each wave since the selection rule $\Delta m_F = 0$ forbids the absorption of two σ^+ or two σ^- photons.[1] One sees that the experimental signal is equal to zero outside the frequency range of the two peaks. The Doppler background disappears by using this polarization configuration. We have performed another test by removing the mirror and observing that the signal disappears since the atom cannot absorb two photons of a σ^+ traveling wave.

These experiments present evidence that we can eliminate Doppler broadening by two-photon transitions. Nevertheless, because of the relatively large spectral bandwidth of our laser, we are not yet able to attain the ultimate precision inherent in this method.

An improvement of our laser stability will permit a comparison between this method and other methods of spectroscopy without Doppler broadening.

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Observation of Two-Photon Absorption without Doppler Broadening on the 3S-5S Transition in Sodium Vapor*

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The $3S$-$5S$ transition of Na atoms is induced by absorption of two photons, one each from two circularly polarized beams traveling in opposite directions through the vapor. The beams are derived from a tunable, narrow-band pulsed dye laser. Doppler broadening is absent and the hyperfine structure is resolved. The hyperfine interaction constant A_{5S} in the $5S$ state of the Na^{23} atom is determined to be 101 ± 15 MHz.

Several authors[1-3] have recently called attention to the predicted absence of Doppler broadening in two-photon absorption processes, if the two photons have equal and opposite momenta. In this note we report the experimental observation of this effect for the $3S$-$5S$ transition in Na vapor. The novel technique permits high-resolution optical spectroscopy of many highly excited states, with energies up to twice the laser frequency, in atomic and molecular spectra. It complements and extends the high-resolution "Lamb-dip" techniques, based on saturation of one-photon transitions.[4]

Two-photon absorption may be described phenomenologically by the imaginary part of a nonlinear susceptibility, $i\chi^{(3)\prime\prime}$. This nonlinearity is relatively large in the alkali-metal vapors, and a variety of other related nonlinear optical processes, such as third-harmonic generation and frequency mixing, have recently been reported.[5-7] The thrust of those investigations was directed toward ultraviolet generation, infrared detection, or other nonlinear optical devices. This note links the nonlinear optical properties of alkali vapors to high-resolution spectroscopy. Since the precise value of the two-photon absorption cross section is not of primary present interest, a rough evaluation of the expected magnitude of the effect should suffice. Tabulated values of the matrix elements[7] and standard expressions for the two-photon absorption cross section indicated that under the experimental conditions described below about $1:10^7$ of the incident beam intensity would be absorbed by two-photon processes in the cell. The occurrence of these events is most conveniently detected by subsequent fluorescence radiation from the excited Na atoms. A cross section of this magnitude should provide an ample signal-to-noise ratio. This type of experiment has become feasible because of the availability of pulsed high-power, narrow-band, tunable dye lasers.

If the laser frequency is tuned so that $2\hbar\omega$ corresponds to the separation of two energy levels with the same parity, each atom in the gas, regardless of its thermal velocity, is at resonance for the two-photon absorption process in which one photon is taken from each of two counter-

propagating beams. The linear Doppler shift for the absorption of a photon from one beam is exactly compensated by the opposite linear Doppler shift for photons from the other beam. In general, this narrow resonance, without inhomogeneous Doppler broadening, is superimposed on a Doppler-broadened background, in which two quanta are absorbed from a beam moving in one direction.[1]

In our experiment this background was eliminated by using circularly polarized light beams. For an S-to-S transition we obviously have the selection rule $\Delta m = 0$. Absorption of the two photons from one circularly polarized light beam could occur only for $\Delta m = \pm 2$ transitions. Thus the two oppositely moving light beams must be given opposite helicities with respect to a fixed laboratory frame to allow $\Delta m = 0$ two-photon transitions. The two counterpropagating beams are both circularly polarized in the same sense, because convention defines sense with respect to the direction of propagation. If the light beams moving in opposite directions had slightly different frequencies, ω_1 and ω_2, respectively, the Doppler-broadened background could also be eliminated by having $\hbar(\omega_1 + \omega_2)$ fulfill the resonance condition, while $2\omega_1$ and $2\omega_2$ fall outside the Doppler profile.

