THEORY OF MULTIPHOTON IONIZATION*

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The production of sparks in air, though not detailed in the literature, has become a part of the repertoire of laser parlor tricks along with razor blade piercing and balloon bursting. Recently Meyerand and Haught[1] have reported measurements of the ionization of Ar and He at the focus of a Q-switched ruby laser. Several attempts have been made to explain the phenomenon qualitatively on the basis of classical microwave breakdown theory.[1,2] Wright[3] has proposed a semiquantitative, semiquantum theory containing, in addition, the idea of inverse bremsstrahlung. Further, Zernik[4] has written a careful quantum treatment of the two-photon ionization of the metastable 2s state of H.

The present Letter presents a theory of the N-photon photoionization of "transparent" gases, explicitly treating systems with N as high as 14. Specifically, we calculate the apparent thresholds for optical ionization of the noble gases, Xe, Kr, Ar, Ne, and He. These processes require the simultaneous absorption of 7, 8, 9, 13, and 14 photons, respectively. The predictions are in reasonable agreement with experimental results for Ar and He insofar as information about peak power levels may be extracted from reported measurements. Preliminary computations set these thresholds at peak fluxes of 7.0×10^{31} and 4.4×10^{32} photons $\mathrm{cm}^{-2}\,\mathrm{sec}^{-1}$ for Ar and He, respectively. For $N=2$, our technique agrees reasonably well with Zernik's work.[4]

Using a semiclassical formulation of the interaction between an atom and a radiation field of frequency ω,[5] and retaining only the lowest order nonvanishing $\vec{p}\cdot\vec{A}$ term, the transition amplitude $a_f^{(N)}$ to a final state f from initial state g is given in Nth-order perturbation theory by

$$a_f^{(N)}=\hbar^{-N}\frac{\{\exp[i(\omega_{fg}-N\omega)t]-1\}}{(\omega_{fg}-N\omega)}\sum_{m_{N-1}}\sum_{m_{N-2}}\cdots\sum_{m_1}\langle f|H_I|m_{N-1}\rangle\frac{\langle m_{N-1}|H_I|m_{N-2}\rangle}{[\omega_{m_{N-1}g}-(N-1)\omega]}$$

$$\times\cdots\times\frac{\langle m_2|H_I|m_1\rangle}{[\omega_{m_2g}-2\omega]}\frac{\langle m_1|H_I|g\rangle}{[\omega_{m_1g}-\omega]}. \tag{1}$$

Here the various m_i run over all possible intermediate states of the atom whose energies, measured with respect to the ground state, are $\hbar\omega_{m_ig}$. H_I is given by

$$H_I=-\frac{e}{mc}A_0e^{i\vec{\eta}\cdot\vec{r}}\vec{\epsilon}\cdot\vec{p}, \tag{2}$$

where $\vec{\eta}$ is the wave vector of the radiation, $\vec{\epsilon}$ the unit polarization vector, and $\vec{p}$ the electronic momentum operator.

The relevant portions of the electronic spectra of Ar and He are shown in Figs. 1 and 2, respectively; energy scales in units of 1.78-eV ruby photons, measured from the ground states, are also included. It will be seen that, for example, the 5p $^3S_1$ states of Ar are very nearly (within ~0.2 eV) eight photon energies above the ground state, while the other energy levels are relatively well separated from integral multiples of $\hbar\omega$. An energy of $9\hbar\omega$ carries one across the threshold of the ionization continuum.

Taking the spectral structure as our cue, we divide the energy denominators occuring in Eq. (1) into two classes. The first contains the "near resonances" in νth ($\nu<N$) order; these denominators are small and make the dominant contribution to the transition amplitude. The second class contains the (weak) remainder. We now assume, in complete analogy with the usual Eisenschitz-London theory of dispersion forces,[6] that the intermediate-state energies $\hbar\omega_{m_ig}$ which fall into the latter class may be replaced by some appropriate average $\hbar\Omega$, independent of state. For simpli-

