



Rydberg carbon clusters prepared by pulsed field recombination

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Abstract

The technique of pulsed field recombination is used to recombine a free electron with carbon cation clusters, ranging from C_{60}^+ to C_{50}^+ . It is shown that after recombination the electron is left in a highly excited state. The recombination method produces a Rydberg state ($n \sim 180$) in a large carbon cluster, such as C_{60} , with an electronic energy spread of ~ 1 K. We measured a recombination efficiency of $\sim 6\%$. © 2000 Elsevier Science B.V. All rights reserved.

The study of core excited cations has gained interest with the introduction of zero kinetic energy (ZEKE) [1,2], mass analyzed threshold ionization (MATI) [3], and photoinduced Rydberg ionization (PIRI) [4] spectroscopy. In PIRI spectroscopy, a core electronic transition is photoexcited in a Rydberg molecule, which then decays by rapid autoionization. Because Rydberg molecules only weakly interact with optical radiation, the absorption wavelengths for a Rydberg molecule are very similar to those of the corresponding cation. A similar technique developed by Fujii et al. is called IR/PIRI [5,6] in which the OH stretching vibration of cations is investigated by means of exciting Rydberg molecules with infrared (IR) radiation. There, the coupling of the vibrational with the electronic energy leads to autoionization. Not all molecular systems are accessible for these studies because the preparation of a Rydberg molecule is not always trivial, due to the fact that at non-zero temperatures of the molecules many vibra-

tional degrees of freedom in the system are occupied. Therefore, until now, it has not been possible to produce Rydberg states of large carbon clusters [7,8] such as C_{60} , nor has the (IR-)photoelectron cation spectrum with the technique of (IR/)PIRI spectroscopy been measured. This would be a major achievement in the IR-spectroscopy of fullerenes [9]. In this Letter, we report on the observation of Rydberg carbon clusters in a Rydberg state ($n = 180$, $\Delta n \approx 20$), by means of pulsed field recombination (PFR) [10,11].

Previously we have experimentally and theoretically shown that an atomic (rubidium) ion can be recombined with a free electron by means of the PFR scheme, the recombined atom being left in a highly excited state with a mean principal quantum number of $n \sim 180 (\pm 20)$ [10,11]. Classical calculations were in excellent agreement with the experimental observations. These calculations showed that the dynamics of the PFR scheme was unaffected by the non-hydrogenic core of the rubidium atoms, thus leading to the prospect that the PFR scheme is a universal method to recombine a free electron with any sort of ion. It was proposed that the PFR scheme

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can be used to produce 100–1000 cold anti-hydrogen atoms in a single experiment [10,11] in the already realized combined trap for particles of opposite charge of Gabrielse et al. [12]. In this Letter, we show that the PFR scheme can also be used to recombine a free electron with an ionic carbon cluster ($C_{50}^+ - C_{60}^+$). An experimental method is presented where excited states in ‘hot’ clusters (~ 750 K) are prepared with an electronically excited state energy spread on the order of 1 K. This observation opens the way for photoelectron spectroscopy (PIRI, IR-PIRI) on large ionic carbon clusters.

The PFR scheme can best be described as the time inverse of pulsed field ionization of Rydberg atoms [13] and is schematically sketched in the upper panel of Fig. 1. An ion is situated in a static electric field. The static electric field modifies the Coulomb potential such that a saddle point is created (Fig. 1a). If an electron passes over the saddle point in the modified Coulomb potential, it will take a small, but

not negligible, amount of time to return to the saddle point and escape from the ion (Fig. 1a). If the static field is turned off (Fig. 1b) before the electron returns to the saddle point, it will remain bound in a highly excited state (Fig. 1c). The time required for the electron to travel from the saddle point, to the nucleus, and back to the saddle point is roughly 1–2 ns for the fields and energies used in this experiment. In Fig. 1d the experimentally determined efficiency (density of recombined carbon clusters atoms divided by the density of free ionic clusters) of this scheme is depicted as a function of the delay of the fast field turnoff. This delay is with respect to the time when the free electron has its turning point in the electric field. Clearly, a maximum number of recombination events is recorded at zero delay. Note that efficiencies up to $6(\pm 4) \times 10^{-2}$ are obtained.

