Production of Multiply Charged Ions by Strong uv Laser Pulses: Theoretical Evidence for Stepwise Ionization

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It is pointed out that the charge-state distribution produced by intense ultraviolet laser radiation is a Poissonian, rather than the binomial which prevails under infrared radiation, and hence that ionization occurs stepwise during the pulse. This result is shown to be consistent with experimental data as well as with recent theoretical advances.

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In the study of matter in strong external fields, the development of high-intensity lasers has opened new perspectives. Picosecond pulses have been focused on small targets of noninteracting atoms, creating electric field amplitudes of the order of one atomic unit (5.14×10^{11} V m^{-1}). Production of multiply charged ions has been observed in such fields, both with irv (infrared and visible) light[1] and with uv (ultraviolet) light.[2,3] A basic question is whether this phenomenon occurs as a consequence of direct multiphoton multielectron ionization of neutral atoms, or of stepwise ionization during the light pulse.

Geltman[4] and Rhodes[5] and co-workers[3,6] have emphasized the direct-ionization mode, but for different reasons. Whereas Geltman[4] has taken both the irv and uv data as evidence for the independent-electron model of the target atoms, Rhodes and co-workers[3,5,6] have related their uv observations to field-induced collective motion of the outer-shell electrons of the target atoms. In contrast, Lambropoulos[7] has suggested that at least the first ionization stages are produced in a stepwise fashion during the rise of the uv and also the irv pulses. This conclusion seems to agree with the statistical analysis of Crance[8] of saturation intensities, emphasizing the time and space variation of the interaction region.

Recently, we have shown[9] that the charge-state distributions of rare-gas atoms irradiated with intense irv pulses[1] are governed by a binomial law, similar to that which describes the recoil charge distributions in single-electron–capture collisions. This analysis was based on an information-theoretical derivation of the most probable distribution, given the average probability of removing one electron from an atom during the pulse, and consistent with the exclusion principle. In this Letter we show that a simple and systematic extension of the work of Ref. 9 leads to an unexpected but physically well-justified interpretation of the uv data. Our results unambiguously answer the question whether the uv charge-state distributions originate from direct or stepwise processes.

The target atoms discussed here are those for which charge-state measurements have been reported,[2,3] viz., Ar, Kr, I, Xe, and U. The large number of alternative routes leading to ionization in multiphoton absorption by these atoms suggests that the ion charge q should be treated as a random Markovian function of time. Thus, the evolution of the charge-state distribution function $P_q(t)$ during the pulse is described by the master equation

$$\begin{aligned}
\frac{dP_0(t)}{dt} &= -\mu P_0(t) = -\left(\sum_{n'=1}^{Z} W_{n'0}\right) P_0(t),\\
\frac{dP_q(t)}{dt} &= \sum_{n=0}^{q-1} W_{qn} P_n(t) \\
&\qquad - \left(\sum_{n'=q+1}^{Z} W_{n'q}\right) P_q(t), \qquad (1)\\
\frac{dP_Z(t)}{dt} &= \sum_{n=0}^{Z-1} W_{Zn} P_n(t).
\end{aligned}$$

Here, $W_{n'n}\Delta t$ is the probability for a transition from charge state n to $n'(>n)$ during a short time Δt. In practice, Z can be identified with the highest measured charge, subject in both experiments[1,3] to a detection limit of $P_Z/P_1 \cong 10^{-4}$. For many-electron atoms, perturbation theory (if applicable) leads to estimates for the generalized cross section σ_{10} which occurs in $W_{10}=\sigma_{10}F^N$, where F is the photon flux, and N the number of absorbed photons.[7] In particular, since we are interested in the prediction of charge states after

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the pulse has elapsed, these cross sections can be used to estimate $P_0(t)$ in Eq. (1) by taking $\mu \cong W_{10}$. It follows that the neutral target atoms cannot survive past the applied peak intensities ($I \gtrsim 10^{13}$ W cm^{-2}) of the irv and uv pulses,[7] except possibly in the case of iodine as indicated below. The lower limit of q is hence taken to be 1 in the following. The task is then to predict $P_q(t)$ at $t=\tau$ [denoted as $P_q(Z,\tau)$ in the following], for $1 \leqslant q \leqslant Z$, where τ is the pulse duration ($\tau = 50$ ps in the irv and 5 or 10 ps in the uv experiments).[1,3]

Charge-state distributions, whether they result from strong radiation fields or from single or multiple collisions with ions, have a common characteristic. Most likely they do not depend on any individual transitions to specific final states of the residual ions, but only on the number of ways in which a given final charge state can be realized within the constraints of quantum conditions and conservation laws.[10] One may thus use general methods of inference, such as the maximum-entropy principle, to predict the most probable distribution, once these constraints are known. If the prediction were to deviate systematically from measured distributions, this would indicate that there is after all a strong specific transition which produces a given charge state.

