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Optical second-harmonic generation in atomic vapors with focused beams

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Processes leading to second-harmonic generation when a single polarized beam is focused into neutral or partially ionized atomic vapor are considered, including electric-field-induced third-order mixing, and quadrupole and magnetic dipole processes. Estimates of the relative strengths of these processes are given. In addition, the polarization properties given by the tensor susceptibilities are discussed in detail.

I. INTRODUCTION

Various nonlinear optical schemes for obtaining second-harmonic generation (SHG), sum-frequency generation (SFG), or difference-frequency generation (DFG) in isotropic media have been demonstrated, despite the fact that $\chi^{(2)}$, the lowest-order susceptibility describing such processes, vanishes in the dipole approximation. These schemes have typically utilized gases or vapors as nonlinear media and have involved applying dc electric fields and using the third-order nonlinearity,[1] or producing quadrupole polarizations which can radiate in a noncollinear geometry,[2] or applying a dc magnetic field to "rotate" driven quadrupole or magnetic dipole moments, allowing them to radiate in a collinear geometry.[3] Interference effects have been observed when combinations of these processes are present, for example, in quadrupole/dc electric-field-induced SFG (Ref. 4) or quadrupole/magnetic-field-induced SFG.[5]

More recently SHG was reported in several experiments when a single beam was focused into a metal vapor with no externally applied electric or magnetic fields. Mossberg, Flusberg, and Hartmann[6] attributed the SHG they observed in thallium vapor (with two-photon pumping on a transition with no quadrupole moment) to a third-order mixing with a radial dc electric field produced by three-photon ionization of the atoms in the focused beam. In a subsequent letter,[7] Miyazaki, Sato, and Kashiwagi (MSK) reported very interesting experimental data on SHG in sodium vapor. Their principal findings were the following: (1) the generated light at frequency 2ω emerges in a ring pattern, (2) the radiation is radially polarized, (3) at high pump intensity the 2ω intensity is proportional to the square of the density N, and (4) the observed intensity dependence at lower pump intensities (I) is faster than I^4. They attributed these results to a new mechanism. In their picture a spontaneous electric field ($\vec{E}_S$) arises during the pump pulse, parallel to the pump intensity gradient and independent of the atomic density, resulting in SHG via third-order mixing.

It is the purpose of this paper to describe and estimate the strength of various processes leading to SHG from a focused beam in an isotropic vapor with no externally applied electric or magnetic fields. In addition, simple physical arguments are given to show that the spontaneous field model proposed by MSK does not give a correct description of the physics involved. The processes described in the present work fall into two classes: those involving free electrons created by photoionization and those which can occur with only neutral atoms present. Within each of these classes a second important distinction exists between processes relying only on the dipole-forbidden susceptibility $\chi^{(2)}$ to produce a second-harmonic polarization which radiates at 2ω, and processes that in some way produce a slowly varying electric field, which induces SHG via the dipole-allowed third-order susceptibility $\chi^{(3)}$. In this paper processes relying on ionization are described in the second section while those involving only neutral atoms are discussed in the third section. Since in typical experiments, visible lasers with $\omega \sim 10^{15}$ sec^{-1} and alkali-metal vapor densities of $\sim 10^{16}$/cm^3 are used, even if all valence electrons are freed, the plasma frequency $\omega_p \sim 10^{13}$ sec$^{-1} \ll \omega$, so that the incident beam is nearly unperturbed by the plasma. In addition, except in the immediate vicinity of an atomic resonance line, the atomic refractive index is small, so that the pump beam is assumed to propagate through the cell undepleted and with a fixed spatial mode (taken here to be lowest-order Gaussian). The fourth section gives a more detailed account of dc induced SHG, and both the tensor properties and frequency dispersion of $\chi^{(3)}$ are given. In the final section, estimates of the strengths of all the various processes are made in order to assess their relative importance.

II. SHG INVOLVING FREE ELECTRONS

In the presence of high power pulses, multiphoton ionization can occur quite readily in alkali-metal vapors,[8] and the free electrons produced can lead in several ways to SHG. As a first possibility the electrons can move after they are freed, creating net charge densities and static electric fields which induce SHG. The movement can be due to either radiation forces exerted on the electrons by the pump light, or due to the initial kinetic energy of the ejected electrons. A second possibility is that the free-electron second-harmonic polarization proportional to the dipole-forbidden second-order susceptibility for plasma can directly give SHG.

Consider first the motion of the free electrons in response to the radiation forces. The radiation force per unit volume on the medium, $\vec{f}$, can be written[9]

$$\vec{f} = \nabla \cdot \vec{\sigma} - \frac{\partial \vec{g}}{\partial t}, \tag{1a}$$

$$\vec{\sigma} = -\frac{1}{8\pi}(E^2 + B^2)\vec{I} + \frac{1}{4\pi}(\epsilon \vec{E}\vec{E} + \vec{B}\vec{B}). \tag{1b}$$

Here $\vec{\sigma}$ is the electromagnetic stress tensor, $\vec{g} = (\vec{E} \times \vec{B})/4\pi c$ is the field momentum density, and ϵ is the dielectric constant, including both atomic and free-electron contributions. The expression for $\vec{f}$ can be rewritten as

$$\vec{f} = \tfrac{1}{2}\chi \nabla(E^2) + \frac{\chi}{c}\frac{\partial}{\partial t}(\vec{E} \times \vec{B}) \tag{2a}$$

$$= (\vec{P} \cdot \nabla)\vec{E} + \frac{1}{c}\frac{\partial \vec{P}}{\partial t} \times \vec{B}, \tag{2b}$$

where χ is the linear susceptibility $(\epsilon - 1)/4\pi$, including both atomic and plasma contributions, and $\vec{P} = \chi \vec{E}$. The last form is recognizable as the Lorentz force on a time varying dipole in an inhomogeneous field. The force on the free electrons is given by Eq. (2a), with $\chi_{fe}^{(1)} = -n_e e^2/m\omega^2$ (where n_e is the free-electron density, m is the electron mass, and ω is the optical angular frequency). These free electrons will move radially outward under the influence of the cycle average $\langle \vec{f} \rangle$ of this force, building up a net charge density and giving rise to an electric field $\vec{E}_S$ and electric forces *opposing* $\langle \vec{f} \rangle$.[10]

In discussing the time development and maximum strength of $\vec{E}_S$, the charge separation induced electric field, three regimes occur according to which of three characteristic times is shortest. These times are the laser pulse length τ_l, the inverse plasma frequency $\tau_p \sim \omega_p^{-1}$ (where $\omega_p = 4\pi \underline{n} e^2/m$ and $\underline{n}$ is the maximum photoelectron density), and the time $\tau_f \sim (2mR/\underline{f}_e)^{1/2}$ required for the maximum cycle averaged radiation force per electron, $\underline{f}_e$, to move an electron one beam radius (R) starting from rest.

If τ_p is shortest, $\vec{E}_S$ increases to a strength $\sim \underline{f}_e/e$. At that strength the outward radiation force is balanced, and as $\vec{E}_S$ increases slightly more, the outward motion is halted with $\vec{E}_S$ at its maximum value in a time $\sim \tau_p$.

If τ_f is shortest, the density of electrons is insufficient to give restoring electrostatic forces strong enough to halt the outward motion, and the photoelectrons are swept from the beam in a time $\sim \tau_f$. The electric field $\vec{E}_S$ saturates at a value given by the positive-ion distribution with all free electrons removed.

If τ_l is shortest, the limits set by electrostatic restoring forces and electron depletion of the beam volume are not reached, so that the electron displacements and the strength of $\vec{E}_S$ increase quadratically in time, attaining values $\propto \tau_l^2$.

Quantitative estimates of the strength of $\vec{E}_S$ for all three cases can be made starting with the continuity equation, Gauss's law, and the force law for the electrons:

$$\frac{\partial n_e}{\partial t} = -\nabla \cdot n_e \vec{v}, \tag{3a}$$

$$\nabla \cdot \vec{E}_S = -4\pi e(n_e - n_0), \tag{3b}$$

$$\frac{d\vec{v}}{dt} = \frac{\partial \vec{v}}{\partial t} + (\vec{v} \cdot \nabla)\vec{v} = (\vec{f}_e - e\vec{E}_S)/m. \tag{3c}$$

Here $n_e(\vec{r}, t)$ and $n_0(\vec{r})$ are the free electron and ion densities, $\vec{v}(\vec{r}, t)$ is the local mean electron velocity, and $\vec{f}_e$ is the cycle-averaged radiation force per electron. For the cylindrically radial motion of the electrons assumed here, no magnetic fields or forces are generated.