The PFR scheme was experimentally realized as follows: a pulsed electron source [14] was created by means of photoionizing lithium atoms in a static electric field of 1.50 V/cm, with a pulsed (9 ns duration) narrowband ($\Delta\lambda < 0.2$ cm $^{-1}$) dye laser (operating at 10 Hz). Typically electron pulses of 9 ns duration, with about $(5 \pm 2) \times 10^4$ electrons in a volume of 0.01 mm 3 were produced. The electric field is created by two parallel capacitor plates (separation: 10.0 mm) over which a voltage is applied (Fig. 2a). The ionizing laser pulse is focussed, creating a focus of 35 μ m diameter. Focussing the laser in the direction of the electric field (z -direction) is important since the focus size determines the energy spread of the created electron pulses. After ionization, the free electrons are pushed towards the anode plate (connected to ground) through which a small hole is drilled. A grid covering the hole minimizes the distortions on the electric field. After this region, the electrons enter a field-free region of 15.0 mm, after which another set of parallel capacitor plates (with small holes, covered by a grid) is situated. Since the final plate is on -1.50 V, the electrons turn around halfway between these plates, separated by 10.0 mm. A cloud of ionic carbon clusters is awaiting the electrons in this region. A magnetic field was applied ($B_z = 2.5$ mT) parallel to the direction of propagation to minimize the perpendicular spread of the electrons during their travel to the ions.

The ionic carbon clusters were produced 500 ns before the photoelectrons were created by photoion-

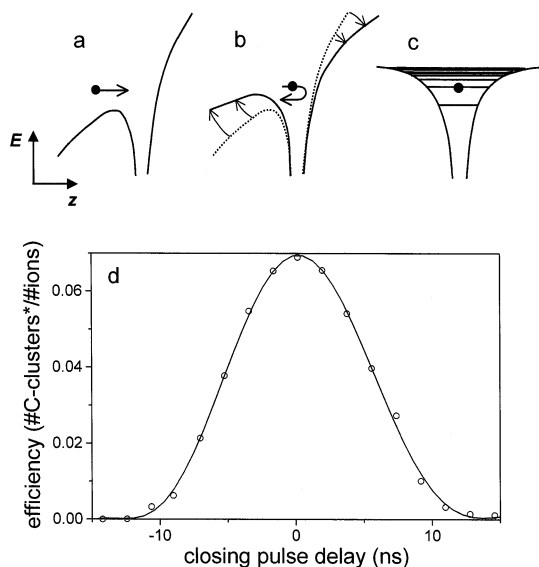


Fig. 1. Schematic representation of the PFR scheme. (a) An electron travels toward a positive ion in a static field; the turning point for the electron is within the ion cloud. (b) When the electrons are at the turning point, the electric field is quickly turned off. (c) If the field is turned off while the electron is near the ion, the electron remains bound. A small electric field bias of 200 mV/cm removes the electrons that did not recombine with an ion. (d) The efficiency (number of recombined carbon clusters divided by the number of free ionic carbon clusters) as a function of the delay of the quick turnoff.

