# Experimental Observation of Excess-Photon Detachment of Negative Ions

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Negative chlorine ions are stored in a Penning trap and are exposed to short (35 ps) and intense (up to $3\times10^{12}$ W/cm$^2$) optical pulses with a wavelength of 1064 nm. The detached electrons are detected in energy-resolved measurements. Absorption is observed of up to two photons in excess of what is required on the basis of the electron affinity.

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Detachment of negative ions has proven to be an intriguing process with unexpected repercussions. It has been studied under quasi-field-free conditions [1], and also in the presence of a magnetic field [2], an electric field [3], a microwave field [4], and a strong radiation field [5–8]. Characteristic for negative ions is the short range of the interaction between the outer electron and the neutral core. A well-known consequence is that only a finite number of bound states exists, in general only one. A long-standing question is whether this short-range nature of the potential will prevent the absorption of excess photons during multiphoton detachment when a negative ion is placed in a strong radiation field. In atoms the phenomenon of additional photon absorption is known under the name "above-threshold ionization" or "excess-photon ionization" and has been studied thoroughly [9]. However, the analogous process of excess-photon detachment (EPD) has not been reported up to now.

Since conservation laws forbid absorption of photons by a free electron, the absorption of any excess photon will have to occur as an integral part of the detachment process, where the electron is still able to exchange momentum with the remaining atom. In the case of detachment this is a much more stringent requirement than in ionization, where the Coulomb tail of the electron-ion potential makes interaction possible to fairly large distances.

It has been shown (Ref. [10]) that in the high-frequency approximation (where the driving frequency is large compared to the average motion of the electron) it is the third derivative of the interaction potential that causes photon absorption. In a negative ion this potential is the interaction between a charge and an induced dipole that falls off as $r^{-4}$. So the region in which the absorption has to occur is very limited. This fact makes negative ions very interesting objects for studying the excess-photon absorption process, since, to a very good approximation, the electron can be described as free immediately after the detachment, as indeed most theories do.

The goal of this Letter is to present measurements that demonstrate that negative ions can indeed absorb more photons than is energetically required for detachment. Despite the lack of experimental observations, there are calculations by Crance [11] that indicate that EPD is feasible indeed. Surprisingly enough, even in the model problem of an electron in a zero-range potential and a strong radiation field, excess-photon absorption can take place [12]. Other predictions of the model of Crance were tested in a series of multiphoton detachment experiments by Blondel *et al.* [7,8]. These experiments, which are the most detailed experiments on negative ions in strong radiation fields up to now, confirm the calculated generalized cross sections for the negative fluoride ion, but show deviations for the heavier halogen negative ions.

The present experiments are performed with negative chlorine ions as the target and the fundamental of a Nd-doped yttrium-aluminum-garnet (Nd:YAlG) laser (1.165 eV photons) as the strong field. Chlorine has an electron affinity of 3.613 eV [6]. After detachment the neutral chlorine atom can be in either the $^2P_{3/2}$ state or the $^2P_{1/2}$ state, 110 meV higher in energy [13]. Therefore we expect after multiphoton detachment an electron energy spectrum with peaks at $1.047+N\times1.165$ and $0.937+N\times1.165$ eV. With the combination of ion and laser frequency used here at least four photons are required for detachment. This prevents the high-intensity observations from being swamped by processes that occur at low light intensities or, an even more fundamental problem, low-intensity processes depleting the ground state before high light intensities are reached. Furthermore, the fourth photon is sufficiently far above threshold to assure that channel closure by ponderomotive shifts cannot occur at the intensities used in this experiment. Thus the excess photon really represents a transition between continuum channels.

To obtain a sufficient density of $Cl^-$ ions a Penning ion trap [14] is used. We combined this Penning trap with a magnetic-bottle electron spectrometer [15] (Fig. 1). The maximum magnetic field is 1 T. Along the symmetry axis the field drops to 1 mT over a distance that is long compared to the Penning trap but short compared to the flight tube. The required electric quadrupole field is not

 

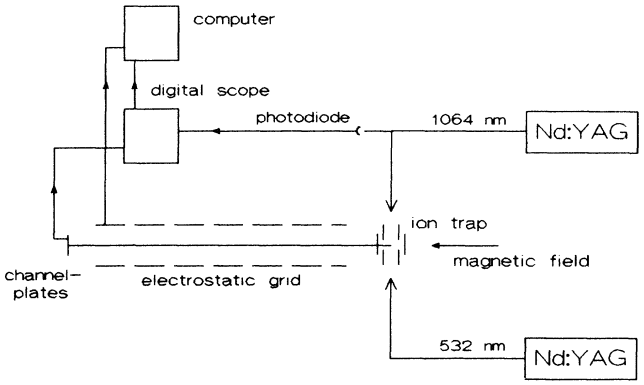


FIG. 1. Schematic outline of the experimental setup with a Penning trap initially used for electrons and subsequently for $Cl^-$, combined with a magnetic-bottle spectrometer for photoelectron energy measurements. The laser indicated at the bottom is used for production of $Cl^-$. The other laser detaches $Cl^-$.