While in reality the ionization and charge separation processes occur simultaneously throughout the laser pulse, to simplify the calculation it is assumed here that (1) at time $t = 0$ during the laser pulse, equal densities $[n_0(\vec{r})]$ of electrons and ions are created by s-photon ionization; (2) the electrons, initially at rest, are accelerated by $\vec{f}_e$ for the remainder of the laser pulse, assumed to have constant intensity until it ends at $t = \tau_l$; and (3) the collisional damping time for the electrons is longer than the time required for $\vec{E}_S$ to build up initially.

The laser electric field $\vec{\mathcal{E}}$ is described by $\vec{\mathcal{E}} = \vec{E} + \vec{E}^*$, where $\vec{E} = \vec{e}E_0 \exp(ikz - i\omega t - r^2/R^2)$, and R denotes the beam radius. The density $n_0(\vec{r})$ is taken to be $\underline{n} \exp(-2sr^2/R^2)$, and the transverse

components of $\vec{f}_e$ are given by the first term of Eq. (2a) with $E^2 = 2E_0^2 \exp(-2r^2/R^2)$. The longitudinal $\vec{E}\times\vec{B}$ term in Eq. (2a) is neglected since it does not give charge separation.

Equation (3) can be solved in successive powers of t. For short times the change of electron density, $\Delta n_e = (n_e - n_0)$, and electric field $\vec{E}_S$ are given by

$$\Delta n_e(r,t) = -\nabla\cdot(n_0\vec{x}_1), \tag{4a}$$

$$\vec{E}_S = 4\pi e n_0 \vec{x}_1, \tag{4b}$$

where $\vec{x}_1 = \vec{f}_e t^2/2m$. Thus the electric field built up during a short laser pulse is $\vec{E}_S \cong 4\pi e n_0 \vec{f}_e \tau_l^2/2m$, which has a maximum of $(\omega_p\tau_l)^2(\underline{f}_e/e)[4(s+1)]^{-1/2}$, where $\underline{f}_e = (2/\sqrt{\underline{e}})(e^2E_0^2/m\omega^2R)$ is the maximum of $\vec{f}_e$, and $\underline{e} = 2.7818\ldots$.

For the case where τ_f is shortest, the field saturates when the electrons are swept out of the beam completely, and only the positive ion density $n_0(\vec{r})$ remains. Gauss's law then gives the radial field, which has a maximum strength of $E_S \cong \pi e \underline{n} R s^{-1/2}$. For electrons to leave the beam, $\underline{f}_e\tau_f^2/2m \cong R$, leading to $\tau_f \cong m\omega R/eE_0$.

Considering now the high-density case where τ_p is the shortest time, Eqs. (3) can be solved through fourth order in t, thus including the electrostatic restoring force. The maximum electric field is then found to be $\vec{E}_S \cong \frac{3}{2}(\vec{f}_e/e)$, and it is attained in a time $\tau_p \cong \sqrt{6}/\omega_p$. If the radial plasma oscillation were damped before the laser pulse ended, a steady state would be reached such that $(-e\vec{E}_S) = -\vec{f}_e$, and the opposing electrostatic and radiation forces would be balanced at each point. Note that in this high-density case $\vec{E}_S$ is independent of n_e and N, the electron and atom densities.

A crossover density n_c, which divides the regime where charge separation is or is not limited by the electrostatic restoring force, can be defined by setting $\tau_p = \tau_f$ and solving for the electron density. The result is $n_c = E_0^2/2m\omega^2R^2 = 2P\times10^7/mc\omega^2R^4$, where P is the peak laser power in watts. For wavelength 1.06 μm and $R = 10^{-2}$ cm, $n_c \cong 230P$ (W). When the electron density is greater than n_c, the electrons are confined within the beam by electrostatic forces.

Sample values of these parameters can be calculated using, for example, parameters corresponding to the experiment of MSK ($R = 10^{-2}$ cm, $\omega = 2\pi c/1.06$ μm, $E_0 = 1.15\times10^5$ esu corresponding to a beam power of 1 GW and an intensity at focus of ~6 TW/cm^2, and $\tau_l = 30$ ps). In this case $\tau_f \cong 280$ ps, $n_c \cong 2.3\times10^{10}$/cm^3, and the limiting field strength is given by $\frac{3}{2}(\underline{f}_e/e) = 0.44$ esu $= 130$ V/cm. The time τ_p decreases as $\underline{n}^{-1/2}$, and has the value $\tau_p = 280$ ps when $\underline{n} = n_c$, the value $\tau_p = 30$ ps $= \tau_l$ when $\underline{n} = 2\times10^{12}$/cm^3, and the value $\tau_p = 0.42$ ps when $\underline{n} = 10^{16}$/cm^3.

This picture can be contrasted to the spontaneous field description of MSK for free electrons. In their description a spontaneous electric field is introduced as an entity which is directly responsible for the force $\vec{f}$ in Eq. (2a) (with $\chi = \chi_{fe}^{(1)}$). MSK assume that *no* charge separation occurs, and that the spontaneous field in the plasma case is obtained by equating $\vec{E}_S = \vec{f}_e/(-e)$. This expression for $\vec{E}_S$ is similar to that obtained in the high-density case discussed above, but is opposite in sign since the field $\vec{E}_S$ *causes* $\vec{f}_e$ in the picture of MSK, rather than arising from net charge density due to electron motion induced by $\vec{f}_e$ and giving an electric force *opposing* $\vec{f}_e$. Fundamentally, however, there is no physical equivalence between an electric force and the cycle averaged radiation force, since as Eq. (2b) shows, the radiation force arises because the electrons are vibrating in space. The first term is proportional to the field gradient and accounts for the local variation of the electric field at different points along an electron's path, and the second term is just the magnetic force on the moving charge. The importance of this vibratory particle motion, and the inadequacy of the spontaneous electric-field description of the radiation force, can be seen from the inverse proportionality of $\vec{f}$ to the electron mass (since $\chi_{fe}^{(1)} \propto m^{-1}$). If we imagine an electron and a very massive particle with unit negative charge near one another in space, they would experience identical forces due to any electric field. But the radiation forces on the two particles are in inverse ratio to their masses. An infinitely massive negative particle would experience *no* radiation force because it could not vibrate under the influence of the applied radiation field. It is clear therefore that the radiation forces in a nonuniform beam cannot be discussed in terms of an equivalent electric field. Similarly, the response of neutral atoms to an inhomogeneous field is not equivalent to their response to an electric field, as will be discussed in Sec. III below.

We next consider a second mechanism leading to separation of charge which relies on the initial kinetic energy of the ejected photoelectrons to carry them away from the beam axis. Kinetic separation of charge was recently suggested as the mechanism leading to dc field induced SHG in atomic thallium vapor with weak (~kW) 7 ns long laser pulses.[6] For these pulses the radiation forces and equilibrium electric field are weak, so that the electric field set up by the ballistic motion of the electrons should dominate. The strength and buildup time of these radial fields can be estimated using the Boltzmann equation

and assuming that photoionization produces at $t=0$ an initial spatial density of photoelectrons n_0, with velocity and energy v and E_v and a uniform angular distribution. For short times ($vt<R$ and $t<\tau_p$) the electrons move without net forces on them and, it is assumed, without collisions. In this case it can be shown that the electron distribution function $f_B(\vec{r},\vec{v},t)=f_B(\vec{r}-\vec{v}t,|v|,0)$. Expanding in powers of $\vec{v}t$ and integrating over $\vec{v}$ gives the lowest-order change in electron density $\Delta n_e(t)=(vt)^2\nabla^2 n_0/6$. Gauss's law then gives the electric field $\vec{E}_S=-\frac{1}{6}4\pi e(vt)^2\nabla n_0$. As in the case of radiation force driven charge separation, three regimes occur depending on which of three times is the shortest. Two of these, τ_l and τ_p, are the same as before, but now the beam escape time $\tau_v=R/v$ replaces the time τ_f.

