There are two collisional processes which can also produce the ionization observed. Direct collisional excitation of the form $Na^*(3p) + Na^*(3p) \rightarrow Na^*(5s) + Na(3s)$ followed by photoionization of the $Na^*(5s)$ is energetically possible but unlikely to have a cross section large enough ($> 10^{-15}$ cm^2) to explain the amount of ionization observed in the experiment because the energies are off resonance by a relatively large amount (700 cm^{-1}). A more promising possibility is that of collisionally induced radiative transitions.[19] In this case the ionization would occur as a photon absorption during the collision of two $Na^*(3p)$ atoms resulting in $Na^*(3p) + Na^*(3p) + h\nu \rightarrow Na(3s) + Na^+(2p^6) + e$. The process is closely related to the work of Lidow *et al.* on collision-induced transitions between discrete levels.[20]

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Optical Quadrupole Sum-Frequency Generation in Sodium Vapor

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We show that second-order coherent sum-frequency generation via quadrupole transitions in metal vapors can be easily detected. The process is as strong as the allowed third-order processes. Our experimental results agree very well with theoretical predictions.

Nonlinear optical effects in atomic vapors have recently been studied quite extensively.[1-4] Because of their large resonant nonlinear susceptibilities, wide ranges of transparency, and high optical breakdown thresholds, atomic vapors are excellent nonlinear media for generation of new coherent radiation. Thus, in atomic vapors, third-harmonic generation has been used to generate vacuum uv radiation, four-wave mixing has been used to generate tunable vacuum uv and infrared,[2] and stimulated Raman scattering has been used to generate tunable infrared.[3] Nevertheless, in all cases reported to date, third-order and occasionally odd-higher-order[4] nonlinearities of the vapors are always responsible for the observed effects. The second-order nonlinear

processes, being forbidden by symmetry under the electric-dipole approximation, were believed to be too weak to be significant. We realize, however, that in many cases, if electric-quadrupole transition matrix elements are taken into account in nonlinear susceptibilities,[5] then an nth-order electric-dipole-forbidden process can often be as strong as or stronger than an $(n+1)$th-order allowed process. Hänsch and Toschek[6] considered collinear sum-frequency generation (SFG) due to dipole-forbidden susceptibilities, and concluded that it will not occur. They, however, did not consider the noncollinear case. In this paper, we present theory and experiment to show that noncollinear second-order SFG in atomic vapors is in fact easily observable. The effect may be used to generate coherent tunable uv radiation over certain narrow ranges.

We consider the case of sodium with two pump laser frequencies ω_1 and ω_2 close to the $3s \rightarrow 3p$ and the $3p \rightarrow 4d$ transitions, respectively. Under the electric-dipole approximation, the second-order nonlinear susceptibility $\vec{\vec{\chi}}^{(2)}$ should vanish. But if we include the electric-quadrupole matrix element between $4d$ and $3s$, then we have

$$\vec{\vec{\chi}}^{(2)} \cong -i(\vec{k}_1+\vec{k}_2)\cdot\frac{Ne^3}{\hbar^2}\sum_{3p_{1/2},3/2}\frac{\langle 3s|\vec{r}\vec{r}|4d\rangle\langle 4d|\vec{r}|3p\rangle\langle 3p|\vec{r}|3s\rangle}{(\omega_1-\omega_{3p})(\omega_3-\omega_{4d}+i\Gamma)} \equiv -i(\vec{k}_1+\vec{k}_2)\cdot\vec{\vec{\chi}}_Q^{(2)}, \tag{1}$$

where $\omega_3=\omega_1+\omega_2$, N is the number of atoms per unit volume, and Γ is an appropriate half-width for the $4d$-$3s$ transition. $\vec{\vec{\chi}}_Q^{(2)}$ is a fourth-rank susceptibility tensor relating two applied electric fields to the induced quadrupole moment density.[5] Since all the matrix elements and transition frequencies in Eq. (1) are known,[7] we can easily calculate $|\chi^{(2)}|$ with given ω_1 and ω_2. For $\omega_1-\omega_{3p_{1/2}}=-10\ \mathrm{cm}^{-1}$, $\omega_3=\omega_{4d}$, and $\Gamma=0.15\ \mathrm{cm}^{-1}$, we find $|\chi^{(2)}|/N=1.6\times10^{-24}$ esu. This value can be compared with the value of $|\chi^{(3)}\boldsymbol{E}|/N$ for a third-order mixing process. For example, in infrared generation by four-wave mixing in potassium, Sorokin and co-workers[2,8] had $|\chi^{(3)}E|/N\sim10^{-25}$ esu for $|E|=20$ esu corresponding to a 100 kW/cm^2 beam. Therefore, we should expect this second-order SFG to be readily observable.

