band. This ultrafast relaxation demonstrates that the inelastic electron-electron scattering lifetimes can be of the same order of magnitude as in solid metals, even in the case of a particle containing only three atoms.

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