For short laser pulses, we have simply $\vec{E}_S \cong -\frac{1}{6}4\pi e(v\tau_l)^2\nabla n_0$. In the next case, where the beam escape time τ_v is less than τ_l and τ_p, the maximum value of $E_S \cong \pi e\underline{n}Rs^{-1/2}$ is again obtained when the electrons have left the beam volume in a time $\sim\tau_v$.

The high-density case can be treated by assuming the density change and $\vec{E}_S$ develop according to the expressions above, until the electrostatic potential energy is equal to the initial radial kinetic energy of the photoelectrons, at which time the outward motion of the electrons is halted. This energy balance $\int E_S^2/8\pi d^3r = E_v(\pi R^2\underline{n}/3s)$ leads to the time for maximum field buildup $\tau_k(2/s)^{1/4}$, where the time $\tau_k=(\tau_v\tau_p)^{1/2}$ can be called the kinetic separation time. The maximum field is then

$$\vec{E}_S \cong \pi e\underline{n}(v\tau_p)\left(\frac{-1}{\sqrt{s}}\frac{R}{\underline{n}}\vec{\nabla}n_0\right)$$

with the maximum value $E_S \cong (2/\sqrt{3})\pi e\underline{n}(v\tau_p) \cong (\underline{n}E_v 4\pi)^{1/2}$. The last expression reflects the fact that the electrostatic potential-energy density $E_S^2/8\pi$ has a maximum value approximately equal to the maximum initial kinetic energy density $\underline{n}E_v$.

A crossover density can again be defined by equating τ_p and τ_v, with the result $n_c \cong E_v/e^2R^2$. The density n_c has the same physical significance as in the radiation force driven case.

The dc fields resulting from kinetic charge separation can be quite strong: for $E_v=1.6\times10^{-12}$ erg (1 eV) and $R=10^{-2}$ cm, $\tau_v=170$ ps, and the crossover density $n_c=6.9\times10^{10}$ cm^{-3}. At that density, the maximum field $E_S\cong1.18$ statvolt/cm (355 V/cm). For $\underline{n}=10^{14}$ cm^{-3}, τ_k is reduced to ~25 ps and E_S rises to 45 statvolt/cm (13.5 kV/cm).

While the mechanisms discussed above rely on charge separation in a focused beam to give dc electric fields which induce SHG via the atomic third-order nonlinearity, the free-electron second-order susceptibility can give a second-harmonic polarization which can directly radiate. Unlike the dc-field-induced processes which require macroscopic motion of charge, this second-order response requires only microscopic electron motion and should be effectively instantaneous. The 2ω polarization for neutral plasma with electron density n_e has been given by Jha[11] and can be written as[12]

$$\vec{P}(2\omega)=\chi_{fe}^{(2)}(2\omega)\left((\vec{E}\cdot\nabla)\vec{E}+\frac{i\omega}{c}\vec{E}\times\vec{B}\right)+\frac{e\vec{E}(\nabla\cdot\vec{E})}{8\pi m\omega^2}, \tag{5a}$$

where

$$\chi_{fe}^{(2)}(2\omega)=\frac{n_e e^3}{4m^2\omega^4}. \tag{5b}$$

The first two terms in Eq. (5a) arise from the variation of the $\vec{E}$ field along the electron path, and the magnetic force, respectively. The last term is important in nonuniform plasma, where the $\vec{E}$ field induces a net charge density at frequency ω, giving a 2ω current when multiplied by the velocity component at frequency ω. By using vector identities and Maxwell's equations to transform the first terms, and the relationship $\nabla\cdot(\epsilon_p\vec{E})=0$ with $\epsilon_p=(1-\omega_p^2/\omega^2)$ to transform the last term, Eq. (5a) can be rewritten

$$\vec{P}(2\omega)=\chi_{fe}^{(2)}(2\omega)[\tfrac{1}{2}\nabla E^2+2\vec{E}(\vec{E}\cdot\nabla\ln n_e)/\epsilon_p]. \tag{5c}$$

The $(\vec{E}\cdot\nabla)\vec{E}$ and $\vec{E}\times\vec{B}$ terms of Eq. (5a) combine to give the gradient term in Eq. (5c), a purely irrotational polarization (having vanishing curl) which cannot radiate in bulk media (although at boundaries it can give a radiating dipole layer[12]). The second term in Eq. (5c) can radiate in a nonuniform plasma. If in the present case ($\epsilon_p\sim1$, Gaussian beam profile) we assume $n_0\propto I^s$, as expected for s-photon ionization, the radiating 2ω polarization becomes

$$\vec{P}(2\omega)=-8s\chi_{fe}^{(2)}(2\omega)\vec{E}(\vec{E}\cdot\vec{r})/R^2. \tag{5d}$$

Owing to the factor $\vec{r}$ in this expression the 2ω radiation will be emitted off axis at an angle approximately equal to the divergence half-angle of the focused pump beam and will have no intensity exactly on axis. For linear polarized pump light the 2ω radiation will have parallel linear polarization, and the radiation pattern will have two lobes oriented along the directions of $\pm\vec{E}$. For circular

polarization the harmonic radiation will emerge in a circularly polarized ring around the beam axis.

III. SHG INVOLVING ONLY NEUTRAL ATOMS

The spatial nonuniformity introduced by focusing a light beam into a homogeneous, unpolarized, neutral atomic vapor, slightly disturbs the rotational symmetry about all lines parallel to the beam direction that rules out SHG or other second-order processes for a plane wave (even if higher multipole orders are considered). With focusing, two mechanisms for SHG are possible. They depend on the dipole-forbidden second-order susceptibilities (quadrupole and magnetic-dipole) of the medium, and they should be equally effective for picosecond or nanosecond pulses since only microscopic electron motion is involved. In the first effect, a *nonuniform* zero-frequency polarization, quadratic in the applied field, gives rise to a net bound-charge density. This in turn gives rise to dc electric fields and leads to 2ω radiation via $\chi^{(3)}$. In the second effect, it is possible for the 2ω polarization quadratic in the nonuniform applied field to radiate second-harmonic directly.

In general, for either quadrupole or magnetic dipole effects in isotropic media, the corresponding susceptibility tensor has only one independent component,[13] so that the polarization properties are independent of frequency. Thus, the polarizations at the sum frequency for a pair of fields $\vec{E}_1$ and $\vec{E}_2$ can be written in forms that explicitly display their vector or tensor dependence on the incident fields:

$$\vec{P}_Q(\omega_1+\omega_2)=\chi_Q(\omega_1,\omega_2)[-\tfrac{2}{3}(\nabla\cdot\vec{E}_1)\vec{E}_2+(\vec{\nabla}\vec{E}_1)\cdot\vec{E}_2+\vec{E}_2\cdot(\vec{\nabla}\vec{E}_1)]$$
$$+\chi_Q(\omega_2,\omega_1)[-\tfrac{2}{3}(\nabla\cdot\vec{E}_2)\vec{E}_1+(\vec{\nabla}\vec{E}_2)\cdot\vec{E}_1+\vec{E}_1\cdot(\vec{\nabla}\vec{E}_2)]\,, \tag{6a}$$

$$\vec{P}_M(\omega_1+\omega_2)=\chi_M(\omega_1,\omega_2)\left(\frac{-i\omega_1}{c}\vec{B}_1\times\vec{E}_2\right)+\chi_M(\omega_2,\omega_1)\left(\frac{-i\omega_2}{c}\vec{B}_2\times\vec{E}_1\right), \tag{6b}$$

$$\vec{M}(\omega_1+\omega_2)=\chi'_M(\omega_1,\omega_2)\vec{E}_1\times\vec{E}_2\,, \tag{6c}$$

$$\vec{\vec{Q}}(\omega_1+\omega_2)=[\chi'_Q(\omega_1,\omega_2)][\vec{E}_1\vec{E}_2+\vec{E}_2\vec{E}_1-\tfrac{2}{3}\vec{\vec{I}}(\vec{E}_1\cdot\vec{E}_2)]\,, \tag{6d}$$

$$\vec{P}'_Q=-\nabla\cdot\vec{\vec{Q}}$$
$$=\chi'_Q(\omega_1,\omega_2)[-(\nabla\cdot\vec{E}_1)\vec{E}_2-(\vec{E}_1\cdot\nabla)\vec{E}_2-(\nabla\cdot\vec{E}_2)\vec{E}_1-(\vec{E}_2\cdot\nabla)\vec{E}_1+\tfrac{2}{3}\vec{\nabla}(\vec{E}_1\cdot\vec{E}_2)]\,. \tag{6e}$$

The expressions in (6a), (6b), and (6e) give the dipole moment/cm^3 due to quadrupole interactions with the field gradients, magnetic dipole interactions with $\vec{B}$, and the nonuniform field-induced quadrupole moment/cm^3, respectively. The atomic susceptibilities for alkali-metal atoms are given in the Appendix. The induced magnetic dipole/cm^3 in Eq. (6c) gives no 2ω contribution, but can give a dc magnetization (essentially parallel to the beam) for circularly polarized beams. Unlike a transverse magnetization, this magnetization induces no appreciable SHG.