The nonlinear polarization for SFG is

$$\vec{P}^{(2)}(\omega_3=\omega_1+\omega_2)=\vec{\vec{\chi}}^{(2)}:\vec{E}_1(\omega_1)\vec{E}_2(\omega_2)=-i(\vec{k}_1+\vec{k}_2)\cdot\vec{\vec{\chi}}_Q^{(2)}:\vec{E}_1\vec{E}_2. \tag{2}$$

Let $\vec{k}_1+\vec{k}_2\cong\vec{k}_3$ be along $\hat{Z}$. From symmetry arguments and the requirement that $\vec{E}_1$ must be perpendicular to $\vec{k}_1$ in an isotropic medium, we immediately find that $(\chi_Q^{(2)})_{xzzx}=(\chi_Q^{(2)})_{yzzy}=(\chi_Q^{(2)})_{xzxz}=(\chi_Q^{(2)})_{yzyz}$ are the only elements of $\vec{\vec{\chi}}_Q^{(2)}$ responsible for SFG. Then, in order to observe SFG, the two pump beams must be noncollinear and at least one of them must have a field component in the plane of $\vec{k}_1$ and $\vec{k}_2$. If either beam is polarized along $\vec{k}_1\times\vec{k}_2$, then the sum-frequency output should also be polarized along $\vec{k}_1\times\vec{k}_2$. Finally, SFG vanishes when $\omega_1=\omega_2$ and both $\vec{E}_1$ and $\vec{E}_2$ lie in the plane of $\vec{k}_1$ and $\vec{k}_2$.

The above SFG process can be phase matched if $\omega_1-\omega_{3p\text{-}3s}<0$ by varying the angle θ between $\vec{k}_1$ and $\vec{k}_2$. From $\vec{k}_1+\vec{k}_2=\vec{k}_3$, we obtain, for the phase-matching angle θ_p,

$$\theta_p^2=2[(1+\omega_1/\omega_2)\Delta n(\omega_1)+(1+\omega_2/\omega_1)\Delta n(\omega_2)], \tag{3}$$

where

$$\Delta n(\omega_{1,2})=n(\omega_{1,2})-1\cong\frac{-2\pi Ne^2}{\hbar}\sum_{3p_{1/2},3/2}\frac{|\langle 3s|x|3p\rangle|^2}{\omega_{1,2}-\omega_{3p}} \tag{4}$$

and we have used the approximations $\theta_p\ll1$ and $n(\omega_3)=1$. Equations (3) and (4) show that θ_p^2 should increase linearly with N, the sodium density.

The output power of SFG is a maximum when $\vec{E}_1$ and $\vec{E}_2$ are orthogonal and one of them lies in the plane of $\vec{k}_1$ and $\vec{k}_2$. If we assume that both pump beams have Gaussian transverse profiles with variance σ, then the output power as a function of θ is given approximately by

$$P_3(\omega_3)=(4\pi^3\omega_3^4/c^5)P_1P_2|(\chi_Q^{(2)})_{xzxz}|^2\exp[-2\sigma^2(\Delta k)^2/\theta^2], \tag{5}$$

where $\Delta k\equiv(k_1+k_2)\cos(\theta/2)-k_3$ is the phase mismatch. Equation (5) shows that P_3 is linearly proportional to the laser powers P_1 and P_2 and to N^2. At phase matching, $\Delta k=0$, P_3 is independent of σ and θ. For fixed k_1 and k_2, the phase-matching factor in Eq. (5) can also be expressed as a Gaussian in $\theta-\theta_p$,

