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LETTER TO THE EDITOR

Multiphoton detachment from negative ions: new theory versus experiment

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Abstract. In this paper we compare the results of our adiabatic theory (Gribakin and Kuchiev 1997 *Phys. Rev.* A **55** 3760) with other theoretical and experimental results, mostly for the halogen negative ions. The theory is based on the Keldysh approach, and shows that the multiphoton detachment rates depend only on the asymptotic parameters A and κ of the bound-state radial wavefunction $R(r) \simeq Ar^{-1}\mathrm{e}^{-\kappa r}$. Simple analytical expressions for the differential and total n-photon detachment cross sections are obtained. They allow us to estimate the cross sections for almost any negative ion. Our approach suggests a new physical interpretation of the nontrivial oscillatory behaviour of the differential cross sections that has been observed in experiments. It also predicts oscillations in the energy dependence of the total n-photon cross sections, due to interplay among different partial waves.

In our recent work (Gribakin and Kuchiev 1997 (GK97)) a simple analytical theory of multiphoton detachment from negative ions has been developed, following the original approach of Keldysh (1964). We checked that for hydrogen our results are in agreement with accurate numerical calculations by other authors. In this paper we use our theory to calculate n-photon detachment cross sections and excess photon detachment (EPD) spectra for some negative ions that have been explored experimentally.

It has been shown in GK97 that the differential cross section of n-photon detachment of an electron from a negative ion by a linearly polarized light of frequency ω is (in atomic units)

$$\frac{\mathrm{d}\sigma_n^{(lm)}}{\mathrm{d}\Omega} = \frac{pA^2\omega(2l+1)}{4\pi^2\sqrt{2n\omega}}\frac{(l-|m|)!}{(l+|m|)!}\left|P_l^{|m|}\left(\sqrt{1+p_\perp^2/\kappa^2}\right)\right|^2\left(\frac{\pi e}{nc\omega^2}\right)^n \times\frac{\exp(p_\parallel^2/\omega)}{\sqrt{\kappa^2+p_\perp^2}}[1+(-1)^{n+l+m}\cos\Xi], \tag{1}$$

where l and m are the orbital angular momentum and its projection of the initial electron state, κ is determined by the energy of the bound state $E_0 \equiv -\kappa^2/2$, A is the asymptotic parameter of the bound-state radial wavefunction $R(r) \simeq Ar^{-1}\mathrm{e}^{-\kappa r}$, $p = \sqrt{2n\omega - \kappa^2}$ is the photoelectron momentum, $p_\parallel = p\cos\theta$ and $p_\perp = p\sin\theta$ are its components parallel and

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perpendicular to the field, $c \approx 137$ is the speed of light, $e = 2.71\ldots$, $P_l^{|m|}$ is the associated Legendre function, and

$$\Xi = (2n+1)\tan^{-1}\frac{p_\parallel}{\sqrt{\kappa^2+p_\perp^2}} + \frac{p_\parallel\sqrt{\kappa^2+p_\perp^2}}{\omega} \tag{2}$$

is the phase that determines the oscillatory behaviour of the photoelectron angular distribution. As shown in GK97, the electron detachment by the periodic external field takes place when the field is close to maximal. There are two such instants in every period, and the oscillations are due to interference between the two corresponding amplitudes. For low photoelectron momenta $p \ll \kappa$ ($n\omega \approx k^2/2$)

$$\Xi \simeq (2n+1)p_\parallel/\kappa + p_\parallel\kappa/\omega \equiv 2Rp\cos\theta,$$

where $R \approx 2n/\kappa \approx \sqrt{2n/\omega}$ is large compared with the size of the negative ion ($\sim \kappa^{-1}$). This phase indeed describes the interference between the electron waves emitted at R and $-R$ from the atom at an angle θ to the field. Note that in accord with the general symmetry properties the cross section (1) vanishes at $\theta = \pi/2$, if $n+l+m$ is odd.

