PHYSICAL REVIEW
LETTERS

VOLUME 31 | 6 AUGUST 1973 | NUMBER 6

Generation of Vacuum-Ultraviolet and Soft—X-Ray Radiation Using High-Order Nonlinear Optical Polarizabilities*

S. E. Harris
Microwave Laboratory, Stanford University, Stanford, California 94305
(Received 30 May 1973)

The harmonic or sum-frequency power generated in the last coherence length of a low-density atomic species is calculated subject to the condition that the applied electric field be bounded by the multiphoton absorption or ionization limit. It is shown that higher-order polarizations may equal or exceed lower-order polarizations. Calculations are given for generation at 1773 and 1064 Å in Xe, and at 236, 169, and 177 Å in Li^+.

In recent years, picosecond-time-scale laser systems have evolved to the point where it is readily possible to produce focused optical pulses with power densities which are greater than the multiphoton ionization threshold of single atoms, and which at the same time have energy densities low enough that inverse bremsstrahlung (avalanche) ionization of the species does not occur.[1] By using the third-order nonlinear polarizability of low-pressure xenon, and operating at peak power densities which approach the multiphoton ionization limit ($P/A \cong 5\times 10^{12}$ W/cm^2), picosecond laser pulses at 3547 Å have recently been used to produce third-harmonic radiation at a conversion efficiency of 3%.[2]

In this Letter, I consider the relative magnitude of the higher-order nonlinear optical polarizabilities; i.e., $\mathcal{P}^{(3)}\sim E^3$, $\mathcal{P}^{(5)}\sim E^5$, $\mathcal{P}^{(7)}\sim E^7$, etc.; where the applied electric field strength, E, is bounded by the condition that it not exceed the multiphoton absorption or ionization limit of the atom. It is shown, for many practical systems where the electronic transition frequencies to ground are greater than the frequency of the applied laser fields, that at incident power densities which approach the multiphoton ionization limit, the higher-order polarizations may equal or exceed lower-order polarizations. There is also often a basic invariance, where the harmonic or sum-frequency power generated in the last coherence length of an atomic species is independent of the position and oscillator strengths of the intermediate levels, and of the order of the nonlinear polarizability involved. As a first experimental test of these ideas, Kung *et al.* have recently demonstrated the fifth-harmonic process 5320 Å → 1064 Å in low-pressure xenon.[3]

We consider an atomic system with certain transition frequencies to ground denoted by ω_{01}, $\omega_{02}, \ldots, \omega_{0n}$. We assume that optical radiation at frequencies $\omega_1, \omega_2, \ldots, \omega_n$ is applied to the system (for nth-harmonic generation $\omega_1=\omega_2=\cdots=\omega_n$). We assume that a single path through the atomic levels dominates the nonlinear optical susceptibility. For a gas with N atoms/cm^3, the dipole moment at the sum frequency $\omega_s=\omega_1+\omega_2+\cdots\omega_n$ is approximately given by[4]

$$\mathcal{P}^n(\omega_s)=N\frac{\mu_{01}\mu_{12}\cdots\mu_{(n-1)n}\mu_{n0}E(\omega_1)E(\omega_2)\cdots E(\omega_n)}{\hbar^n(\omega_1-\omega_{01})(\omega_1+\omega_2-\omega_{02})\cdots(\omega_s-\omega_{0n})}, \tag{1}$$

where μ_{ij} are the dipole matrix elements connecting the various levels (0 denotes ground, and is the

only level which is populated). We calculate the power density $P/A(\omega_s)$ which is generated in one coherence length at the sum frequency. (The coherence length is $L_c \equiv |\pi/\Delta k|$, where Δk is the difference in the propagation vectors of the driving polarization and the free electromagnetic wave at ω_s.) Experimentally, this is the power density which will be generated when a Gaussian laser beam is focused to the center of a negatively dispersive media with a confocal parameter equal to L_c.[5,6] We assume that the sum frequency ω_s is sufficiently close to ω_{0n} that this transition, by itself, approximately determines L_c; then