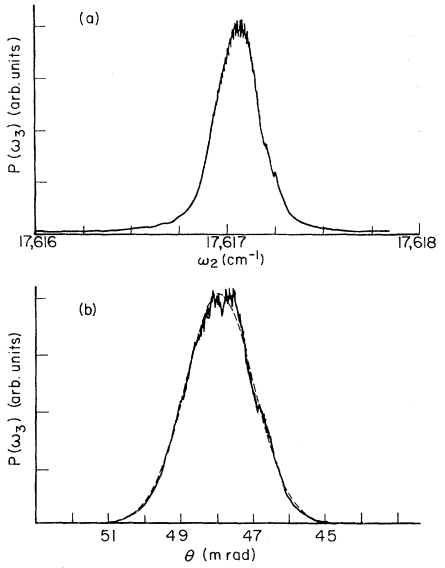

FIG. 1. (a) Sum-frequency output $P(\omega_3)$ as a function of ω_2 showing the sharp resonance at $\omega_1+\omega_2=\omega_{4d}$ $=34\,548.8$ cm^{-1}. $P_1=2$ W; $P_2=25$ W; $\theta=47.9$ mrad; N $=1.6\times10^{16}$ cm^{-3}. (b) Phase-matching curve $P(\omega_3)$ versus θ. $P_1=2$ W; $P_2=25$ W; $\omega_1-\omega_{3p_{1/2}}=-25.6$ cm^{-1}; ω_1 $+\omega_2=\omega_{4d}$; $N=1.6\times10^{16}$ cm^{-3}. The dashed curve is a theoretical curve calculated from Eq. (5), with $\sigma=0.1$ mm.

with variance $\sigma_\theta=2/(k_1+k_2)\sigma$. The output power should also show a sharp resonance at $\omega_3=\omega_{4d}$ resulting from the resonant denominator $\omega_3-\omega_{4d}$ $+i\Gamma$ in $\chi^{(2)}$.

In the above theoretical discussion, we have not considered absorption, laser-induced saturation, self-defocusing, etc. These effects should become important when the laser intensities are too strong and as ω_1 approaches the $3s\rightarrow3p$ transitions.

We have carried out an experiment to verify the above predictions. Two flash-pumped dye lasers were used as the pump sources; one was tunable around 16 956 cm^{-1} and the other around 17 593 cm^{-1}. Each had a linewidth of about 0.3 cm^{-1}. The two beams were focused by long-focal-length lenses into a common 0.24-mm spot in a heat pipe containing sodium vapor with pressure varying from ~0.3 to 10 Torr. The divergence of the focused beams was about 3 mrad. The two beams crossed each other with an angle θ ~40 mrad in the focal region. The coherent SFG from the sodium vapor was monitored by a detection system composed of a monochromator, a photodetector, and a gated integrator. Variables in the experiment were the laser frequencies ω_1 and ω_2, the laser powers P_1 and P_2, the angle θ, and the sodium vapor pressure (or density N).

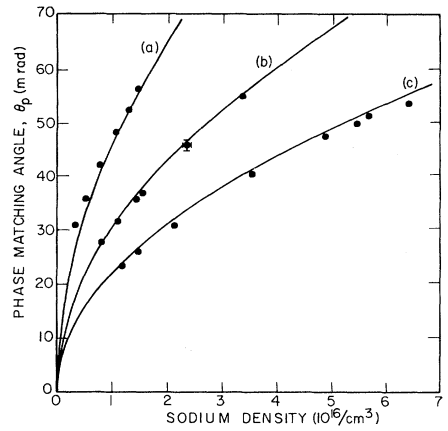

FIG. 2. Phase matching angle θ_p versus the sodium density N at $\omega_1+\omega_2=\omega_{4d}$ and curve a, $\Delta\omega_1\equiv\omega_1-\omega_{3p_{1/2}}$ $=-14.9$ cm^{-1}; curve b, $\Delta\omega_1=-40.8$ cm^{-1}; curve c, $\Delta\omega_1=-80.4$ cm^{-1}. The dots are the data points and the curves are calculated from Eq. (3).

When $\omega_1+\omega_2$ was tuned near ω_{4d}, and the angle θ was adjusted close to the phase-matching angle θ_p, we could easily detect, in addition to the strong visible $3p\rightarrow3s$ fluorescence, a coherent sum-frequency uv beam at ~34 549 cm^{-1}, even if the laser powers were as small as 1 W. We found that the predicted selection rules for SFG were indeed strictly obeyed. The sum-frequency output was polarized along $\vec{k}_1\times\vec{k}_2$. Since $\omega_1\cong\omega_2$ in our case, the output was very small if both pump beams were polarized in the plane of $\vec{k}_1$ and $\vec{k}_2$. We obtained the maximum output signal when one beam was polarized along $\vec{k}_1\times\vec{k}_2$ and the other in the plane of $\vec{k}_1$ and $\vec{k}_2$.