After the detachment from a closed-shell negative ion the neutral atom is left in either of the two fine-structure states with the total angular momentum $j = l \pm \frac{1}{2}$, e.g. $^2\mathrm{P}_{3/2}$ and $^2\mathrm{P}_{1/2}$ for halogens. In this case the n-photon detachment cross section summed over the projections of the angular momentum is given by

$$\frac{\mathrm{d}\sigma_n^{(j)}}{\mathrm{d}\Omega} = \frac{2j+1}{2l+1}\sum_{m=-l}^{l}\frac{\mathrm{d}\sigma_n^{(lm)}}{\mathrm{d}\Omega}, \tag{3}$$

where different values of κ and binding energies $|E_0|$ should be used for $j = l \pm \frac{1}{2}$, since the two sub-levels have different detachment thresholds. The main contribution to the sum in equation (3) comes from $m = 0$, since these orbitals are extended along the direction of the field.

The sum over m can be carried out analytically†, yielding

$$\frac{\mathrm{d}\sigma_n^{(j)}}{\mathrm{d}\Omega} = \frac{pA^2\omega(2j+1)}{4\pi^2\sqrt{2n\omega}}\left(\frac{\pi e}{nc\omega^2}\right)^n \frac{\exp(p_\parallel^2/\omega)}{\sqrt{\kappa^2+p_\perp^2}}[P_l(1+2p_\perp^2/\kappa^2) + (-1)^{n+l}\cos\Xi], \tag{4}$$

where P_l is the Legendre polynomial, $P_0(x) = 1$, $P_1(x) = x$, etc.

The total n-photon detachment cross section $\sigma_n^{(j)}$ is obtained by integrating equation (4) over the emission angles of the photoelectron. The result can be presented in the following form

$$\sigma_n^{(j)} = (2j+1)\frac{pA^2}{4\pi n}\left(\frac{\pi e}{nc\omega^2}\right)^n \exp(p^2/\omega)F_{nl}(p^2/2\omega), \tag{5}$$

where F_{nl} is a dimensionless function of the electron energy in units of ω, $\varepsilon = p^2/2\omega$,

$$F_{nl}(\varepsilon) = \int_{-1}^{1}\frac{\mathrm{e}^{2\varepsilon(x^2-1)}}{\sqrt{1-\varepsilon x^2/n}}\left\{P_l\left(1+\frac{2\varepsilon(1-x^2)}{n-\varepsilon}\right)\right.$$
$$\left.+(-1)^{n+l}\cos\left[(2n+1)\tan^{-1}\left(\frac{x\sqrt{\varepsilon}}{\sqrt{n-\varepsilon x^2}}\right)+2x\sqrt{\varepsilon(n-\varepsilon x^2)}\right]\right\}\mathrm{d}x. \tag{6}$$

† Note that $P_l^{|m|}$ in equation (1) is a function of the imaginary angle ϑ, $\cos\vartheta = \sqrt{1+p_\perp^2/\kappa^2}$, so that $[P_l^{|m|}(\cos\vartheta)]^* = (-1)^m P_l^{|m|}(\cos\vartheta)$.