$$L_c = 2\pi\hbar(\omega_s - \omega_{0n})/N\eta\omega_s\mu_{0n}^2, \tag{2}$$

where $\eta=(\mu/e_0)^{1/2}$. From Maxwell's equations, the power density generated in one coherence length of atoms is $P/A(\omega_s)=(1/2\pi^2)\eta\omega_s^2[\mathcal{P}(\omega_s)]^2L_c^2$. Define $\gamma_{ij}=(\mu_{ij}E_j/\hbar\Delta\omega_j)^2$, where $\Delta\omega_j=\omega_{0j}-\omega_1-\omega_2-\cdots-\omega_j$. Using Eqs. (1) and (2), the conversion efficiency from the highest applied frequency ω_n to the sum frequency ω_s is given by

$$\mathcal{E}=\frac{P/A(\omega_s)}{P/A(\omega_n)}=4\gamma_{01}\gamma_{12}\cdots\gamma_{n-2,n-1}\frac{\mu_{n-1,n}^2}{\mu_{0n}^2}. \tag{3}$$

The maximum conversion efficiency to ω_s is determined by the maximum allowed value of $E(\omega_1)$, $E(\omega_2),\ldots,E(\omega_n)$. These are assumed to be limited by the nth-order absorption probability $W^{(n)}$ which, again subject to the assumption of a single dominant path, is given by[7,8]

$$W^{(n)}=\hbar^{-2}\gamma_{01}\gamma_{12}\cdots\gamma_{n-2,n-1}\mu_{n-1,n}\rho_nE^2(\omega_n), \tag{4}$$

where ρ_n is the density of states of the upper transition. Note that the single-photon cross section for absorption of ω_s by the transition ω_{0n} is given by $\sigma_{0n}(\omega_s)=\eta\omega_s\mu_{0n}^2\rho_n/2\hbar$. Using Eq. (4), Eq. (3) may be written

$$\mathcal{E}=\frac{\hbar\omega_s}{\sigma_{0n}(\omega_s)}\frac{W^{(n)}}{[P(\omega_n)/A]}=\frac{\hbar\omega_s}{2\sigma_{0n}(\omega_s)}\frac{1}{J(\omega_n)/A}, \tag{5}$$

where $J(\omega_n)/A$ is the incident energy density at the highest applied frequency ω_n. The second equality in Eq. (5) follows by multiplying numerator and denominator by the length of the laser pulse, Δt_p, and allowing the applied fields to increase until $W^{(n)}\Delta t_p=\frac{1}{2}$, i.e., 50% of the atoms are excited to the upper level. (It is assumed that Δt_p is shorter than the decay time of the upper level.) The quantity $\hbar\omega_s/2\sigma_{0n}(\omega_s)$ is often termed the saturation energy density, and is that density which if incident from the outside would approximately saturate the transition.

Note that this conversion efficiency is independent of the order of the nonlinear polarizability, and also of the oscillator strengths and positions of the intermediate levels. If intermediate levels have smaller oscillator strengths or resonant denominators, the incident applied fields are allowed to increase to yield the same conversion efficiency.

The foregoing has assumed that the generated frequency ω_s is sufficiently close to some upper level ω_{0n}, and that this level both determines the coherence length and most severely limits the allowable incident power density. More generally, the maximum allowable power density will be determined by multiphoton absorption to some other discrete level, or, most often, by multiphoton ionization to the continuum. Equation (3) still applies, but the maximum allowable E fields are now shown to be determined by the condition that

$$\gamma_{01}\gamma_{12}\cdots\gamma_{q-2,q-1}=\frac{1}{8}\frac{\hbar\omega_q}{\sigma_{q-1,q}}\frac{1}{J/A(\omega_q)}, \tag{6}$$

where q denotes that level or point in the continuum which most severly limits the allowable fields. The quantity $\gamma_{01}\gamma_{12}\cdots\gamma_{n-2,n-1}$ is then substituted into Eq. (3) to determine the conversion efficiency. [If $q=n$, then Eqs. (6) and (3) combine to give Eq. (5).]

Before applying the foregoing, two qualifications are in order. First, at the level of applied electric field strengths, Stark shifts may be significant. In principle, these can be included in the frequency denominators.[9] In practice, allowing that the electric field is a free variable, the predicted conversion efficiencies are not very sensitive to the exact position of the upper atomic levels. There are also certain questions with regard to the applicability of the perturbation theory at these high field strengths. These same questions apply to multiphoton ionization theories,[7-9] which experimentally have proven to be reasonably accurate.