First, consider the zero-frequency polarization from Eq. (6)

$$\vec{P}(0)=\chi_a^{(2)}(0)\nabla(\vec{E}^*\cdot\vec{E})+\chi_b^{(2)}(0)\left(\frac{2\omega}{c}\mathrm{Im}(\vec{E}\times\vec{B}^*)\right)$$
$$+\chi_c^{(2)}(0)[\vec{E}(\nabla\cdot\vec{E}^*)+\vec{E}^*(\nabla\cdot\vec{E})]\,, \tag{7}$$

where

$$\chi_a^{(2)}(0)=2\chi_Q(-\omega,\omega)-\tfrac{1}{3}\chi'_Q(-\omega,\omega)\,, \tag{8a}$$

$$\chi_b^{(2)}(0)=-\chi_Q(-\omega,\omega)+\chi'_Q(-\omega,\omega)+\chi_M(-\omega,\omega)\,, \tag{8b}$$

$$\chi_c^{(2)}(0)=-\tfrac{2}{3}\chi_Q(-\omega,\omega)-\chi_{Q'}(-\omega,\omega)\,, \tag{8c}$$

and use is made of the formula

$$(\vec{E}^*\cdot\nabla)\vec{E}+(\vec{E}\cdot\nabla)\vec{E}^*=\nabla(\vec{E}^*\cdot\vec{E})-\frac{2\omega}{c}\mathrm{Im}(\vec{E}\times\vec{B}^*). \tag{9}$$

Any static fields due to this polarization arise from the net bound charge density

$$\rho_b=-\nabla\cdot\vec{P}(0)$$
$$=-\chi_a^{(2)}(0)\nabla^2(E^*E)-\chi_b^{(2)}(0)2k^2\left(\frac{B^*B}{\epsilon}-E^*E\right). \tag{10}$$

In a uniform neutral vapor the term $\propto\chi_c^{(2)}(0)$ in Eq. (7) vanishes. While for plane waves both terms on the right side of Eq. (10) vanish, in a focused beam they are comparable. To study quadrupole effects it is necessary to use vector

electric and magnetic fields rather than the scalar Gaussian beam used for most purposes.[14] Fields satisfying $\nabla \cdot \vec{E} = 0$ and $\nabla \cdot \vec{B} = 0$ may be found by defining a vector potential $\vec{A} = \vec{A}_0 \psi$ and a scalar potential $\phi = \nabla \cdot \vec{A}/ink$ (from the Lorentz condition, with n the index of refraction) and taking for ψ the scalar Gaussian beam wave function

$$\psi = \zeta \exp\left(ikz - \zeta \frac{r^2}{R^2} - i\omega t\right), \tag{11}$$

where $\zeta = (1 + iz/z_0)^{-1}$, $z_0 = kR^2/2$ is the confocal parameter (when $z = z_0$ the amplitude $1/e$ radius increases by $\sqrt{2}$), and R is the minimum amplitude $1/e$ radius. The beam divergence half-angle (field amplitude $1/e$) is $\theta = \tan^{-1}(2/kR) \sim 2/kR$. The wave function ψ is a correct solution of the wave equation through terms of order θ^3. For a linearly polarized beam $(\vec{A} \| \vec{e}_x)\vec{E}$ and $\vec{B}$ to lowest order in θ, are found to be

$$\vec{E} = E_0 \psi \left(\vec{e}_x - \frac{i\theta x \zeta}{R} \vec{e}_z\right), \tag{12a}$$

$$\vec{B} = B_0 \psi \left(\vec{e}_y - \frac{i\theta y \zeta}{R} \vec{e}_z\right), \tag{12b}$$

where $B_0 = nE_0$.

The charge density from Eq. (10) and corresponding scalar potential ϕ are then

$$\rho = \frac{8\zeta_R}{R^2} E_0^2 |\psi|^2 \left[\chi_a^{(2)}(0)\left(1 - \frac{2r^2\zeta_R}{R^2}\right) - 2\chi_b^{(2)}(0) \frac{\zeta_R (y^2 - x^2)}{R^2}\right], \tag{13a}$$

$$\phi = 2\pi E_0^2 |\psi|^2 \left\{2\chi_a^{(2)}(0) - \chi_b^{(2)}(0) \frac{R^2}{\zeta_R} \left(\frac{y^2 - x^2}{r^4}\right) \times \left[\exp\left(\frac{2r^2\zeta_R}{R^2}\right) - \left(1 + \frac{2r^2\zeta_R}{R^2}\right)\right]\right\}, \tag{13b}$$

where $\zeta_R = \mathrm{Re}(\zeta) = |\zeta|^2 = (1 + z^2/z_0^2)^{-1}$. For the linearly polarized case, the polarization charge is not cylindrically symmetric, and the dc fields corresponding to the two terms will add along one axis and partially cancel along the orthogonal axis. For circular polarization the terms $\propto \chi_b^{(2)}(0)$ in Eqs. (7), (10), and (13) vanish. We may compare the strength of this static field to the field induced by the radiation force for the high-density free-electron case. The ratio of the static field from the cylindrically symmetric term in Eq. (13) to the static field for the free-electron case, $\vec{E}_S \cong \vec{f}_e/e$ (independent of n for large enough n), is

$$\left(\frac{m\omega^2}{e}\right) 4\pi \chi_a^{(2)}(0) . \tag{14}$$

A typical nonresonant value of $\chi_a^{(2)}(0)$ for Na density $10^{16}/\mathrm{cm}^3$ and 1.0 μm wavelength light is 10^{-20}, giving a ratio $\sim 10^{-6}$. This means that very little ionization will overwhelm the bound charge effect.

However, while the free-electron effect varies slowly with frequency, resonant enhancements of $10^4 - 10^5$ in $\chi_a^{(2)}(0)$ are possible near resonant frequencies. If ω were tuned exactly to a quadrupole transition, for example, one could obtain strong resonant enhancement of the neutral atom response with much less ionization than would occur if ω were near an allowed transition.

The description of the dc distortion of the atoms and the resulting static electric field due to the nonuniform field given above can be compared to the discussion given by MSK for neutral atoms. Considering just the cylindrically symmetric term in Eq. (13b), the static field $\vec{E}_S = -4\pi\chi_a^{(2)}(0)\nabla E^* E$ is proportional to the second-order dipole forbidden susceptibility $\chi^{(2)}$. In contrast, MSK argue that the net force on the neutral atoms given by $\vec{f} = \chi^{(1)} \nabla E^* E$ can be written in terms of a static field $\vec{E}_S = \vec{f}/(-eN)$ so that $\vec{E}_S = -(\chi^{(1)}/eN)\nabla E^* E$. Again the result obtained with the spontaneous field model is not equivalent to that obtained by considering the inhomogeneous field. The atomic response is different in the two situations since an E field mixes only states of opposite parity while an inhomogeneous field mixes states of the same parity. Thus, to describe the static *distortion* of the atom induced by the nonuniform field, it is necessary to use $\chi^{(2)}$ rather than $\chi^{(1)}$, even though the net *force* on the neutral atoms can be found from $\chi^{(1)}$ alone.