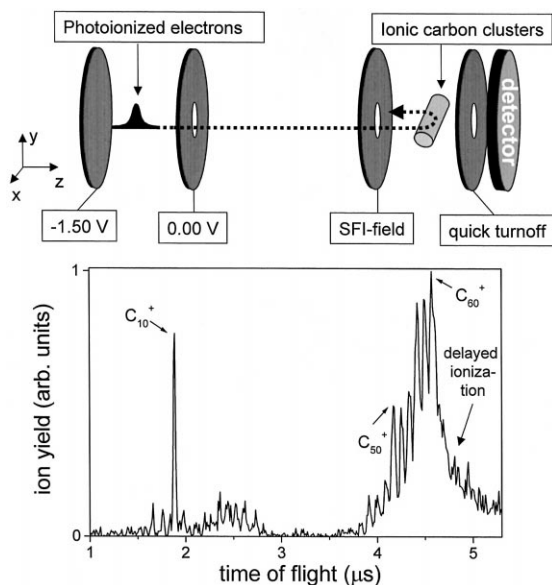


Fig. 2. Upper panel: Experimental setup. A static electric field of 1.50 V/cm pushes the electrons towards the ion region, where the ions await the electrons in an opposite electric field. The cathode plate is connected to a fast pulse generator so the field can be turned off within 1.0 ns. The anode plate is connected to a slow pulse generator so that after the quick turnoff the population distribution of the created Rydberg atoms can be probed. Lower panel: Mass spectrum of the produced carbon clusters by photoionization of C_{60} molecules with 266 nm.

izing and fragmenting gas-phase C_{60} molecules ($T \sim 750$ K) in a static electric field of 1.50 V/cm. The gas-phase C_{60} molecules were produced by a resistively heated oven. We photoionized C_{60} molecules (IP = 7.6 eV) by the fourth harmonic (266 nm) of a Nd:YAG laser. A typical mass spectrum of the created ions is depicted in Fig. 2. The multiple ionization with 266 nm mainly produces the higher ionic carbon clusters. Successful recombination experiments were also performed where ionic carbon clusters were produced by photoionizing C_{60} molecules with the second harmonic (532 nm), resulting in average cluster sizes of C–C₇. The smaller cluster size, in the 532 nm experiment, can be understood by the fact that the absorption of multiple photons opens up another decay channel of the C_{60} molecules: fragmentation. Also the effect of delayed ionization is seen in the C_{60}^+ mass peak, which is due to thermionic emission of the highly excited molecular

core [15,16]. Detailed studies of the fragmentation and ionization dynamics of C_{60} are reported in Ref. [15–19]. The decay time of this delayed ionization is measured to be ~ 240 ns. By producing the ionic carbon clusters 500 ns prior to the arrival of the electron pulses assures that the major fraction of the excited C_{60} molecules have ionized at the moment of the recombination event. The static electric field of 1.5 V/cm assures that all the electrons of the ionized carbon clusters have left this interaction region at the time the lithium photoelectrons are created. However, the heavy ionic carbon clusters are virtually standing still during our experiment ($\Delta l = 10$ μm in 100 ns due to thermal velocity and $\Delta l = 0.1$ μm in 100 ns due to the static electric field).

The ionic carbon cloud resembles a cylinder with a radius of 35 μm in the z - and y -direction and a length of 10 mm in the x -direction, with a density of $2.4(\pm 0.4) \times 10^7 \text{ cm}^{-3}$. In the ion source region, the electrons are decelerated by the electric field of 1.50 V/cm, and have their turning point at the position of the ion cloud. At that time, the field is turned off by dipping the voltage on the cathode plate from -1.50 V to -0.20 V in $1.0(\pm 0.2)$ ns. The electric field turnoff is realized by connecting an impedance matched, fast pulse generator (Stanford Research Systems, model DG 535) to the cathode plate. The density of ionic carbon clusters is kept low with respect to the density of free electrons to prevent the effect of ‘trapping’ the electrons in the attractive potential of the ion cloud. For the given volumes and densities, the electrons feel an attractive field of < 30 mV/cm at the edge of these volumes. Such a low density plasma is therefore not stable when the ion region is biased with an electric field of 200 mV/cm. The experiments were performed in a vacuum chamber with a background pressure of 5×10^{-7} Torr.