With ω_1 fixed and ω_2 varied over a narrow range, the phase-matching angle θ_p, as given by Eq. (3), should remain essentially unchanged, and the sum-frequency output should have a sharp resonance at $\omega_1+\omega_2=\omega_{4d}$. We show in Fig. 1(a) such a resonant curve obtained with $P_1=2$ W and $P_2=25$ W. In this case, the width of the curve was apparently dominated by the laser spectral widths. A typical phase-matching curve, obtained by varying the angle θ and keeping the other variables fixed, is shown in Fig. 1(b), together with the theoretical phase-matching curve calculated from Eq. (5) using $\sigma=0.1$ mm. This σ corresponds to an overlap-region diameter of ~0.2 mm, which agrees with the measured value within the experimental uncertainty. The peak of the curve appears at an angle θ_p within 1.2 mrad of the value predicted by Eq. (3).

We also measured the phase-matching angle θ_p as a function of the sodium density N and the la-

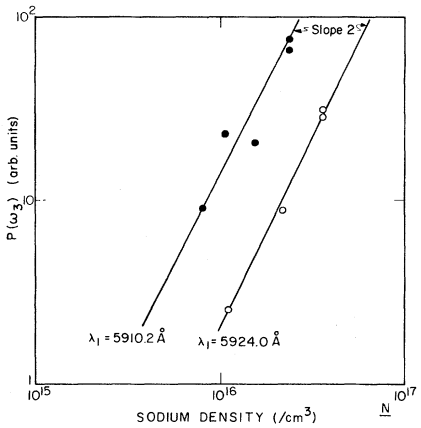

FIG. 3. Phase-matched sum-frequency output $P(\omega_3)$ as a function of sodium density N at $\omega_1 - \omega_{3p_{1/2}} = 40.8$ and -80.4 cm^{-1}. The other parameters fixed in the experiment are $P_1 \simeq 2$ W, $P_2 \simeq 20$ W, and $\omega_1 + \omega_2 = \omega_{4d}$.

ser frequency ω_1. The results are shown in Fig. 2 in comparison with the theoretical curves calculated from Eq. (3). The agreement between theory and experiment is within 4 mrad in all cases. The phase-matched sum-frequency output power was measured as a function of N and ω_1. As shown in Fig. 3, the results show both the predicted N^2 dependence and the intermediate-state resonant enhancement due to the denominator $\omega_1 - \omega_{3p}$ in $\chi^{(2)}$.

At sufficiently low laser powers (depending on $\omega_1 - \omega_{3p}$ and N), the sum-frequency output P_3 was linear with P_1 and P_2 as expected. With $P_1 = P_2 = 10$ W at $\omega_1 - \omega_{3p_{1/2}} = -10$ cm^{-1} and $\omega_1 + \omega_2 = \omega_{4d}$, the phase-matched output was approximately 1 μW, in reasonable agreement with the value predicted from Eq. (5). At high P_1 (for example, above 100 W at $\omega_1 - \omega_{3p_{1/2}} = -40$ cm^{-1} and $N = 10^{16}$ cm^{-3}), the laser beam at ω_1 strongly self-defocused in the cell. As a result, the output P_3 versus P_1 was appreciably lower than the theoretical prediction of Eq. (5); the phase-matching curve P_3 versus θ also became appreciably broader. Since ω_2 was always sufficiently far away from resonance, no such self-defocusing effect occurred for the ω_2 laser beam for P_2 as high as 500 W. However, when the product P_1P_2 was sufficiently large, a broadening of the resonant curve, P_3 versus ω_2, in Fig. 1(a) was clearly observed. This was direct evidence of saturation due to resonant two-photon transitions[9] from $3s$ to $4d$ in sodium. Quantitative results and discussion on self-defocusing and saturation of two-photon transitions will be given elsewhere.

In conclusion, we have successfully demonstrated for the first time that resonant second-order sum-frequency generation in atomic vapor, though forbidden, is easily observable. Our experimental results agree very well with the theoretical predictions. Similar processes such as difference-frequency generation and parametric amplification via quadrupole transitions should also occur and are now under investigation.

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