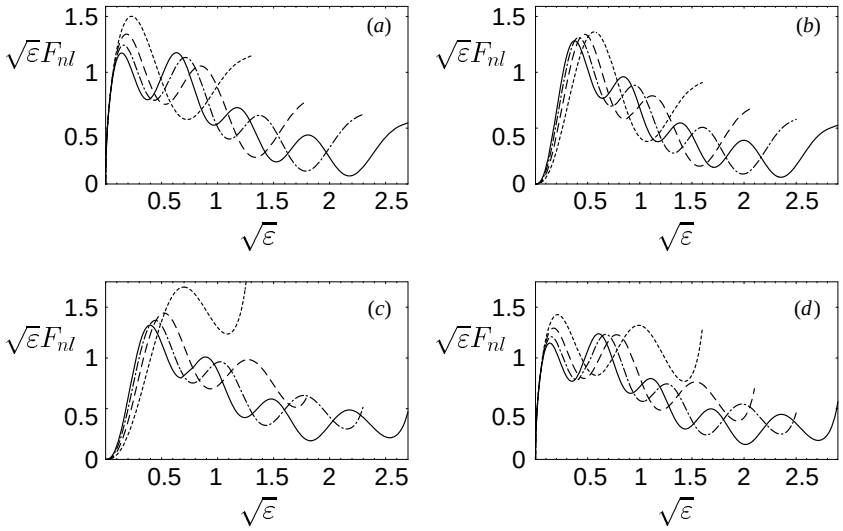

Figure 1. Dependence of $\sqrt{\varepsilon}F_{nl}(\varepsilon)$ on the scaled photoelectron momentum $\sqrt{\varepsilon} = p/\sqrt{2\omega}$ for the n-photon detachment of s ($l = 0$) and p ($l = 1$) electrons. (a) and (c): - - - -, $n = 2$; — — —, $n = 4$; — · —, $n = 6$; ——, $n = 8$; (b) and (d): - - - -, $n = 3$; — — —, $n = 5$; — · —, $n = 7$; ——, $n = 9$.

Figure 1 shows the dependence of $\sqrt{\varepsilon}F_{nl}(\varepsilon)$ on the scaled photoelectron momentum $\sqrt{\varepsilon} = p/\sqrt{2\omega}$ for $l = 0, 1$, and $n = 2$–9. The difference between the behaviour of $\sqrt{\varepsilon}F_{nl}(\varepsilon)$ at small ε in figures 1(a) and (d) and figures 1(b) and (c) illustrates different threshold behaviour of the cross section for even and odd $n + l$. For even $n + l$ only even photoelectron orbital angular momenta $l_{\rm p} = 0, 2, \ldots, n+l$ are allowed; hence, the dominant contribution to the cross section near the threshold is given by the s wave, $\sigma \propto p$. For odd $n + l$ the photoelectron is represented by the odd partial waves, $l_{\rm p} = 1, 3, \ldots, n + l$, and the p wave dominates in the near-threshold region, $\sigma \propto p^3$.

Figure 1 predicts that the n-photon detachment cross section should oscillate as a function of the photoelectron energy. The maxima observed at $p \approx (l_{\rm p} + \frac{1}{2})/R_1$ correspond to contributions of different photoelectron partial waves $l_{\rm p}$ to the total cross section, and the characteristic distance $R_1 = \frac{2}{\pi}\sqrt{2n/\omega} \sim R$ is much greater than the size of the atomic system.

Both the photoelectron angular distribution and the energy dependence of the cross section illustrate the fact that the escape of an electron from the atomic system in a low-frequency laser field takes place at large distances. Because of this property established in GK97, the multiphoton detachment rate depends only on the long-range asymptotic behaviour of the bound-state wavefunction. Of course, this behaviour is ultimately determined by electron correlations at small distances in the negative ion ground state. To apply our theory one can obtain accurate κ values from experimental binding energies, and take A from handbooks, e.g. Radtsig and Smirnov (1986). Note that possible corrections to our theory, e.g. due to re-scattering of the electron from the atomic residue, are proportional to some inverse powers of R.

Equation (5) enables us to estimate the saturation intensity $I_{\rm S}$ defined by $\sigma_n^{(j)}(I_{\rm S}/\omega)^n\tau =$

Table 1. Parameters of the negative ions used to calculate the n-photon detachment cross sections.

				Final atomic state and κ[b]			
Ion	Term	l	A[a]	j	κ	j	κ
O^-	^2P	1	0.65	0.5[c]	0.328	—	—
Cu^-	$^1S_0$	0	1.2	0.5	0.301	—	—
Ag^-	$^1S_0$	0	1.3	0.5	0.3094	—	—
Au^-	$^1S_0$	0	1.3	0.5	0.4119	—	—
F^-	$^1S_0$	1	0.7	1.5	0.4998	0.5	0.5035
Cl^-	$^1S_0$	1	1.3	1.5	0.5156	0.5	0.5233
Br^-	$^1S_0$	1	1.4	1.5	0.4973	0.5	0.5300
I^-	$^1S_0$	1	1.8	1.5	0.4742	0.5	0.5423

[a] Values from Radtsig and Smirnov (1986) for O^-, Cu^-, Ag^-, and Au^-, and from Nikitin and Smirnov (1988) for F^-, Cl^-, Br^-, and I^-.
[b] Calculated using electron affinities from Hotop and Lineberger (1985), and fine-structure intervals from Radtsig and Smirnov (1986).
[c] This value gives correct cross sections for oxygen, when the fine structure of the final ^3P state is neglected.