Next, consider the possibility of direct SHG by the 2ω polarization resulting from the dipole-forbidden second-order susceptibility. From Eq. (6),

$$\vec{P}(2\omega) = \chi_a^{(2)}(2\omega)\nabla E^2 + \chi_b^{(2)}(2\omega)(\vec{E} \cdot \nabla)\vec{E} + \chi_c^{(2)}(2\omega)\vec{E}(\nabla \cdot \vec{E}), \tag{15}$$

where

$$\chi_a^{(2)}(2\omega) = \tfrac{1}{2}\chi_Q(\omega, \omega) + \tfrac{1}{2}\chi_M(\omega, \omega) + \tfrac{1}{3}\chi_Q'(\omega, \omega), \tag{16a}$$

$$\chi_b^{(2)}(2\omega) = \chi_Q(\omega, \omega) - \chi_M(\omega, \omega) - \chi_Q'(\omega, \omega), \tag{16b}$$

$$\chi_c^{(2)}(2\omega) = -\tfrac{2}{3}\chi_Q(\omega, \omega) - \chi_Q'(\omega, \omega). \tag{16c}$$

Only the second term can radiate for a focused beam in a bulk, uniform vapor, since the gradient term of Eq. (15) is a purely irrotational polarization which cannot radiate, and the divergence term vanishes for a uniform medium. If a beam is especially prepared, for example, by orthogonally polarizing the two halves of the beam, the polarization transverse to $\vec{k}$ will be proportional to θ, the beam divergence half-angle. This is essential-

ly the geometry used for quadrupole sum-frequency generation by Bethune, Smith, and Shen.[2] However, for a single Gaussian beam with linear or circular polarization, it can be shown by keeping terms in $\vec{E}$ and $\vec{B}$ through order θ^3, that the *transverse* part $[\vec{P}_\perp(2\omega)]$ of the second-order polarization $\vec{P}(2\omega)$ will be smaller by a factor θ^2 and will have the same polarization as the pump beam. For example, for a pump beam polarized along $\hat{e}_x$, the transverse, radiating component of $\vec{P}(2\omega)$ is found to be

$$\vec{P}_\perp(2\omega) = \chi_b^{(2)}(2\omega)\,\frac{\theta^2\zeta}{4}\,\hat{e}_x\,\frac{\partial}{\partial x}\,(E^2)\,. \tag{17}$$

Since θ will typically be $\sim 3\times10^{-3}$, the intensity of generated 2ω radiation will be reduced by about 10 orders of magnitude from the case of near collinear, but cross-polarized beams.

IV. dc FIELD-INDUCED SHG IN A FOCUSED BEAM

The case of dc induced 2ω generation due to the third-order susceptibility $\chi^{(3)}$, will now be considered in more detail. If we consider the second-harmonic polarization resulting from a static field $\vec{E}_S$ and a field $\vec{E}(\omega)$ with angular frequency ω, it has the general form (neglecting spin-orbit effects)

$$\vec{P}^{(3)}(2\omega) = \chi_a^{(3)}(2\omega)\vec{E}(\omega)[\vec{E}_S\cdot\vec{E}(\omega)] + \chi_b^{(3)}(2\omega)\vec{E}_S[\vec{E}(\omega)\cdot\vec{E}(\omega)]\,. \tag{18}$$

The susceptibilities $\chi_a^{(3)}$ and $\chi_b^{(3)}$ (defined in the Appendix) have different dispersions, so that the second-harmonic polarization character and angular distribution are frequency dependent.

Suppose $\vec{E}(\omega)$ is linearly polarized along $\hat{e}_x$ and $\vec{E}_S$ is radial. Then it follows that

$$\vec{P}^{(3)}(2\omega)=\chi_a^{(3)}(2\omega)[(1+R_\chi)\cos\phi\hat{e}_x+R_\chi\sin\phi\hat{e}_y]E_S E^2(\omega), \tag{19a}$$

$$|\vec{P}^{(3)}(2\omega)|^2 \propto (1+2R_\chi)\cos^2\phi+R_\chi^2\,, \tag{19b}$$

where ϕ is the azimuthal angle about the beam axis and $R_\chi=\chi_b^{(3)}/\chi_a^{(3)}$. The quantities $|\chi_a^{(3)}(2\omega)|^2$, $|\chi_b^{(3)}(2\omega)|^2$, and $R_\chi(\omega)$, calculated for Na with $N=10^{16}/\mathrm{cm}^3$, and including principal quantum numbers $n=3$–8, are plotted in Fig. 1. R_χ takes all values between $-\infty$ and ∞, and approaches the value $\frac{1}{2}$ for $\omega\to0$. The resonances in R_χ occur at frequencies $2\omega=\omega_{ns,3s}$, where $\chi_b^{(3)}$ has a two-photon resonance to an intermediate s state. At these values one would expect perfect radial polarization of the output beam. However, for $R_\chi=-1$ we expect y polarized light, for $R_\chi=0$, x polarized light, and for other values of R_χ, more complicated polarization patterns. Only for $R_\chi\to\pm\infty$ or $R_\chi=-\frac{1}{2}$ do we obtain a uniform intensity around the ring.

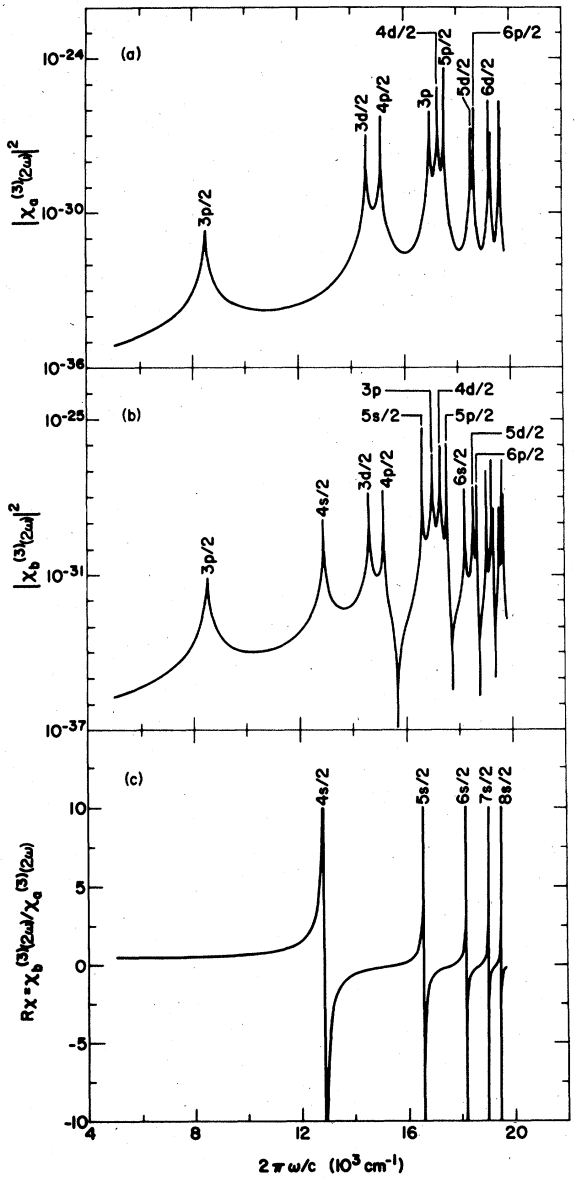

FIG. 1. (a) The magnitude squared of the third-order susceptibility $|\chi_a^{(3)}(2\omega)|^2$ (esu), calculated using s, p, and d states with $n=3$–8, for Na vapor with density $10^{16}/\mathrm{cm}^3$. This susceptibility governs generation of 2ω light polarized parallel to $\vec{E}(\omega)$. (b) $|\chi_b^{(3)}(2\omega)|^2$ (esu), for the same conditions as in (a). This susceptibility governs generation of 2ω light polarized parallel to $\vec{E}_S$, the dc field. (c) The ratio $R_\chi=\chi_b^{(3)}(2\omega)/\chi_a^{(3)}(2\omega)$.

For circularly polarized $\vec{E}(\omega)$, the second term of Eq. (18) vanishes, while the first term gives a polarization

$$\vec{P}^{(3)}(2\omega) = \chi_a^{(3)} \frac{e^{i\phi}}{2} (\vec{e}_x + i\vec{e}_y) E_S E^2 \tag{20}$$

leading to a cylindrically symmetric ring of circularly polarized second-harmonic light. In this case the s-state two-photon resonances disappear since they occur only in $\chi_b^{(3)}(2\omega)$, a result that follows directly from angular momentum conservation.