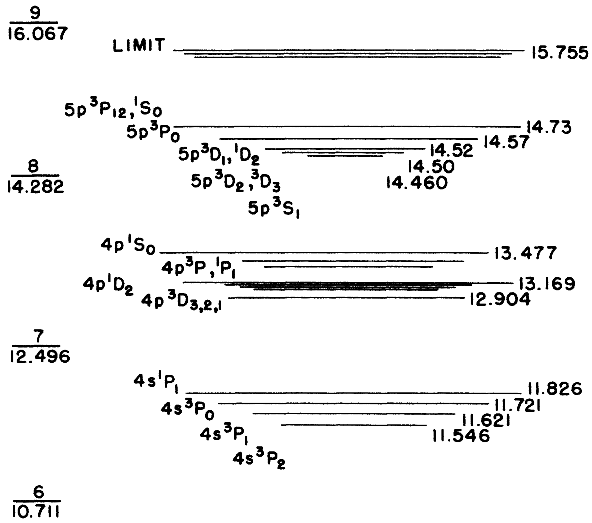

FIG. 1. Relevant portions of the spectrum of Ar. All energies are in eV relative to the ground state. *LS* term designations are given for simplicity, even though *jl* coupling is more appropriate to the atom [G. Racah, Phys. Rev. 62, 438 (1942)]. Energies are also marked in integral numbers of ruby-laser quanta. Data taken from C. E. Moore, Atomic Energy Levels, Nat. Bur. Std. (U.S.) Circ. No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

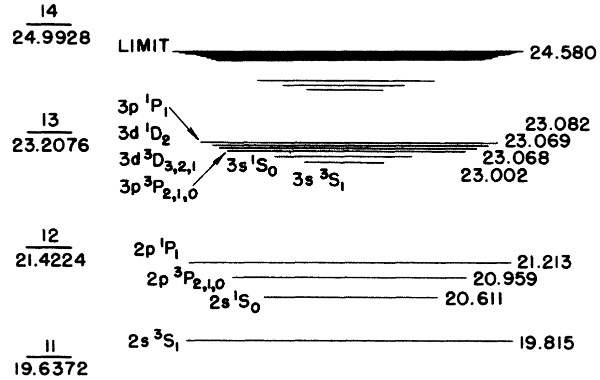

FIG. 2. Relevant portions of the spectrum of He.

city, we first discuss the case of a near resonance occurring in only one order, ν (cf. Ar). In this instance our assumption (really a definition of "average") allows the sums in (1) to be reduced, via matrix multiplication, to the form

$$\prod_{\substack{\lambda=1\\ \lambda\neq\nu}}^{N-1}(\Omega-\lambda\omega)^{-1}\sum_m\frac{\langle f|H_I^{N-\nu}|m\rangle\langle m|H_I^{\nu}|g\rangle}{(\omega_{mg}-\nu\omega)}. \quad (3)$$

In the simplest approximation we assume that only one nearly resonant state contributes to (3), and rewrite (1) as

$$a_f^{(N)}=\hbar^{-N}\frac{\{\exp[i(\omega_{fg}-N\omega)t]-1\}}{(\omega_{fg}-N\omega)}$$

$$\times\frac{\langle f|H_I^{N}|g\rangle}{(\omega_{\nu g}-\nu\omega)}\prod_{\substack{\lambda=1\\ \lambda\neq\nu}}^{N-1}(\Omega-\lambda\omega)^{-1}, \quad (3a)$$

where $\omega_{\nu g}$ is the frequency of the state in νth order near resonance (e.g., 14.30 eV for $\nu=8$, $N=9$ in Ar).

If, for simplicity, the final, ionized state is approximated by a plane wave of wave vector k, the total cross section for Nth-order ionization becomes

$$\sigma^{(N)}=\frac{(2m/\hbar)^{3/2}(4\pi r_0C)^N(N-\omega_0/\omega)^{N+1/2}|S(\vec{q},g)|^2F^{N-1}}{2\pi(2N+1)\omega^{-1/2}|(\omega_{\nu g}-\nu\omega)\prod_{\substack{\lambda=1\\ \lambda\neq\nu}}^{N-1}(\Omega-\lambda\omega)|^2}. \quad (4)$$

