# Observation of resonantly enhanced sum-frequency generation involving sodium Rydberg states

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A large, dc-electric-field-induced nonlinear optical susceptibility is exploited to produce ultraviolet radiation in the range 2453–2476 Å by the process of sum-frequency generation in sodium. The interaction is resonantly enhanced at the first intermediate level by the $3\,^2P_{3/2}$ state and at the second intermediate level by a Rydberg state. Conversion efficiencies of $10^{-5}$ have been obtained; improvement of this value by a factor of $10^3$ should be possible.

It has been known for many years that the application of a dc electric field to a medium possessing inversion symmetry can lead to the existence of a second-order nonlinear optical susceptibility $\chi^{(2)}$, which in the absence of such a field would vanish by reasons of symmetry.[1–4] In most previous demonstrations of this phenomenon, only nonresonant interactions were studied, and hence only modest values of the induced nonlinearity were obtained. Recently, however, it was proposed that extremely large values of $\chi^{(2)}$ could be obtained by applying a dc electric field to an atomic vapor and exploiting the strong resonance enhancement that occurs when the incident lasers are tuned to atomic-transition frequencies.[5] Furthermore, it was shown that only modest values of the dc field are required if the interaction involves atomic Rydberg states. In this Letter, we present the first reported experimental verification of this process, and we briefly discuss potential applications of this interaction.

The highly excited, one-electron states of atoms, known as Rydberg states, possess several properties that suggest their usefulness in mediating tunable, resonantly enhanced, nonlinear optical interactions. These properties include closely spaced energy levels, large dc Stark effects, and large electric-dipole transition moments connecting nearby levels. The first two properties offer the potential of continuously tunable, resonantly enhanced nonlinear optical mixing processes since the Rydberg levels can be Stark tuned into exact coincidence with any desired resonance frequency.

The nonlinear optical process considered in this Letter involves the mixing of optical fields at frequencies $\omega_1$ and $\omega_2$ to produce a sum-frequency output at frequency $\omega_3 = \omega_1 + \omega_2$, as illustrated in Fig. 1. The resonant contribution to the nonlinear susceptibility describing this process is given in lowest order by[6]

$$\chi^{(2)} = \frac{N\mu_{ik}\mu_{kj}\mu_{ji}}{2\hbar^2(\omega_{ji} - \omega_1)(\omega_{ki} - \omega_2 - \omega_1)}, \qquad (1)$$

where $N$ denotes the number density of atoms in the initial state, $\mu_{\alpha\beta}$ denotes the electric-dipole matrix element connecting levels $\alpha$ and $\beta$, and the transition frequencies $\omega_{\alpha\beta}$ are defined by Fig. 1. If each of the levels $i$, $j$, and $k$ has definite parity, at least one of the $\mu_{\alpha\beta}$'s must be equal to zero, and hence $\chi^{(2)}$ vanishes. However, a dc electric field can mix states of opposite parity, permitting the existence of a nonzero value of $\chi^{(2)}$. It has been shown[7] for sodium Rydberg levels with $n \cong 16$ that field strengths of the order of only 1000 V/cm are required to obtain complete mixing of such levels.

An estimate of the magnitude of the resulting nonlinearity can be obtained by treating the Rydberg levels in the hydrogenic approximation. In the presence of a dc electric field, the Schrödinger equation describing atomic hydrogen is separable in parabolic coordinates, leading to energy eigenstates $|n_1, n_2, m\rangle$ specified by electric quantum numbers $n_1$ and $n_2$ and magnetic quantum number $m$, which are related to the principal quantum number $n$ by

$$n = n_1 + n_2 + |m| + 1. \qquad (2)$$

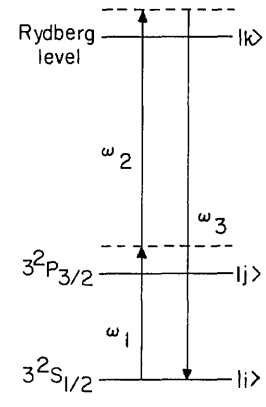


Fig. 1. Optical waves at frequencies $\omega_1$, $\omega_2$, and $\omega_3 = \omega_1 + \omega_2$ interact by means of the nonlinear response of an atom with energy eigenstates $|i\rangle$, $|j\rangle$, and $|k\rangle$. In the experimental work, these states correspond to the $3\,^2S_{1/2}$, $3\,^2P_{3/2}$, and a Rydberg level, respectively.