made by means of hyperbolic electrodes but is mimicked by flat ring electrodes. A thin golden plate with a hole of 1.5 mm is mounted on the tip of each pole piece and grounded. On top of these plates a golden ring electrode (outer diameter 15 mm, inner diameter 7 mm) is mounted which is set at a voltage of +1.2 V. The distance between the two electrodes is 3 mm. Despite higher multipole moments this configuration gives good results and has the advantage that the trap volume is much more accessible than with the conventionally shaped electrodes. Apart from the obvious function of trapping the negative ions, the Penning trap has a second purpose, namely, trapping electrons that are required to form the ions. The trap is filled with $Cl^-$ ions by the following procedure: A continuous flow of $CCl_4$ gas provides a pressure of $1\times10^{-6}$ mbar, which is of the same order of magnitude as the background pressure. A frequency-doubled laser pulse from a mode-locked Nd:YAlG laser is focused into the center of the trap (pulse duration 35 ps, energy per pulse 6 mJ, focused with a lens of focal length 15 cm) at a repetition rate of 10 Hz. Because of the ionization potential of 11.47 eV of $CCl_4$ [16], ionization by five 2.33-eV photons fills the trap with 0.2-eV electrons. $CCl_4$ has a large dissociative attachment cross section for low-energy electrons [17] under formation of $CCl_3$ and $Cl^-$. At the $CCl_4$ pressure used in the experiment no free electrons could be detected 500 $\mu$s or later after the 532-nm laser pulse. We estimate the trapping volume to be 1 $mm^3$, containing roughly 1000 ions. This estimation is based on an assumed energy of $Cl^-$ of 0.4 eV maximum after dissociation. A 1064-nm laser pulse from a second mode-locked Nd:YAlG laser (pulse duration also 35 ps) is focused on the cloud of ions 2 ms after every 532-nm laser pulse. The ion trap is electrically turned off 15 ns before this second laser pulse arrives. About 8 mJ of energy is focused with a planoconvex lens of focal length 50 cm. The diameter of the focused beam at half maximum is measured to be 90 $\mu$m and the maximum intensity is calculated to be $3\times10^{12}$ W/$cm^2$. Linearly polarized light is used. Detachment takes place in a volume of $1\times10^{-2}$ $mm^3$, which is roughly 1% of the size of the ion cloud. The photoelectrons are energy analyzed on the basis of their time of flight over a 50-cm-long flight path. In order to obtain optimum resolution, retarding voltages are applied to the flight tube. The high-resolution part of the time-of-flight spectrum is then converted to energy. The electrons are detected with two channel plates in tandem and further amplified. The analog signal from the electron detector is recorded on a LeCroy 9450 digital oscilloscope. A typical signal consists of five electrons per shot. Calibration of the time-of-flight spectra is done by recording the known photoelectron spectrum after multiphoton ionization of xenon with 532-nm light. The energy of the detachment laser is measured on a shot-to-shot basis and the electron spectra are binned accordingly. At every retardation voltage 2000 laser shots are used, divided over ten "intensity bins." A schematic outline of the experimental setup is given in Fig. 1.

Figure 2 shows the energy spectrum of the detached electrons. Indeed, more than one peak is observed. All peaks are due to the interaction of $Cl^-$ and the 1064-nm light. In addition there is a smooth background due to ionization of, probably, water. The width of the peaks is about 200 meV, and the two energy spectra corresponding to the neutral chlorine atom left in the $^2P_{3/2}$ and $^2P_{1/2}$ states are indistinguishable. This substantial width has various causes.

(1) Because of the unusually long region of 1 mm in which electron production occurs there is some degradation of the performance of the electron spectrometer.