In (4) r_0 is the classical election radius, ω_0 the first ionization potential, F the flux in photons $\mathrm{cm}^{-2}\,\mathrm{sec}^{-1}$, given in terms of the vector potential by $\omega|A_0|^2/2\pi\hbar C$, and

$$S(\vec{q},g)=\int e^{i\vec{q}\cdot\vec{r}}\psi_g d\tau, \quad (4a)$$

where $\vec{q}=N\vec{\eta}-\vec{k}$, and ψ_g is the ground-state wave function of the "jumping" electron. Because of the high-order dependence on photon flux, practically any reasonable estimate of the matrix element is adequate for predicting the breakdown flux. (For example, an error of four orders of magnitude in the matrix element for Ar will still give a breakdown prediction within a factor of five of the correct value—well within the experimental uncertainty in the flux.)

In the event that near resonances occur in more than one order, the (small) denominators arising from the various orders appear as products in expressions like (3) and (4). For several, perhaps degenerate, near resonances of the same order, one obtains a sum of terms as in (3). More precise evaluations of (3) have been carried out; there seems to be little effect on predictions. A fuller exposition will be presented in a future publication. For now, the simple, approximate formalism suffices to present and clarify significant results.

We present numerical results in four forms: the cross section, the "threshold" for breakdown, defined as the flux required to produce 10^{13} electrons in the focal region within the (~10^{-8}-sec) duration of the pulse (the criterion of reference 1), and "underestimated" values for the cross section and the corresponding thresholds obtained by completely neglecting the near resonances and replacing $\omega_{\nu g}$ by Ω. These last fluxes, incidentally, are very near those which the theory would predict as necessary to ionize every atom in the focus. Once more, the high order of flux appearing makes the predicted threshold relatively insensitive to the somewhat arbitrary choice of criterion.

Predictions according to (4) for a density of 10^{20} atoms cm^{-3} are listed in Table I, together with the order of the transition and the ionization potential for each atom. In all cases $|S|^2$ has been taken as $64\pi a^3$, the form given by a hydrogenic $1s$ function for ψ_g, where a is the atomic radius[7]; Ω has everywhere been set equal to ω_0 for the atom. The orders and "strengths" of the near resonances are also tabulated. From Fig. 1 we see that Ar has a single near resonance of strength 0.18 eV in eighth order, while ionization occurs in ninth. The fourteenth-order ionization of He takes place through the agency of energy denominators of 0.81 and 0.12 eV in twelfth and thirteenth order, respectively, as shown in Fig. 2.

Meyerand and Haught[1] quote 10^{29}-10^{30} photons $\text{cm}^{-2}\,\text{sec}^{-1}$ as average fluxes in their pulses required to cause discharges in He and Ar. However, it seems clear that they are not operating their laser in a single axial mode but rather in several. In this event, peak fluxes one or two orders of magnitude larger than the average may be expected.[8] These uncertainties are further compounded by the difficulty of estimating the true beam diameter by burning holes in a foil. In view of these experimental difficulties, the predicted values for Ar and He based on conservative criteria must be regarded as being in reasonable agree-

Table I. Summary of calculated thresholds for optically ionizing rare gases. The word "underestimate" refers to transition rates (cross sections) and hence corresponds to an overestimate of thresholds. The j-l state designations (where appropriate) are included in parentheses. For further explanation see text. The numbers in parentheses indicate powers of 10 and F refers to the photon flux measured in units of photons $\text{cm}^{-2}\,\text{sec}^{-1}$.