1, where τ is the laser-pulse duration,

$$I_S = \frac{nc\omega^3}{\pi e}\left[\frac{4\pi n \exp(-p^2/\omega)}{(2j+1)pA^2F_{nl}\tau}\right]^{1/n}. \tag{7}$$

For low photoelectron energies $p^2/2 \sim \omega$, $F_{nl} \sim 1$, the n-dependence of I_S is basically determined by the first factor with $\omega \approx |E_0|/n$,

$$I_S \propto n^{-2}. \tag{8}$$

This dependence was first noticed by Crance (1988) in numerical calculations.

In what follows we use equations (4), (5) and parameters from table 1 to calculate the cross sections for those negative ions and photon frequencies where experimental data are available.

The angular distributions in multiphoton detachment from the halogen negative ions were studied by Blondel *et al* (1991, 1992), Blondel and Delsart (1993a) and Dulieu *et al* (1995). For a linearly polarized light the angular distributions can be parametrized using n asymmetry parameters β_{2p} as $C[1 + \sum_{p=1}^{n} \beta_{2p} P_{2p}(\cos\theta)]$ (Blondel *et al* 1992). Table 2 shows the values of β_{2p} obtained in two successive experiments by Blondel *et al* (1992) and Blondel and Delsart (1993a) at $\lambda = 532$ nm, $n = 2$, for the lightest and heaviest of the halogens, together with the results of calculations. For F^- the experimental data look firmly established, and our values of β_2 and β_4 are in excellent agreement with the experiment. In contrast, the experimental values for I^- are not as reliable as those for F^- (Blondel and Delsart 1993a). Nevertheless, our theory shows much better agreement with the results of the second measurement. It would be tempting to say that the discrepancy between our theory and the experiment for I^- is due to re-scattering or many-electron correlations, which are expected to be much larger in I^- than in F^-. However, the present level of experimental accuracy does not permit us to make this conclusion.

Note that determination of β_{2p} does not require absolute normalization of the cross section. Absolute measurements of multiphoton cross sections are very difficult and the values usually contain large error bars, mostly due to the uncertainty in the intensity of the detaching light (Blondel and Delsart 1993b). The experimental error bars are typically about

Table 2. Parameters of the photoelectron angular distributions of the two-photon detachment from F^- and I^- at $\omega = 2.331$ eV.

Ion and final atomic states	Parameter	Experiment[a]		Theory[b]			
		E1	E2	AT	HF1	HF2	PS91
F^-	β_2	1.02	1.03	1.04	1.45	1.28	1.26
$(^2P_{3/2} + {}^2P_{1/2})$	β_4	−0.61	−0.59	−0.60	−0.38	−0.44	−0.57
I^-	β_2	0.2	0.46	0.79	0.89	0.19	–
$(^2P_{3/2})$	β_4	−0.42	−0.85	−0.81	−0.76	−0.97	–

[a] Experiments by Blondel *et al* (1992) (E1) and Blondel and Delsart (1993a) (E2).
[b] AT is our adiabatic-theory results, equation (4); HF1 is the calculation based on the Hartree–Fock wavefunction of the initial bound state and the plane-wave approximation for the photoelectron, and HF2 includes the first Born correction (Blondel *et al* 1992); PS91 is the calculation by Pan and Starace (1991).

a factor of two or four between the extreme possible values. Theoretically, our absolute values of the cross sections are also less reliable because of the uncertainty in the values of A (usually about 10% or more).