As a first example, consider the third-harmonic process 3547 Å $\rightarrow$1182 Å in xenon. To evaluate Eq. (6), I choose the four-photon path $5p^6[^1S]0$-$6s[1\frac{1}{2}]1$-$6p[0\frac{1}{2}]1$-$7s[1\frac{1}{2}]2$-continuum[8,10] as that which will most severely bound the allowable incident power density. I assume unity oscillator strength for all transitions and estimate $\sigma_{7s\text{-continuum}}$ at 3×10^{-19} cm^2.[8] Then assuming an incident 30-psec pulse at 3547 Å yields $(P/A)_{\max}=1.32\times10^{12}$ W/cm^2. At this density, Eq. (3) predicts a conversion efficiency of 0.34%. Experimentally, us-

TABLE I. Conversion efficiency and limiting power density for some higher-order nonlinear processes.

Process	Species and path	Limiting P/A (W/cm^2)	Conversion efficiency (%)
3×5320 Å $\rightarrow$ 1773 Å	Xe[a], $5p$-$6s$-$5p$-$6s$-$6p$-$8d$-c	1.94×10^{12}	0.084
5×5320 Å $\rightarrow$ 1064 Å	As above	As above	0.051
5×1182 Å $\rightarrow$ 236 Å	Li^{+}[b], $1s$-$2p$-$1s$-$2p$-$3s$-$2p$-$3s$-$4p$-c	1.68×10^{15}	0.002
7×1182 Å $\rightarrow$ 169 Å	As above	As above	0.004
15×2660 Å $\rightarrow$ 177 Å	Li^{+}[c], $(1s$-$2p)^7$-$(2p$-$3s)^7$-$3p$-$4d$-c	3.47×10^{15}	4×10^{-7}

[a] $5p=5p^6[^1S]0$; $6s=6s[1\frac{1}{2}]^0 1$; $6p=6p[2\frac{1}{2}]2$; $8d=8d[2\frac{1}{2}]^0 3$; c = continuum.
[b] $1s=1s^2[^1S]0$; $2p=2p[^1P^0]1$; $3s=3s[^1S]0$; $4p=4p[^1P^0]1$; c = continuum.
[c] $3p=3p[^1P^0]1$, others as in b.

ing tight focusing to the center of a xenon cell at a pressure of 3 Torr, a conversion efficiency of 0.9% has been measured.[2]

A number of other examples of the theory are summarized in Table I. The first two are concerned with generation of vacuum ultraviolet radiation in Xe. Assuming an incident laser pulse with a peak power of 10^8 W, then to exceed the multiphoton ionization limit we must focus to an area less than about 5×10^{-5} cm^2, and thus (at 5320 Å) to a confocal parameter less than 3.7 cm. For focusing to the center of a negatively dispersive media we set the coherence length L_c equal to the confocal parameter of the focus.[5,6] For Xe in this region of the spectrum this will require an atom density between 10^{15} and 10^{16} atoms/cm^3, and thus Xe pressures in the range of 0.1 Torr. At this pressure, and for a pulse length of 30 psec, avalanche breakdown would require a power density of about 5×10^{15} W/cm^2 [11]; the assumption of multiphoton breakdown is thus well satisfied.

In recent weeks the processes 3×5320 Å $\rightarrow$ 1773 Å and 5×5320 Å 1064 Å have been demonstrated experimentally. Conversion efficiencies are comparable and measurements will be reported subsequently.[3]

The final three examples in Table I are 5th-, 7th-, and 15th-order processes in singly ionized Li to generate radiation at 236 Å, 169 Å, and 177 Å. Ionization will be accomplished by the incident laser pulse. At ion densities of $\sim 10^{18}$ ions/cm^3, recombination times are several nanoseconds,[12] and each atom need be ionized only once during the incident laser pulse. Because of the tight focus, this will require only about 10^{-6} of the incident pulse energy.