Most recombination processes are characterized by cross-sections. In our PFR scheme, it is more appropriate to give the volume in which the electron has to be at the moment of the quick turnoff to recombine with the ion. We define this volume as the interaction volume. The interaction volume is the volume of space for which an electron with an initial velocity $(0,0,v_z)$ will recombine with the ion after the electric field is ramped down to 200 mV/cm; it is not necessary to use a distribution in velocity due

to the very low effective temperature of the electron source. This interaction volume can be estimated with the following formula:

$$N(\tau) = \rho_{\text{ion}} \rho_e V_{\text{over}} \int_{-\infty}^{\infty} f(t' - \tau) V_{\text{int}}(t') dt' \quad (1)$$

where $N(\tau)$ is the number of recombinations at a certain delay (τ) of the quick turnoff, ρ_{ion} is the ion density, ρ_e is the electron density, V_{over} is the macroscopic overlap volume of the electron and ion clouds, and

$$f(t) = \sqrt{\frac{4\ln 2}{\pi\alpha^2}} \exp\left(-\frac{t^2 4\ln 2}{\alpha^2}\right)$$

is a function which describes the time profile of the electron pulses (α is the duration of the electron pulses, 9 ns). In the case of ionic carbon cluster production with 266 nm ($\text{C}_{60}^+ - \text{C}_{50}^+$), we have measured typically $15(\pm 5)$ recombination events per 5×10^4 electrons in an overlap volume of 0.01 mm^3 and an ion density of $2.4 \times 10^7 \text{ cm}^{-3}$. Using Eq. (1), this observation yields an interaction volume is $(1.3 \pm 1.2) \times 10^{-11} \text{ cm}^3$. A theoretical estimate of V_{int} is obtained by solving Newton's equations, with a force equal to: $\mathbf{F}(t) = q(\mathbf{E}(t) + \mathbf{v}(t) \times \mathbf{B}/c)$. The electric field (\mathbf{E}) is the superposition of the Coulomb potential of the ions and external field, \mathbf{v} is the velocity of the electrons and \mathbf{B} is the magnetic field. An interaction volume of $2.5 \times 10^{-11} \text{ cm}^3$ is theoretically calculated for a 9 ns electron pulse, which is more than the estimation from the experimental data, the explanation for this will be discussed below. We note that the spatial extent of such an interaction volume corresponds to Rydberg states around $n \approx 180$. The radius of the interaction volume is two orders of magnitude smaller than the average distance between neighboring ionic carbon clusters, which means perturbations from unrecombined ionic carbon clusters are negligible in this experiment.

A detailed picture of the final state distribution of the pulsed field recombined Rydberg clusters was obtained with the technique of selective field ionization (SFI) [13,20]. A Rydberg state of an atom or molecule can be ionized if an electric field is applied. Each state of an atom or a molecule has an associated field strength at which it ionizes. The

relation between the value of the static electric field at which ionization classically occurs and the principal quantum number, n , of a state is in atomic units: $F = (E/2)^2 = 1/16n^4$. When the electric field is slowly ramped in time and the field at which Rydberg molecules decay is monitored, the populated Rydberg states can be approximately deduced; changes from $F = (E/2)^2$ arise because the energy of the electron changes during the ramp and because the electron is not immediately stripped from the ion when the energy condition is satisfied. In our experiment, we use a field ramp of 1.50 V/cm in 1.8 μs , 900 ns after the fast field turnoff. This was realized by connecting a voltage ramp to the anode plate of the ion region. The field ramp pushes the field ionized electrons towards the cathode plate through which a hole was drilled covered with a grid. Directly after this plate a set of micro-sphere-plates (MSP) is situated that record the ionized electrons. In this way, we record at which times, and hence at what field strengths, electrons are being field ionized. During the 900 ns after the quick turnoff and before the SFI ramp, effects of three body recombination and radiative recombination are ruled out since the rates of these processes (1 s^{-1}) are far too low at our densities.