(2) At the maximum light intensity used in the reported experiments, $3\times10^{12}$ W/$cm^2$, the quiver energy of a

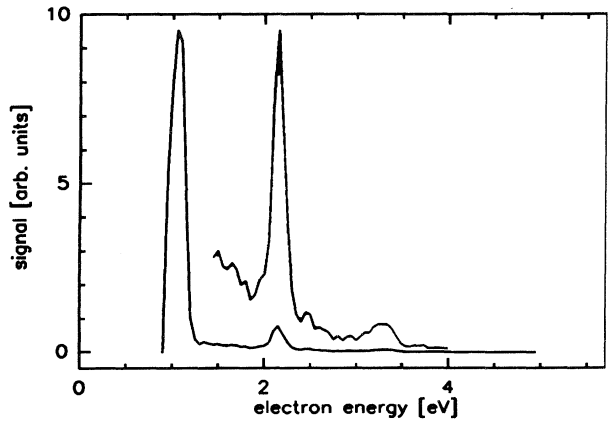


FIG. 2. Electron energy spectrum measured after multiphoton detachment of $Cl^-$ with 1064-nm light at an intensity of $2.4\times10^{12}$ W/$cm^2$. For the excess-photon peaks an enlargement of the signal is shown with the same energy scale.

free electron is 300 meV (much smaller than the photon energy). This experiment is done in the intermediate-pulse-duration regime where a fraction of the detached electrons do not leave the focal region before the laser intensity has changed significantly [18]. Therefore there is an imperfect cancellation of the ponderomotive threshold shift and the quiver energy of the electron. The resulting shift can be in either direction because the detachment process is saturated so that detachment does not necessarily take place at the peak intensity. The various shifts in the electron energies result in a broadening of the peaks that is asymmetric with respect to the spectroscopic positions. A simple calculation shows that space charge does not contribute more than 5 meV and therefore is completely negligible. The resulting width makes the two fine-structure components coalesce, so that the experimental width is hardly intensity dependent because it is dominated by the fine-structure splitting.

Within the resolution of the energy spectrum the distance between the peaks for 4-, 5-, and 6-photon detachments equals the photon energy of 1.165 eV. For comparison with our experimental results we calculated, on the basis of theoretical cross sections [11], ratios between 4-, 5-, and 6-photon detachments at various light intensities. The values were obtained by integration over space and time of the light intensities in the trap, assuming Gaussian distributions over two spatial dimensions, a Gaussian distribution in time, and a constant distribution in the direction of the laser beam. The following cross sections have been used: $\sigma(4)=4.6\times10^{-56}\,s^{-1}W^{-4}m^{8}$, $\sigma(5)=3.4\times10^{-72}\,s^{-1}W^{-5}m^{10}$, and $\sigma(6)=2.6\times10^{-89}\,s^{-1}W^{-6}m^{12}$. Figure 3 shows the ratio between 4- and 5-photon detachments obtained in our experiment together with the calculations on the basis of the theoretical cross sections as a function of the peak intensity. In lowest-order perturbation theory and without saturation effects due to depletion of the ground state, the ratio between the 4- and 5-photon processes is directly proportional to the light intensity. At higher intensities saturation becomes visible. Although the various light intensities are well defined with respect to each other, there is an uncertainty in the overall scaling of 50%. Therefore the experimental results are in good agreement with the theoretical predictions. The yield of the 6-photon process was too small to extract a confident order of nonlinearity from the data. At the peak intensity of $2.4\times10^{12}$ W/cm$^2$, we measured for the ratio of 4- and 6-photon detachments a value between 70 and 200. The theoretical calculations of Crance predict a ratio of 70.

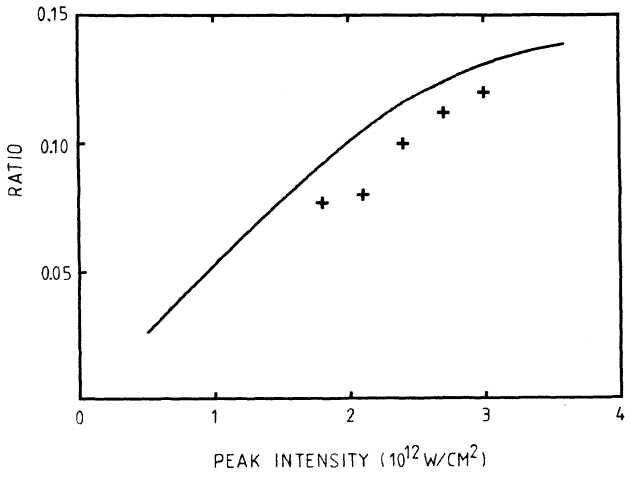


FIG. 3. Ratio between 4- and 5-photon detachments as a function of the peak intensity. Plusses: experimental results; continuous line: theoretical calculations [11].

In conclusion, we report the experimental observation of absorption by a negative ion of more photons than minimally required for photodetachment. This process could very well be called excess-photon detachment. The occurrence of this process in negative ions is less self-evident than the analog process in atoms (excess-photon ionization) that caused widespread surprise and attention when it was first observed by Agostini *et al.* [19]. In the intensity regime that has been investigated up to now there is good agreement between experiment and theory. The experiments will be continued in the direction of higher intensities and more photons involved in the detachment process.

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