This was the strategy used in our prediction[9] of the binomial law for $P_q(Z,\tau)$,

$$P_q(Z,\tau) = \binom{N}{q}\exp(\lambda q)\left[\sum_{n=1}^{Z}\binom{N}{n}\exp(\lambda n)\right]^{-1}, \quad (2)$$

where $\lambda = \lambda(\tau)$ is an adjustable parameter, and $N=6$ is the number of electrons in the outer shell of the rare-gas atoms. The distribution (2) can be interpreted as the most probable charge-state distribution following multiple ionization, given the average probability $p = \langle n \rangle N^{-1}$ of removing one electron from a rare-gas atom during the pulse. According to Eq. (1), we have $P_0(\infty) = 0$ and $P_q(\infty) = W_{q0}/\mu$ for $1 \leqslant q \leqslant Z$ if all $W_{n'n} = 0$ for $n \neq 0$. Otherwise, this stationary distribution is given by $P_q(\infty) = \delta_{q,Z}$. Equation (2) therefore represents the choice $W_{n0} = \binom{N}{n}\exp(\lambda n)$ for the purely *direct* multiple multiphoton ionization process. It should be noted that the untruncated binomial distribution would imply $Z=N$ and $P_0(N,\tau) = (1-p)^N$, which is unphysical. Equation (2) was found to represent the irv data very well.[9]

Application of Eq. (2) to the uv data reveals a notable feature. While there are no systematic deviations, the least-squares fits of the data become *progressively* better as N is made larger and larger in Eq. (2); simultaneously, λ becomes smaller. Very good fits are in fact obtained if N is taken to be the total number of electrons in the target atom, which is unphysical. The significance of this result lies in the fact that we have

$$\mathscr{P}_q(Z,\tau) = \lim_{\substack{N\to\infty \\ \lambda\to-\infty}} P_q(Z,\tau) = (q!)^{-1}a^q\left[\sum_{n=1}^{Z}(n!)^{-1}a^n\right]^{-1}, \quad (3)$$

where $a = N\exp(\lambda)$ stays constant. Instead of the binomial of Eq. (2) we have a truncated Poissonian of Eq. (3). In Figs. 1 and 2 this distribution is tested

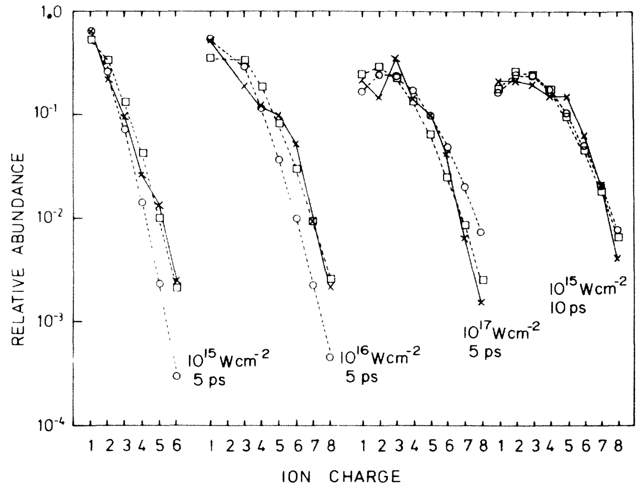

FIG. 1. Experimental data of Rhodes *et al.* (Refs. 2 and 3) for the relative abundance of charge states Xe^{q+} produced by different laser intensities and pulse durations (crosses), compared with a least-squares fit (circles) and a logarithmic least-squares fit (squares) of the theoretical distribution according to Eq. (3).

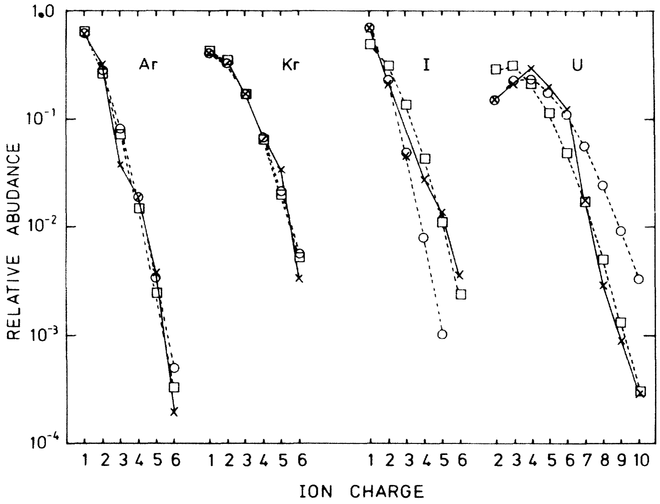

FIG. 2. Experimental data of Rhodes *et al.* (Refs. 2 and 3) for the relative abundance of charge states A^{q+} (A = Ar, Kr, I, U) produced by a laser intensity of 10^{15} W cm^{-2} and a pulse duration of 10 ps, compared with a least-squares fit (circles) and a logarithmic least-squares fit (squares) of the theoretical distribution according to Eq. (3).