In Fig. 3, the Rydberg state distribution as a result of the PFR by the 1.0 ns turnoff is depicted for recombination of the carbon clusters ($\text{C}_{50} - \text{C}_{60}$),

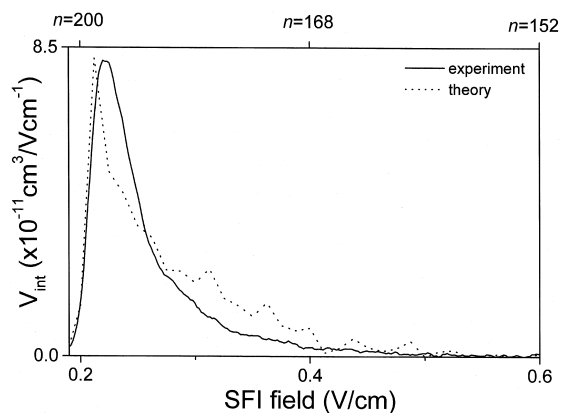


Fig. 3. Calculated state distribution (dotted line) of the recombined Rydberg clusters, compared with experimental state distribution (solid line). The experimentally determined interaction volume is varied within its uncertainty to optimize the comparison with theory.

showing that the state distribution peaks for small SFI fields. Since the 1 ns turnoff reduces the electric field to 0.2 V/cm, states with a principal quantum number beyond $n = 200$ are not stable. From Fig. 3, it is deduced that Rydberg states are produced around $n = 190$. The calculation depicted in Fig. 3 shows a direct comparison between theory and experiment, and clearly good agreement is obtained. Starting out with the state distribution obtained from solving Newton's equations ($\langle n \rangle = 180$ with $\Delta n = \sqrt{\langle n^2 \rangle - \langle n \rangle^2} = 20$) the SFI trace is calculated (using the Landau-Zener approximation [20]). To obtain this level of agreement, the polarizability of the ionic carbon clusters and autoionization of the recombined carbon clusters is implemented. The polarizability is included through a local potential $-\alpha/2r^4$ at large distances; $\alpha \sim 540$ atomic units [21,22]. Autoionization of the Rydberg states by interactions of the electron with the hot C_{60}^+ is included through a model that allows the electron energy to change: every time the recombined electron gets within 5 a.u. of the center, it gets a kick in a random direction so that the energy of the electron is just as likely to increase as to decrease. If the kick increases the energy, the electron leaves (autoionization). If the kick decreases the energy, the electron will be in a lower Rydberg state. For this deeper bound state the time to return to the C_{60}^+ decreases, so the electron will rapidly get kicked again. This is like a random walk where the time between steps decreases in one direction and the time between steps increases in the other direction. The resulting V_{int} from this calculation is $0.7 \times 10^{-11} \text{ cm}^3$, in good agreement with the experimental observation: $(1.3 \pm 1.2) \times 10^{-11} \text{ cm}^3$. From the calculation, roughly 2/3–4/5 of the originally recombined electrons are ejected before the SFI detection.

In Fig. 4, we present the result of three calculations showing the effect of the large polarizability and autoionization on the SFI signal. The polarizability of Rb^+ , ~ 9 a.u., is 60 times smaller than for C_{60} . When we include the huge polarizability of C_{60} molecules, we observe a dramatic change in the shape of the SFI signal. The total Rydberg population remains about the same as can be seen from the unchanged integrated SFI yield. The electron does not get very close (< 20 a.u.) to the ion during the recombination event; V_{int} only depends on the the

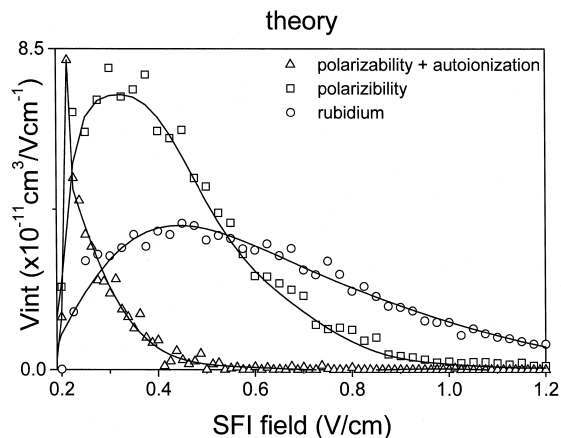


Fig. 4. Calculated SFI traces. \circ : Rb model, weak, elastic interactions with the core. This resulted in an V_{int} of $2.5 \times 10^{-10} \text{ cm}^3$. \square : The same model, but now the huge polarizability of C_{60}^+ is included in the capturing step and in the calculation of the SFI trace. This resulted in a V_{int} of $2.7 \times 10^{-10} \text{ cm}^3$. \triangle : Calculation including the polarizability of C_{60}^+ and autoionization due to the hot C_{60}^+ core, during the 900 ns waiting time. Resulting in a recombination signal loss of about 70%.