Gas	$\hbar\omega_0$	N	ν	State	Strength ($\hbar\omega_{\nu g}-\nu\hbar\omega$)	Underestimates: Cross section (cm^2)	Underestimates: Threshold (10^{30} photons $\text{cm}^{-2}\,\text{sec}^{-1}$)	Present approximation: Cross section (cm^2)	Present approximation: Threshold (10^{30} photons $\text{cm}^{-2}\,\text{sec}^{-1}$)	Expt.[a] Threshold (10^{30} photons $\text{cm}^{-2}\,\text{sec}^{-1}$)
Xe	12.127	7	6	$7p\,^3S_1$ ($7p[0\frac{1}{2}]_1$)	0.188	$6.15(-214)F^6$	18.9	$8.76(-211)F^6$	6.62	···
			5	$6s\,^3P_0$ ($6s[0\frac{1}{2}]_0$)	0.219					
Kr	13.966	8	7	$6s\,^3P_1$ ($6s[1\frac{1}{2}]_1$)	0.114	$6.99(-249)F^7$	54.4	$3.52(-245)F^7$	18.9	···
			6	$5p\,^3S_1$ ($5p[0\frac{1}{2}]_1$)	0.59					
Ar	15.755	9	8	$5p\,^3S_1$ ($5p[\frac{1}{2}]_1$)	0.18	$2.15(-283)F^8$	100	$1.37(-281)F^8$	69.7	0.1-0.2
Ne	21.559	13	12	$11p\,^1D_2, ^3D_1$ ($11p[1\frac{1}{2}]_{2,1}$)	0.007	$9.33(-409)F^{12}$	67.0	$4.25(-406)F^{12}$	42.0	···
He	24.580	14	13	$3p\,^1P_1$	0.116	$3.28(-455)F^{13}$	720	$5.41(-452)F^{13}$	439	0.3-0.5
			12	$2s\,^1S_0$	0.811					

[a]See reference 1.

Table II. Comparison of the predictions of the present theory with that of Zernik for the two-photon ionization of metastable 2s hydrogen. Again, "underestimate" refers to cross section and hence gives too large a flux.

	σ/F (photon^{-1} cm^4 sec)	Threshold flux (photons cm^{-2} sec^{-1})
Underestimate	5.92×10^{-49}	9.47×10^{26}
Present approximation	1.43×10^{-46}	6.09×10^{25}
Zernik[a]	1.53×10^{-47}	1.86×10^{26}

[a]See reference 5.

ment with the observations. It is significant to note that the theory gives good agreement for the relative thresholds for Ar and He.

The apparent "threshold" character of the ionization process, as previously noted, arises from the very high power of the flux which enters. For example, in a ninth-order process, a relative flux change of 33% changes the cross section by a full order of magnitude. Any quenching processes in the gas[9] will tend to make the apparent onset even sharper. The predicted thresholds are quite insensitive to the choice (within reason) of the average energy parameter $\hbar\Omega$.

In Table II we compare the present theory with Zernik's for the two-photon ionization of metastable 2s hydrogen. In a process of such low order we expect greater sensitivity to the particular values of matrix elements and energy denominators and to the approximations used in their computation. The value marked "present approximation" is based on the use of (3a) with a plane-wave final state and the 3p near resonance. The resulting cross section is an overestimate, as expected in low order. The "underestimate" consists of neglecting the near resonances altogether by replacing ω_{mg} with Ω in (3).

High-order atomic quantum effects alone will surely not explain the details of the entire optical-discharge process. After the onset of absorption a very high-temperature plasma is produced, and complicated effects can be expected to ensue. Nonetheless, it is highly likely that multiphoton ionization provides at least the trigger for the breakdown. A crucial test of the proposed mechanism would seem to be provided by the measurement of the breakdown of all the rare gases. In particular, Ne, although it ionizes in thirteenth order, is expected to break down more easily than Ar because of some very strongly coupled twelfth-order states (see Table I). Further details and results will be presented in a forthcoming communication.

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[1]R. G. Meyerand, Jr., and A. F. Haught, Phys. Rev. Letters 11, 401 (1963); 13, 7 (1964).

[2]R. W. Minck, J. Appl. Phys. 35, 252 (1964).

[3]J. K. Wright, Proc. Phys. Soc. (London) 84, 41 (1964).

[4]W. Zernik, Phys. Rev. 135, A51 (1964).

[5]The validity of the procedure is discussed in reference 4 and references cited therein.

[6]See, for example, the review by H. Margenau, Rev. Mod. Phys. 11, 1 (1939).

[7]Taken from tables in Handbook of Chemistry and Physics (Chemical Rubber Publishing Company, Cleveland, Ohio, 1950), 32nd ed.

[8]M. M. Hercher, private communication.

[9]See, for example, W. Zernik, Phys. Rev. 132, 320 (1963); 133, A117 (1964) for discussions of some competing processes in H.