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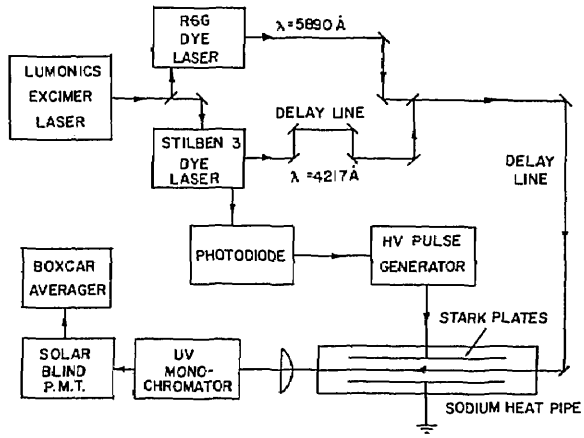


Fig. 2. Block diagram of experimental setup.

The energy eigenvalues associated with state $|n_1, n_2, m\rangle$ are given in inverse centimeters by [8]

$$W = \frac{-1.097 \times 10^5}{n^2} + \frac{E}{15620} n(n_1 - n_2), \qquad (3)$$

where $E$ denotes the applied electric field strength in volts per centimeter. Closed-form expressions for the values of the electric-dipole matrix elements connecting these levels are similarly obtained. These expressions should provide good approximate values for the matrix elements connecting the Stark-mixed Rydberg states of any atom since Rydberg-state wave functions are nearly hydrogenic because of the limited penetration of the excited electron into the atomic core. These closed-form expressions are rather complicated, however, and are not reproduced here; they are displayed in full in Ref. 5. Instead, let us consider as a numerical example a mixing process that is resonantly enhanced by levels with principal quantum numbers equal to 3, 4, and 13. We choose these levels because they correspond roughly to those used in our experimental work with sodium. We find by explicit evaluation that the product of the three matrix elements appearing in Eq. (1) is maximized for an interaction involving the Stark sublevels $|2, 0, 0\rangle$, $|3, 0, 0\rangle$, and $|12, 0, 0\rangle$ and that the value of this product is $-0.18e^3a_0^3$, where $e$ denotes the charge of the electron and $a_0$ denotes the first Bohr radius. Assuming an initial-state population of $1 \times 10^{14}$ atoms/cm$^3$ and equal detunings of 5 GHz, the nonlinear susceptibility of Eq. (1) is predicted to have a value of $1.5 \times 10^{-7}$ esu, which is several hundred times greater than that of potassium dihydrogen phosphate (KDP).

Figure 2 shows the experimental setup. A commercial excimer laser (Lumonics Model TE-861-2) operating at 308 nm with XeCl is used to pump two Littman-style[9] tunable dye lasers. One dye laser utilizes rhodamine 6G and the other Stilben 3, and both produce output pulses of a few nanoseconds' duration. A stray reflection from one of the lasers triggers a pulse generator that applies 1500-V pulses of 1-nsec rise time and ~10-nsec duration to Stark plates located inside a sodium heat pipe. A short pulse duration was chosen to avoid the establishment of an electrical breakdown in the vapor. Synchronization among the high-voltage pulse and the two laser pulses is accomplished through the use of optical delay lines. The output from the heat pipe is focused onto the entrance slit of an ultraviolet monochromator, which, together with two interference filters and a solar-blind photomultiplier, provides a discrimination of $10^9$ between the incident laser pulses and the generated sum frequency.