V. SUMMARY AND CONCLUSIONS

All of the mechanisms described here for SHG in a single focused beam depend on the transverse nonuniformity of the pump intensity. This is reflected in the fact that the second-harmonic polarizations are proportional to components of the transverse gradient of either the pump intensity or the photoelectron density. The presence of this gradient operator has the consequence that the radiated power has a distribution $\propto |\vec{K}_T|^2$, where $\vec{K}_T$ is the component of the 2ω wave vector perpendicular to the pump beam axis. There is therefore no 2ω light exactly on axis, and the output has either off-axis lobes or a ring structure, depending on the input light polarization and tuning. Since the pump intensity and initial photoelectron density both are cylindrically symmetric and have transverse dimension $\sim R$, to first approximation the transverse gradient operator ∇_T brings down a factor proportional to $\vec{r}/R^2$, whether it is applied to n_0 or to E^2. With the approximation $n_0 \propto E^2$ (i.e., $s=1$) this allows us to factor out $(\nabla_T E^2)$ from all of the expressions for $\vec{P}(2\omega)$, leaving effective susceptibilities which may be compared. These effective susceptibilities contain various parameters which are external to the atoms, namely, the atomic and free-electron number densities, the pump power ($\propto E^2$), the energy E_v of ejected photoelectrons, the pump divergence half-angle θ and the beam radius R, and these must be fixed to allow comparisons. In Table I the orders of magnitude of the effective susceptibilities leading to the various processes described here are given. The atomic density is taken as 10^{16} cm^{-3}, a value typical for metal vapor experiments and in the middle of the range (0.1–1 Torr) used by MSK. The beam radius and divergence angle are chosen to be appropriate for a focal length ~50 cm with 1.06μm wavelength, and are fixed at $R = 10^{-2}$ cm and $\theta = 3.4$ mrad ($z_0 = 2.94$ cm). The photoelectron energy E_v depends on the pump wavelength and the ionization mechanism. For comparison purposes the value $E_v = 5\times10^{-13}$ erg (~0.3 eV) is taken somewhat arbitrarily. This quantity appears only in the case of kinetic charge separation, and in that case $\chi_{\text{eff}} \propto E_v^{1/2}$. Two values are taken for the pump peak power and pulse length: The "low power" case (10^6 W, 5 nsec) is appropriate for excimer or doubled-YAG laser pumped dye lasers, while the "high power" case (10^9 W, 30 ps) approximates the highest power mode-locked pulse used in the experiment of MSK. The free-electron processes naturally are strongly dependent on the density n. To give some feeling for the range involved, the susceptibilities are given for a moderate density ($n = 10^{10}$/cm^3), and for the case of nearly complete ionization ($n = 10^{16}$/cm^3). The expressions for the static fields $\vec{E}_S$ used with the third-order susceptibilities are the *peak* values of the field $\vec{E}_S$ for the given cases, as estimated in Sec. II.

The actual powers radiated can be calculated for second-order polarizations $\vec{P}^{(2)} \propto \zeta\chi_Q \nabla_T E^2$ and third-order polarizations $\vec{P}^{(3)} \propto \chi^{(3)}(\nabla_T E^* E)E^2$. For a Gaussian beam focused into a medium of length $L \gg z_0$, the second-harmonic power can be expressed as

$$P(2\omega)\times10^{-7} = (2\pi)^4 \frac{K^4}{c} |\chi_{\text{eff}}|^2 P^2(\omega) F(\Delta k z_0) S \ , \tag{21}$$

where $P(2\omega)$ and $P(\omega)$ are the second-harmonic and input powers (in watts), K is the second-harmonic wave-vector magnitude, $\Delta k = (2k - K)$, $F(\Delta k z_0)$ is a phase-matching function with maximum value 1, S is a numerical factor which depends on the process assumed, and χ_{eff} is an effective susceptibility (specific forms are given in the table).

For a polarization $\propto \zeta\chi_Q \vec{\nabla}_T E^2$, the second-harmonic beam would be radially polarized, and its angular distribution and dependence on $\kappa \equiv \Delta k z_0$ would be given by

$$\frac{dP}{d\Omega}(2\omega) \propto F(\kappa)\Theta^2 e^{-4\Theta^2/\theta^2}, \tag{22a}$$

where $\Theta = (K_T/K)$ and the phase-matching function $F(\kappa)$ would be

$$F(\kappa) = \begin{cases} (\kappa e^{1-\kappa})^2 & (\kappa \geq 0) \\ 0 & (\kappa < 0) \end{cases} \tag{22b}$$

with maximum value at $\kappa = 1$. The factor $S = \frac{1}{2}e^{-2} \cong 0.068$. These results also hold for second-order polarizations $\propto \chi_Q(\vec{E}\cdot\nabla)\vec{E}$ (as discussed in Sec. III), except (assuming $\vec{E}$ along $\vec{e}_x$) the angular distribution has an additional factor $\cos^2\phi$, S is multiplied by $\frac{1}{2}$, the second-harmonic is polarized parallel to $\vec{E}$ rather than radially, and the effective susceptibility is $\chi_{\text{eff}} = [\chi_b^{(2)}(2\omega)(\theta^2/4)]$. Values for this susceptibility are given in the table.

For the third-order case (with $\vec{E}$ along $\vec{e}_x$) the angular distribution and dependence on κ are given by

TABLE I. Forms and magnitudes (in esu) of effective susceptibilities for processes giving SHG for a beam focused into sodium vapor.

Process		χ_{eff} $[P(2\omega)=\chi_{eff}\nabla_T E^2]$	$S^{1/2}\chi_{eff}$ ($\lambda=1.06\ \mu$m) (10^6 W, 5 ns)	(10^9 W, 30 ps)	$S^{1/2}\chi_{eff}$ (resonant[a]) (10^6 W, 5 ns)	(10^9 W, 30 ps)	λ (nm)
dc induced SHG, free electrons driven by radiation force	$\underline{n}=10^{10}$	$\chi^{(3)}(2\omega)(eE_0^2/m\omega^2)$	3.2×10^{-24}	4.8×10^{-23}[b]	3.2×10^{-19}	4.8×10^{-18}[b]	570.6
	$\underline{n}=10^{16}$	$(\times\omega_p^2\tau_l^2/2,\ \tau_l<\tau_p)$		3.2×10^{-21}		3.2×10^{-16}	$(2\lambda_{5p})$
dc induced SHG, photoelectrons ejected with kinetic energy E_v ($E_v=5\times10^{-13}$ erg)	$\underline{n}=10^{10}$	$\chi^{(3)}(2\omega)[R(3\pi\underline{n}E_v)^{1/2}]$	4.8×10^{-21}	2.2×10^{-23}[b]	2×10^{-15}	9×10^{-18}[b]	570.6
	$\underline{n}=10^{16}$	$(\times\frac{2}{3}\tau_l^2/\tau_k^2,\ \tau_l<\tau_p)$	4.8×10^{-18}	4.8×10^{-18}	2×10^{-12}	2×10^{-12}	$(2\lambda_{5p})$
Direct SHG due to nonuniform free-electron density	$\underline{n}=10^{10}$	$2\chi_{fe}^{(2)}(2\omega)$	7×10^{-26}	7×10^{-26}	4×10^{-27}	4×10^{-27}	530
	$\underline{n}=10^{16}$		7×10^{-20}	7×10^{-20}	4×10^{-21}	4×10^{-21}	
dc induced SHG, nonuniform static polarization of neutral atoms $\propto\chi^{(2)}$ leading to dc E field		$\chi^{(3)}(2\omega)(4\pi\chi_{(0)}^{(2)}E_0^2)$	1.6×10^{-30}	1.6×10^{-27}	1.6×10^{-22}	1.6×10^{-19}	570.6 $(2\lambda_{5p})$
Direct SHG due to 2ω polarization of neutral atoms $\propto\chi^{(2)}$		$\chi^{(2)}(2\omega)(\theta^2/4)$	8.8×10^{-27}	8.8×10^{-27}	2×10^{-21}	2×10^{-21}	685.6 $(2\lambda_{3d})$
As in preceding case, for two noncollinear cross-polarized beams		$\frac{1}{2}\chi^{(2)}(2\omega)$	4.7×10^{-21}	4.7×10^{-21}	1.1×10^{-15}	1.1×10^{-15}	685.6 $(2\lambda_{3d})$

[a]Resonant values are for best cases, with minimum detunings 0.1 cm^{-1} assumed.