long range Coulomb interaction to a good approximation. The large polarizability of C_{60} causes that the same Rydberg states ionize at lower SFI field strength. The SFI signal does differ because the SFI signal for Rb does not follow the $F = (E/2)^2$ rule very well; the relatively small region of space where the potential is non-Coulombic allows the electron to remain attached to the Rb^+ ion for a longer time and it thus emerges at a higher field. When autoionization is included in the C_{60} -model together with the polarizability, we find that high n -states (lower SFI fields) are almost unaffected but the lower n -states (higher SFI fields) are sensitive to autoionization and we lose a part of the recombined clusters by autoionization. The autoionization rate scales as $\sim n^{-4}$ since it depends on the number of core passages per unit time ($\sim n^{-3}$) and how often the angular momentum is low per unit time ($\sim n^{-1}$). The effect of m_l -mixing is not included in our model since the electric field of 200 mV/cm reduces the collisional effect of ions inducing m_l -mixing [23,24]. M_l -mixing occurs when the electric field axis is modified sufficiently by the Coulomb field of a perturbing ion. From the ion density an average ion distance is estimated: 50 μm . The ions have a thermal velocity

of $v = \sqrt{2kT/m} = 10^2$ m/s. The amount by which the field axis is changed ($\Delta\theta$) when an ion is moving towards a Rydberg carbon cluster with a velocity ($v = 100$ m/s) perpendicular to the static electric field, after 10 angular momentum oscillation times ($\tau_{\text{osc}} = 6$ ns for $n = 200$ and $F = 0.2$ V/cm [13]) is: $\Delta\theta = 10\tau_{\text{osc}}\partial\theta/\partial t = 10^{-2}$ RAD. This amount is sufficiently low, compared to the effect of angular momentum mixing, to omit the effect of m_l -mixing in our model. However, if the Rydberg clusters are produced to be stored for an extended period of time (> 1 μ s), m_l -mixing will occur.

Besides the potential application of this new recombination technique in the creation of atomic anti-hydrogen, we propose that our scheme can be used in the formation of Rydberg carbon clusters for (IR)-spectroscopy. The way the carbon clusters are prepared leaves them with an internal energy of 750 K, and thus the clusters are excited to various hot bands. This means that laser excitation of a cluster to a Rydberg series with a very well-defined energy, needed for infrared spectroscopy experiments, is impossible. The PFR scheme leaves the recombined clusters in a Rydberg state with an electronic energy spread of 1 K ($\Delta n = 20$ at $n = 180 \rightarrow \Delta E \sim 1$ K). This resembles a narrowband laser excitation (< 1 cm^{-1}) of a carbon clusters to the Rydberg series, making it possible to prepare a well-defined Rydberg cluster.

In summary, we have observed recombination of ionic carbon clusters with free electrons with the use of fast field pulses, resulting in Rydberg carbon clusters. Efficiencies as high as 6.0×10^{-2} have been achieved and a simple improvement (matching the electron pulse duration with the capturing time) can probably raise the efficiency significantly. The recombination can be understood with arguments which do not require mechanisms relying on the magnitude of the quantum defects of non-hydrogenic atoms or molecules. This indicates that the PFR mechanism works for any atom or molecule and yields recombined clusters in a Rydberg state with an energy spread of 1 K. Although we restricted the discussion in this letter to the recombination of ionic carbon clusters and electrons, and we have presented the recombination of rubidium atoms elsewhere [10,11], the technique of PFR is in principle also

applicable for the formation of anions [25], and ion-pair states [26].

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