Figure 1(a) presents the two-photon detachment cross sections for O^-, Cu^-, Ag^- and Au^- measured by Stapelfeldt *et al* (1991a, b) at $\omega = 1.165$ eV, together with our values, and the theoretical result of Robinson and Geltman (1967) for O^-. In the latter calculation the electron wavefunctions were calculated in a model potential chosen to reproduce the electron affinity. Figure 2(b) shows the three-photon cross sections for F^-, Br^- and I^-, measured by Blondel *et al* (1989) and Kwon *et al* (1989) (F^- only) at $\omega = 1.165$ eV, and the results of our calculations and those of Crance (1988). In the latter work the Hartree–Fock (HF) wavefunctions were used to describe the initial bound state, and the plane-wave approximation applied to the photoelectron. On the whole, our theory predicts cross section values consistently higher than those obtained experimentally. On the other hand, the relative magnitudes of the cross sections for different ions, given by the theory and experiment, are quite close. There is also a reasonable agreement between the calculations for O^-, Br^- and I^-.

The large discrepancy between our value for F^- and that of Crance (1988) is, as discussed in GK97, due to incorrect behaviour of the HF bound-state wavefunction, which decreases much faster than the true one (the HF value of κ for F^- is 0.6, versus the true $\kappa = 0.5$). Among the halogen negative ions this discrepancy is the largest for F^-. Accordingly, the theoretical cross sections for Br^- and I^- are in better agreement (HF values of $\kappa = 0.528, 0.508$ respectively; compare these with the true values of $\kappa = 0.497, 0.474$ for $j = \frac{3}{2}$, see table 1). Therefore, we have to conclude that the agreement between the theoretical HF values and the experiment for F^- is probably fortuitous, caused by the significant error in the previous calculations.

Unlike other halogens, the minimal number of quanta needed for the detachment of Cl^- at the Nd:YAG laser frequency is four. In this instance the calculated value $\sigma_4 = 10.2 \times 10^{-124}$ cm^8 s^3 is also greater than the experimental $\sigma_4 = 0.97^{+0.68}_{-0.41} \times 10^{-124}$ cm^8 s^3 (Blondel and Trainham 1989), as well as that by Crance (1988), $\sigma_4 = 5.6 \times 10^{-124}$ cm^8 s^3. In order to compare the results for all four halogens at this frequency, one can calculate the saturation intensities I_S for some τ, e.g. $\tau = 2\pi/|E_0|$, as in Blondel and Trainham (1989). Using our cross sections and the data from Blondel and Trainham (1989) we complete table 3. The existing discrepancy between the theory and experiment is characterized by

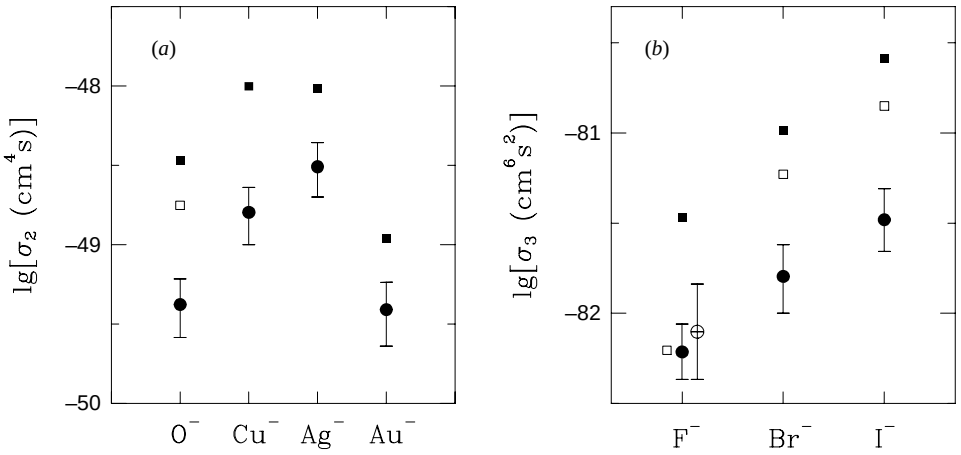

Figure 2. Comparison of the theoretical and experimental n-photon detachment cross sections at $\omega = 1.165$ eV. (a) $n = 2$, ■, our calculation; □, calculation by Robinson and Geltman (1967); ●, experiment by Stapelfeldt *et al* (1991). (b) $n = 3$, ■, our calculation; □, calculation by Crance (1988); ●, experiment by Blondel *et al* (1989); ○, experiment by Kwon *et al* (1989).

Table 3. Saturation intensities for the multiphoton detachment of the halogen negative ions by $\omega = 1.165$ eV linearly polarized light.