[b]Short pulse forms used. S is a weighting factor [see text, Eq. (21)]. Numerical values calculated with ionization order $s=1$.

$$\frac{dP}{d\Omega}(2\omega) \propto [(1+2R_\chi)\cos^2\phi + R_\chi^2] \begin{cases} \alpha(2+3\kappa+\alpha)^2 e^{-2(\kappa+\alpha)} & (\kappa \geq 0) \\ \alpha[f(\alpha,\kappa)]^2 & (\kappa < 0) \end{cases} \tag{23a}$$

where $\alpha = 2\Theta^2/\theta^2$ and

$$f(\alpha,\kappa) = e^{2(\kappa-\alpha)} \sum_{m=0}^{\infty} \frac{\alpha^m}{m!} \sum_{l=0}^{(m+1)} \frac{(-3\kappa)^l}{l!}(2+m-l). \tag{23b}$$

For large angles $f(\alpha,\kappa)$ falls off approximately as a Gaussian in Θ. The phase-matching function $F(\kappa)$, exact for $\kappa \geq 0$ and fit for $\kappa < 0$, is

$$F(\kappa) = 0.997 \begin{cases} e^{-2\kappa}(1 + \frac{36}{19}\kappa + \frac{18}{19}\kappa^2) & (\kappa \geq 0) \\ e^{1.168\kappa}(1 - 1.26\kappa) & (\kappa < 0). \end{cases} \tag{23c}$$

The phase-matching maximum occurs at $\kappa \simeq -0.069$. In this case $S = 0.0262$. The maximum in the angular distribution occurs at $\Theta_m = 0.64\theta$ for optimum phase-matching. The quantity $[\chi_a^{(3)}(2\omega)(\frac{1}{2}+R_\chi+R_\chi^2)^{1/2}]$ should be used for $\chi^{(3)}(2\omega)$ in the table expressions for χ_{eff}.

The product $(S^{1/2}\chi_{\text{eff}})$ giving one second-harmonic photon/pulse, at optimal phase matching and $\lambda = 1.06$ μm, is $\sim 10^{-23}$ esu for the 1 GW pulse and $\sim 10^{-21}$ esu for the 1 MW/pulse.

In the table, the quantity $S^{1/2}\chi_{\text{eff}}$ is given for the various processes. Direct quadrupole SHG in a cross-polarized, two-beam geometry is included at the bottom for comparison purposes with $S = \pi^{-1}$. The other combinations of susceptibilities describe processes occurring in a single, polarized, focused beam.

Inspection of the table shows that SHG in a pure neutral vapor will be very weak. Direct SHG for a single, polarized, focused beam is almost completely suppressed by the nearly uniform polarization of the beam, while the quadrupole and magnetic-dipole induced dc polarizations give very weak static fields. The magnitudes given in the table indicate that neutral-atom SHG will only be observable (>1 photon/pulse) in very resonant cases. However, if the symmetry of the beam is destroyed by cross polarizing one-half of the beam with respect to the other, or equivalently, using two noncollinear cross-polarized beams, a dramatic increase in second-harmonic power by nearly 10 orders of magnitude should result.[15]

When ionization is present, much stronger processes are possible, led by SHG induced by the electric field arising when photoelectrons are ejected from atoms with finite energy E_v and fly out of the beam. The electric field produced by charge separation driven by radiation forces on the free electrons gives dc induced SHG next in strength, although only at high intensity does the induced dc field driven by the radiation forces approach that arising from kinetic charge separation with modest initial electron energies, (0.3 eV is assumed in the table.)

It should be noted that in comparing the processes giving polarizations proportional to $\chi^{(2)}$ to those involving bulk charge separation for short pulses, the former respond essentially instantaneously, while the field $\vec{E}_S$ builds up quadratically with time as the free electrons move. The short pulse correction factors are given in parentheses in the table, and are used in calculating χ_{eff} where necessary. At high free-electron densities, however, the kinetic separation time τ_k can be quite short (~8.6 ps at $n_e = 10^{16}/\text{cm}^3$ for example), and the time τ_p can be even shorter (~0.2 ps at $n_e = 10^{16}/\text{cm}^3$).

A comparison can now be made between the characteristics of the various mechanisms proposed and the principal features of the SHG observed by MSK, namely the pump intensity dependence, the radiation pattern and polarization of the second-harmonic radiation, and the atomic density dependence.

First of all, the extremely steep intensity dependence at lower intensities $[I(2\omega) \sim I^9(\omega)]$, together with the nonresonant laser tuning, seem to rule out the neutral atom mechanisms, which are very weak in this case and proportional to I^2 or I^4. The most reasonable explanation for the strong intensity dependence is that multiphoton ionization must be essential, and the free electrons generated are responsible for the observed SHG.

The radiation pattern and polarization properties (ring emission, radially polarized for directions parallel or perpendicular to $\vec{E}$) seem to rule out SHG solely due to the second-order response of the nonuniform distribution of free electrons, which would give two lobes along the $\pm\vec{E}$ directions, with the second-harmonic linearly polarized parallel to $\vec{E}$. However, at very high ionization levels this mechanism should make some contribution. The other two free-electron mechanisms (radiation force induced and kinetic charge separation) presumably act in combination to produce a radial electric field $\vec{E}_S$ by depleting the electron density at the center of the pump laser

beam. The second-harmonic induced by $\vec{E}_S$ should emerge in a nonuniform ring pattern, radially polarized for azimuthal directions parallel or perpendicular to $\vec{E}$. These predictions are in accord with the observations of MSK, except since for $\lambda = 1.06$ μm $R_\chi \cong 0.63$, the power around the ring should vary by a factor of ~6.7, and it is unclear why no noticeable nonuniformity was found.

Finally, the N^2 density dependence at high intensity can be neatly accounted for by the radiation force mechanism, since $\vec{E}_S$ in this case is independent of N and $\underline{n}$ for high enough electron densities. Since MSK measured the density dependence at maximum power (~1 GW), quite high electron densities were certainly present. MSK suggest that under these conditions phase matching is achieved independent of N, so that $I(2\omega) \propto N^2$. Under the same phase-matched conditions, the nonuniform free-electron second-order process should give $I(2\omega) \propto \underline{n}^2$. If it is assumed that $\underline{n} \propto N$, this mechanism could also give an N^2 dependence. The kinetic charge separation mechanism described here gives $I(2\omega) \propto N^2 \underline{n}$, since the field $\vec{E}_S \propto \underline{n}^{1/2}$. This could give this mechanism a somewhat stronger dependence on N [$I(2\omega) \propto N^3$, for example, if it is assumed that $\underline{n} \propto N$], but without direct measurements of electron density it is unclear how $\underline{n}$ depends on N for a fixed (high) pump laser power. If $I(2\omega)$ and $\underline{n}$ were measured together it would be very helpful in trying to sort out contributions made by the various free-electron SHG mechanisms. It is not possible to give a reasonable account of the complete pump intensity dependence here since this would require inclusion of both the ionization intensity dependence and saturation effects.

In conclusion, this paper has described processes which can lead to SHG in a focused beam in terms of charge separation produced electric fields inducing SHG via $\chi^{(3)}$ on the one hand, and processes involving the dipole-forbidden second-order susceptibilities on the other. Both types of processes can contribute to SHG, but the former are potentially much stronger when a highly polarized beam is used and even small amounts of photoionization occur.

Note added in proof. Dr. M. Matsuoka has privately informed me that his group has done experimental and theoretical work on SHG in Li vapor. They conclude that ionization induced electric fields are responsible for the effect.