In the experiment, the rhodamine 6G dye laser was tuned to the $D_2$ line ($3\,^2S_{1/2} \rightarrow 3\,^2P_{3/2}$), whereas the Stilben 3 laser was tuned to the transition connecting the $3\,^2P_{3/2}$ level to one of the Rydberg levels listed in Table 1. Precise tuning of the Stilben 3 dye laser was achieved by applying a 5-V dc potential between the Stark plates and maximizing the photoionization current. At this point, the 5-V potential was replaced by the high-voltage pulse generator, and strong sum-frequency generation was observed for each of the cases listed in Table 1. The generated ultraviolet signal is emitted as a collimated beam at the expected wavelength and with a pulse length equal to that of the dye laser (to within the 2.5-Å resolution of the monochromator and the 6-nsec rise time of the photomultiplier). The signal vanishes if either of the dye lasers is blocked or if the high-voltage pulse generator is turned off. A weak ultraviolet signal is observed in the absence of the high-voltage pulse only if the laser beams are tightly focused inside the sodium-vapor cell. Second-harmonic generation in the absence of applied dc fields was reported recently[10] and is currently the subject of considerable interest. A strong sum-frequency signal is observed only when the lasers are at or near resonance. In addition, the sum-frequency signal displays a strong dependence on the temporal overlap of the laser and high-voltage pulses, as shown in Fig. 3. The relative timing of the pulses was varied by changing the length of the coaxial cable connecting the triggering photodiode and the high-voltage pulse generator. A sum-frequency signal is observed only if the laser and high-voltage pulses are applied simultaneously to the sodium vapor. These observations rule out the possibility that the observed signal is due to fluorescence excited by the lasers or by a high-voltage discharge.

A typical measured value of the power-conversion efficiency is ~$10^{-5}$. No attempt was made to phase match the nonlinear mixing process, and hence the co-

**Table 1. Rydberg Levels Used to Resonantly Enhance Sum-Frequency Generation in Sodium[a]**

| Rydberg Level | $\lambda_2$ (Å) | $\lambda_3$ (Å) |
|---|---|---|
| 11*p* | 4272 | 2476 |
| 12*s* | 4254 | 2470 |
| 11*f* | 4243.5 | 2467 |
| 11*d* | 4243.2 | 2467 |
| 12*p* | 4239 | 2465 |
| 13*s* | 4224 | 2460 |
| 12*d* | 4217 | 2458 |
| 14*s* | 4202 | 2453 |

[a] $\lambda_2$ gives the wavelength of the Stilben 3 dye laser, which connects the $3\,^2P_{3/2}$ level with the Rydberg level. $\lambda_3$ gives the measured wavelength of the sum-frequency radiation, which is in good agreement with theory.

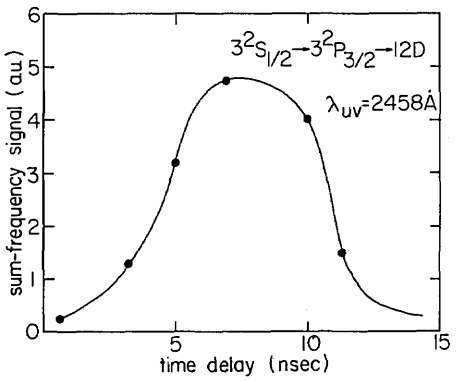


Fig. 3. Intensity of the sum-frequency signal plotted against the time delay between the high-voltage pulse and the optical pulses. The origin of the time-delay scale is arbitrary.

herence length of the interaction was rather short. The estimated value of this length is of the order of 1 mm. Through the use of phase matching, we hope to increase the coherence length to the full 5-cm length of the interaction region, leading to an increase in the efficiency by a factor of ~2500. The inferred value of $\chi^{(2)}$ is $10^{-8}$ esu, which is ~10 times larger than that of KDP but 10 times smaller than the predicted value quoted above. This discrepancy is likely to result from several distinct effects: (1) the theory assumes the hydrogenic approximation, whereas the experiment was conducted in sodium, (2) the dye-laser stability and linewidth were perhaps insufficient to permit complete resolution of the extremely narrow resonances of the Stark-split Rydberg levels, and (3) the applied field strength obtainable from the present apparatus has been determined to be too small to mix Rydberg states of opposite parity completely. Through the use of higher dc field strengths, a complete mixing of opposite-parity states can be obtained, leading to increased efficiency and broader wavelength tunability.

The technique described in this Letter offers the possibility of efficient nonlinear mixing even at low power levels because of the extremely large values of $\chi^{(2)}$ that can be obtained. In addition, this technique can be applied at wavelengths at which conventional mixing crystals do not transmit. Generation of shorter ultraviolet wavelengths can be obtained by using atoms other than sodium, and generation of submillimeter radiation is possible through difference-frequency mixing.

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