Ion	n	τ (fs)	I_S^{exp} (10^{13} W cm^{-2})	I_S^{theor} (10^{13} W cm^{-2})	$R = I_S^{exp}/I_S^{theor}$
F^-	3	1.22	4.4	2.50	1.76
Cl^-	4	1.14	3.2	1.79	1.79
Br^-	3	1.23	3.2	1.72	1.86
I^-	3	1.35	2.4	1.23	1.95

the ratio R, which remains almost constant, $R \approx 1.8$–1.9.

In a more recent work by Davidson *et al* (1992) the two- and three-photon detachment cross sections for Cl^- by 2 eV photons have been measured. Their value $\sigma_2 = 16^{+29}_{-8} \times 10^{-50}$ cm^4 s is in good agreement with ours, $\sigma_2 = 9.44 \times 10^{-50}$ cm^4 s, whereas the values predicted by other theories are notably smaller: $\sigma_2 = 5.5 \times 10^{-50}$ cm^4 s (Crance 1987), and $\sigma_2 = 2.5 \times 10^{-50}$ cm^4 s (Jiang and Starace 1988). Our cross section also agrees with the result of a much earlier measurement by Trainham *et al* (1987) at a smaller photon energy, $\omega = 1.874$ eV, $\sigma_2 = 1.3 \pm 0.9 \times 10^{-50}$ cm^4 s (experiment), $\sigma_2 = 2.19 \times 10^{-50}$ cm^4 s (theory). The result of Robinson and Geltman (1967) is $\sigma_2 = 1.68 \times 10^{-50}$ cm^4 s. The three-photon cross section from Davidson *et al* (1992), $\sigma_3 = 1.84^{+6.3}_{-1.2} \times 10^{-82}$ cm^6 s^2, is also close to our value, $\sigma_3 = 10.35 \times 10^{-82}$ cm^6 s^2.

In the earlier experimental work devoted to the EPD Davidson *et al* (1991) measured the ratio between the five-photon and four-photon detachment signals in Cl^- at $\omega = 1.165$ eV. If the energy of the laser pulse is below the saturation limit, then for a pulse with a Gaussian spatial and temporal profile this ratio is given by $(\frac{4}{5})^{3/2}(\sigma_5/\sigma_4)I/\omega$, where I is the peak intensity in the pulse. Indeed, the experimental points in figure 3 of Davidson *et al* (1991) display an approximately linear dependence on the intensity. The corresponding slope can be estimated as 0.0415, if the intensity is in units of 10^{12} W cm^{-2}, which is quite close to our theoretical estimate of 0.0466. When the cross sections of Crance (1988) are used, a

value of 0.053 is obtained. The difference between our theory and that based on the HF description of the negative ion is not as large for the ratio of the cross sections, as it is for the cross sections themselves. At the peak intensity of 2.4×10^{12} W cm^{-2}, well into the saturation regime, we calculated the ratio of four- and six-photon detachments to be 120, with the experimental value between 70 and 200.

In summary, our theory of multiphoton detachment in a linearly polarized laser field shows that for a given ω and n the cross section depends only on the basic properties of the ionic bound-state wavefunction: the electron orbital angular momentum l and the two constants A and κ which characterize the behaviour of the wavefunction at large distances. The correct asymptotic behaviour of the bound-state wavefunction at large distances is crucial for obtaining accurate absolute values of the n-photon cross sections. Our theory explains the oscillatory photoelectron angular distribution and predicts oscillations in the energy dependence of the total cross section.

We have applied the theory to the negative ions and processes studied experimentally, and found that our results are in reasonable, and in some cases, very good agreement with the experimental data. The difference between the theoretical and experimental absolute values of the n-photon cross section is quite large for some ions, whereas the relative cross section magnitudes for different ions look much more consistent. When more sophisticated calculations are performed our formulae can be used as a benchmark, to demonstrate the role of various possible corrections, which are expected to be small for the processes considered. Of course, there are other processes where many-electron correlations play a decisive role, e.g. multiple photodetachment or ionization (Kuchiev 1987, 1995, 1996).

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