Even at its lower efficiency, the process 15×2660 Å $\rightarrow$ 177.3 Å may be an attractive early source of coherent soft-x-ray radiation. It makes use of a fortuitious coincidence with the $1s^2[^1S]0$-$3p[1P^0]1$ transition of Li^+ at 178.015 Å [10] (2160 cm^{-1} below the generated frequency). As a result of longer coherence lengths in this region of the spectrum, it is almost essential that coincidences of this type be utilized. Assuming an incident peak power of 10^{10} W, to attain the limiting power density, the laser must be focused to a confocal parameter = 0.43 cm. For L_c = confocal parameter, at an oscillator strength of 0.07 (equal to that of the comparable $1s$-$3p$ transition in He), this requires an ion density of 1.5×10^{18} ions/cm^3. At this high density the condition on inverse bremsstrahlung ionization[11] is close to being violated.

By using sum-frequency processes, one photon of a tunable dye laser might be utilized to allow close frequency coincidences and thus to reduce the required ion or atom density. Sum-frequency processes might also be used to inject high-power, lower-frequency radiation and thus to reduce the required power density at the highest applied frequency. Phase-matching techniques[2,6] may also be used to increase the conversion efficiencies of Table I.

The author gratefully acknowledges helpful and interesting discussions with H. Bebb, D. M. Bloom, G. C. Bjorklund, A. Gold, A. H. Kung, A. E. Siegman, E. A. Stappaerts, and J. F. Young.

*Work supported by the U. S. Office of Naval Research, the U. S. Air Force Cambridge Research Laboratories, and the U. S. Army Research Office.

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Accommodation Coefficient of Unsaturated He I Films*

T. G. Wang
Jet Propulsion Laboratory, Pasadena, California 91103
(Received 6 June 1973)

This thickness dependence of the accommodation coefficient γ of unsaturated He I films has been determined by measuring the time constant of a magnetically levitated, slowing, rotating superconducting sphere situated in helium vapor and covered with an unsaturated helium film. The deviation of γ from unity and the linear temperature dependence of the experimental values are in direct contrast to the saturated condition. The abrupt drop of γ at the film thickness of two atomic layers for all the temperatures that we have measured has been interpreted as a direct evidence of solid layers (or the solidlike layers) of helium film.

A new method of measuring the accommodation coefficient γ of liquid helium film, defined as the fraction of incident gas molecules that stick on the surface, has been reported recently.[1] The results confirmed that γ for saturated He I film is not far from unity and has no temperature dependence. The purpose of this Letter is to report that the behavior of the accommodation coefficient of unsaturated He I films deviates significantly from the saturated condition.

The accommodation coefficient of unsaturated He I film was obtained by measuring the decay time constant α of a rotating ultrapure superconducting sphere 1 in. in diameter with a sphericity of 5 μin. A liquid helium film, in equilibrium with its own vapor and whose thickness ranged from 100 to 1.5 atomic layers, covered the rotating sphere.

The unsaturated He film was formed by adsorption on the sphere surface in equilibrium with its own vapor at a pressure below the saturated vapor pressure. Assuming the unsaturated He vapor obeys the ideal gas law, the chemical potential difference $\Delta\mu$ between the film and the bulk liquid at the same temperature is given by

$$\Delta\mu = \Gamma/d^3 = (RT/M)\ln(P_0/P). \quad (1)$$

The middle term is the Van der Waals potential at the surface of a film of thickness d, where Γ is a constant,[2] R is the Boltzmann's gas constant, M is the molecular weight of He, P_0 is saturated vapor pressure, and P is the pressure of the vapor in equilibrium with the film.

The general experimental procedures are similar to those described in detail in Ref. 1; therefore, only a brief description of the difference from the previous report will be included here.

The sphere was spun up to approximately 60 rpm after the helium bath had come to equilibrium at the operating temperature in the range of 3.991 to 2.174°K. Helium gas was then introduced into the chamber to form an adsorbed saturated film on the substrate. Helium gas was pumped out a little at a time while monitoring the pressure difference between the bath and the chamber by a T. I. Precision pressure gauge. The decay constant was measured over a time span of sixty minutes or more after each change of the can pressure. The bath pressure was held constant during the course of the measurements. Thus, the decay constant was determined as a function of film thickness at a given temperature. The measurements of α were always made at low enough angular velocity ω (ranging from 6 to