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APPENDIX

Adopting the convention

$$\vec{\mathcal{E}} = \vec{E}_0 + \sum_j \vec{E}(\omega_j) e^{-i\omega_j t} + \vec{E}^*(\omega_j) e^{i\omega_j t}, \tag{A1}$$

$$\vec{\mathcal{P}} = \vec{P}_0 + \sum_j \vec{P}(\omega_j) e^{-i\omega_j t} + \vec{P}^*(\omega_j) e^{i\omega_j t}, \tag{A2}$$

and defining the wave number frequencies $\nu_i \equiv \omega_i / 2\pi c$, the susceptibility χ_Q in Eq. (6) can be written

$$\chi_Q(\omega_1, \omega_2) = -\left(\frac{Ne^3 a_0^4}{h^2 c^2}\right) \frac{1}{30}\left(\sum_{n'p, np} R_{gn'} R^{(2)}_{n'n} R_{ng} f_{pQ} + \sum_{n'd, np} R^{(2)}_{gn'} R_{n'n} R_{ng} f_{dQ}\right), \tag{A3}$$

where R and $R^{(2)}$ refer to radial integrals of r and r^2, respectively,[16] between appropriate pairs of s-, p-, and d-state radial wave functions, (successive pairs of gs, $n'p$, np, and gs in the first sum, and gs, $n'd$, np, and gs in the second, where g refers to the ground state). The symbols N, e, a_0, h, and c are the atomic density, proton charge, Bohr radius, Planck constant, and speed of light, respectively, and electrostatic units are used. The frequency factors are

$$f_{pQ}(n', n, \omega_1, \omega_2) = [(\nu_{n'p} - \nu_1 - \nu_2)(\nu_{np} - \nu_2)]^{-1} + [(\nu_{n'p} + \nu_2)(\nu_{np} + \nu_1 + \nu_2)]^{-1}, \tag{A4a}$$

$$\begin{aligned} f_{dQ}(n', n, \omega_1, \omega_2) = {} & [(\nu_{n'd} - \nu_1)(\nu_{np} + \nu_2)]^{-1} + [(\nu_{n'd} - \nu_1)(\nu_{np} - \nu_1 - \nu_2)]^{-1} \\ & + [(\nu_{n'd} + \nu_1)(\nu_{np} - \nu_2)]^{-1} + [(\nu_{n'd} + \nu_1)(\nu_{np} + \nu_1 + \nu_2)]^{-1}. \end{aligned} \tag{A4b}$$

$\chi'_Q(\omega_1, \omega_2)$ is obtained by replacing f_{pQ} and f_{dQ} in Eq. (A3) with

$$f'_{pQ} = [(\nu_{n'p} + \nu_1)(\nu_{np} - \nu_2)]^{-1} + [(\nu_{n'p} + \nu_2)(\nu_{np} - \nu_1)]^{-1}, \tag{A5a}$$

$$\begin{aligned} f'_{dQ} = {} & [(\nu_{n'd} - \nu_1 - \nu_2)(\nu_{np} - \nu_2)]^{-1} + [(\nu_{n'd} - \nu_1 - \nu_2)(\nu_{np} - \nu_1)]^{-1} \\ & + [(\nu_{n'd} + \nu_1 + \nu_2)(\nu_{np} + \nu_2)]^{-1} + [(\nu_{n'd} + \nu_1 + \nu_2)(\nu_{np} + \nu_1)]^{-1}. \end{aligned} \tag{A5b}$$

For the magnetic dipole susceptibility,

$$\chi_M(\omega_1,\omega_2)=\frac{1}{2\pi}\left(\frac{Ne^2\mu_B a_0^2}{h^2c^2}\right)\tfrac{1}{3}\sum_{np}|R_{ng}|^2 f_M(\omega_1,\omega_2), \tag{A6a}$$

$$f_M(\omega_1,\omega_2)=\frac{1}{\nu_1}\{[(\nu_{np}-\nu_1-\nu_2)(\nu_{np}-\nu_2)]^{-1}-[(\nu_{np}+\nu_2)(\nu_{np}+\nu_1+\nu_2)]^{-1}\}. \tag{A6b}$$

Similarly,

$$\chi'_M(\omega_1,\omega_2)=\left(\frac{-iNe^2\mu_B a_0^2}{h^2c^2}\right)\tfrac{1}{3}\sum_{np}|R_{ng}|^2 f'_M(\omega_1,\omega_2), \tag{A7a}$$

$$f'_M(\omega_1,\omega_2)=\left(\frac{2\nu_{np}(\nu_1-\nu_2)}{(\nu_{np}^2-\nu_1^2)(\nu_{np}^2-\nu_2^2)}\right). \tag{A7b}$$

In the case of second-harmonic generation $\omega_1=\omega_2$ and we must divide the right sides of Eqs. (6a), (6d), and (6e) by 2 to eliminate the redundant permutation. No 2ω magnetic moment is induced since $\chi'_M(\omega,\omega)=0$.

The third-order susceptibility for atoms with s ground states has contributions from both s and d second-intermediate states. For dc induced SHG:

$$\vec{P}(2\omega)=\chi_a^{(3)}(2\omega)\vec{E}(\omega)[\vec{E}(\omega)\cdot\vec{E}_{dc}]+\chi_b^{(3)}(2\omega)\vec{E}_{dc}[\vec{E}(\omega)\cdot\vec{E}(\omega)], \tag{A8}$$

where

$$\chi_a^{(3)}(2\omega)=\frac{Ne^4a_0^4}{(hc)^3}\left(\sum_{n'p,n''d,np}\frac{R_{gn'}R_{n'n''}R_{n''n}R_{ng}}{45}(6f_0+f_1+f_2)+\sum_{n'p,n''s,np}\frac{R_{gn'}R_{n'n''}R_{n''n}R_{ng}}{9}(f_1+f_2)\right) \tag{A9}$$

and

$$\chi_b^{(3)}(2\omega)=\frac{Ne^4a_0^4}{(hc)^3}\left(\sum_{n'p,n''d,np}\frac{R_{gn'}R_{n'n''}R_{n''n}R_{ng}}{45}(-2f_0+3f_1+3f_2)+\sum_{n'p,n''s,np}\frac{R_{gn'}R_{n'n''}R_{n''n}R_{ng}}{9}(f_0)\right). \tag{A10}$$

The frequency factors are

$$f_0=[(\nu_{n'}-2\nu)(\nu_{n''}-2\nu)(\nu_n-\nu)]^{-1}+[\nu_{n'}(\nu_{n''}-2\nu)(\nu_n-\nu)]^{-1}+[(\nu_{n'}+\nu)(\nu_{n''}+2\nu)\nu_n]^{-1}$$
$$+[(\nu_{n'}+\nu)(\nu_{n''}+2\nu)(\nu_n+2\nu)]^{-1}, \tag{A11a}$$

$$f_1=[(\nu_{n'}-2\nu)(\nu_{n''}-\nu)(\nu_n-\nu)]^{-1}+[(\nu_{n'}+\nu)(\nu_{n''}-\nu)\nu_n]^{-1}+[\nu_{n'}(\nu_{n''}+\nu)(\nu_n-\nu)]^{-1}$$
$$+[(\nu_{n'}+\nu)(\nu_{n''}+\nu)(\nu_n+2\nu)]^{-1}, \tag{A11b}$$

$$f_2=[(\nu_{n'}-2\nu)(\nu_{n''}-\nu)\nu_n]^{-1}+[(\nu_{n'}+\nu)(\nu_{n''}-\nu)(\nu_n-\nu)]^{-1}+[(\nu_{n'}+\nu)(\nu_{n''}+\nu)(\nu_n-\nu)]^{-1}$$
$$+[\nu_{n'}(\nu_{n''}+\nu)(\nu_n+2\nu)]^{-1}, \tag{A11c}$$

and the indices n' and n refer to p states, and n'' refers to d states in the first sum and s states in the second sum. The vector form given in Eq. (A8) and the following equations, (A9), (A10), and (A11) are derived using the basic relations between the tensor components given by group theory (see, for example, Yuratich and Hanna[17]). For Cartesian tensors, if only d second-intermediate state contributions are included,

$$\tfrac{3}{4}\chi^{(3)}_{1111}=-\tfrac{3}{2}\chi^{(3)}_{1122}=\chi^{(3)}_{1212}=\chi^{(3)}_{1221}, \tag{A12}$$

and similarly, if only s second-intermediate state contributions are included,

$$\chi^{(3)}_{1111}=\chi^{(3)}_{1122}\quad\chi^{(3)}_{1212}=\chi^{(3)}_{1221}=0. \tag{A13}$$

Note that for a given set of intermediate states, $f_0\to f_1\to f_2$ as $\omega\to 0$, so that $\chi_a^{(3)}(0)=2\chi_b^{(3)}(0)$. Also, it can be seen that $\chi_b^{(3)}(2\omega)$ has two-photon resonances to intermediate s states (in f_0) not present in $\chi_a^{(3)}(2\omega)$ (in f_1 or f_2).

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