against the available uv data.[3] We show not only least-squares fits to the relative abundances of charge states, but also fits to the logarithms of these abundances. The latter procedure is justified by the minimization of the relative (rather than absolute) deviations). It is apparent from Figs. 1 and 2 that the predictions from Eq. (3) agree very well with the data, certainly better than predictions based on the binomial law [Eq. (2)].[4] In Table I we list the optimized values of a for both ordinary and logarithmic least-squares fits; from these, the average ionization rates $g = a\tau^{-1}$ can be obtained.

From a general probabilistic point of view, $\mathscr{P}_q$ in Eq. (3) with $a = g\tau$ represents the probability that an atom loses q electrons at random, one by one, during the laser pulse of duration τ. It is normalized with respect to the total ion yield and represents the most probable distribution, given the mean time g^{-1} between two sequential ionization events.[11] If one, however, assumes $\mu \cong W_{10} >> g$ and a pure *step* process for $q \geqslant 1$, i.e., $W_{n'n} = g\delta_{n+1,n'}$, then Eq. (3) is an approximate solution of Eq. (1) for intermediate times. In contrast to the binomial it is not the stationary solution, which in this case would be $\mathscr{P}_q(Z,\infty) = \delta_{q,Z}$. By taking the time derivative of Eq. (3), one finds that $\dot{\mathscr{P}}_q = g(\mathscr{P}_{q-1} - \mathscr{P}_q)$ within 30%, provided $a = g\tau \geqslant 1.5$ and $\mathscr{P}_Z << 1$. According to Table I, only for Ar is a clearly smaller than 1.5, especially if one considers that I may exist in the form of negative ions at the beginning of the pulse (see footnote b of Table I). The fits are found to be extremely good even for $a < 1.5$, which indicates that the constraint on a is less significant when $\mathscr{P}_q(Z,\tau)$ is a strongly decreasing function of q.

At first glance, the distributions (2) and (3) seem to be mutually exclusive. According to the derivation of Eq. (1), however, the probabilities of the direct and step processes only exclude each other to the order of Δt^2.[12] In fact, a reexamination of the irv data in terms of the Poissonian (3) shows that this even leads to a somewhat better fit than the binomial for high-intensity ($\gtrsim 10^{14}$ W cm^{-2}) visible light. Combined with the results of Figs. 1 and 2 and Table I, this means that the ion formation is predominantly governed by the process $q \rightarrow q+1$ beyond $q \geqslant 1$ when the intensity exceeds 10^{14} to 10^{15} W cm^{-2} in the visible and ultraviolet range. This conclusion does not exclude the possibility that ions with $q \geqslant 2$ are formed from neutral atoms as a consequence of the direct multiphoton process at the beginning of the pulse, but the probability for the direct process is much smaller than for the step process via the $q = 1$ stage. This result agrees with recent experimental data on the double multiphoton ejection of the $5s^2$ electrons in Sr.[13]

TABLE I. Values of $a = g\tau$ in the Poisson distribution of Eq. (3), obtained from the statistical analysis of the uv data.

Target atom	Intensity (10^{15} W cm^{-2})	Pulse length τ (ps)	Method I[a]	Method II[a]
Xe	1	5	0.81	1.2
Xe	10	5	1.6	2.0
Xe	100	5	2.9	2.4
Xe	1	10	2.9	2.8
I[b]	1	10	0.64	1.3
Kr	1	10	1.6	1.4
Ar	1	10	0.90	0.78
U	1	10	3.1	2.1

[a] Method I is based on the minimization of the absolute deviations, whereas method II is based on minimizing relative deviations.

[b] If it is assumed that the charge starts with $q = -1$, one finds (I) $a = 0.84$ and (II) $a = 1.6$.

In the infrared region, where the number of absorbed photons is very large, the direct multiple ionization process is favored even at rather high intensities. Here this process is associated with tunneling of several electrons along the field axis, similar to transfer ionization in single-electron capture.[9]

In conclusion, we have shown by a detailed statistical analysis of measured ionic charge distributions produced in strong visible and ultraviolet picosecond laser pulses that these states are predominantly created by the *step* process. Contrary to earlier analyses, there is no indication of any specific direct multiple multiphoton ionization processes in the uv laser experiments.

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