Since $\hbar\omega + E_{3S} - E_{3P}$ is large compared to the multiplet splitting of the $3P$ state, and the same holds true for all other virtual intermediate states ($4P$, etc.) in our experiments, the effect of spin-orbit coupling on the two-photon transition is negligible in first approximation. Since the electric dipole matrix elements themselves do not change the electron and nuclear spin states, it may be concluded that the induced transitions obey the selection rule $\Delta F = 0$. No changes or projections of the spin-state configurations occur. The allowed two-photon transitions form a hyperfine doublet. From the $F = 2$, $3S$ state we can only reach the $F = 2$, $5S$ states, and similarly $F = 1$. Because of the statistical weight, the doublet components should have the intensity ratio 5:3.

The two-photon absorption cross section could be considerably enhanced by choosing two different frequencies for the two counterpropagating light beams. If ω_1 is chosen close to the resonant frequency of the $3S \rightarrow 3P$ transition, a large increase in the two-photon absorption cross section would be observable in addition to a breakdown of the ΔF selection rule.

Figure 1 depicts the experimental apparatus.

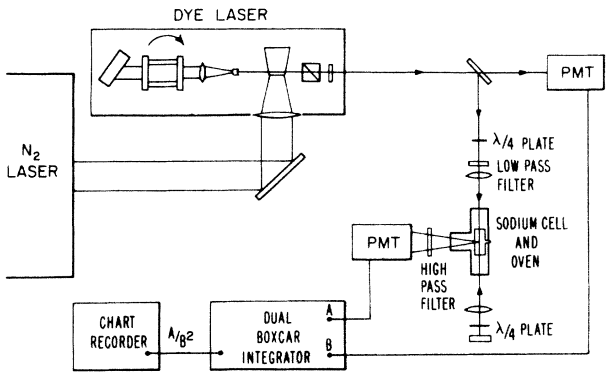

FIG. 1. Schematic diagram of the experimental apparatus used to detect two-photon absorption without Doppler broadening. The curved arrow represents the direction of rotation of the Fabry-Perot etalon. The photomultipliers employed as light detectors are labeled PMT. Feedback of the reflected pulse into the laser cavity was avoided by providing sufficient optical delay.

A Molectron UV-1000 nitrogen laser pumps a modified Hänsch-type dye laser.[8] One reflector in the dye-laser cavity is a grating which limits the width of the output spectrum to roughly 0.5 cm^{-1} near $\lambda = 602.23$ nm, corresponding to half the energy separation of the $3S$ and $5S$ levels. Within the cavity is a high-finesse plane Fabry-Perot etalon with a 5.00-cm plate spacing. This etalon allows the laser to oscillate in a number of bands of width 80 MHz separated by the 3000-MHz free spectral range of the interferometer. As the etalon is rotated, the frequencies of these modes move through the gain band permitted by the grating.

The 2.4-kW, 3-nsec length dye-laser pulses are focused by a 15-cm–focal-length lens into the sodium-vapor sample. A quarter-wave plate is placed between the laser and sodium cell to convert the incident radiation to circular polarization. The transmitted beam is collimated and passed through a second $\lambda/4$ plate placed before the mirror which reflects the beam back into the vapor cell. This second $\lambda/4$ plate assures that both counterpropagating beams have the same sense of circular polarization. No signal is observed if it is omitted.

The spontaneous emission radiated at 330 nm by the $4P$-$3S$ transition following the excitation of the $5S$ level is detected by an EMI 9750Q photomultiplier. Sodium pressures of roughly 5 mTorr are required for adequate signal levels. Colored-glass filters reject extraneous long-wavelength radiation.

To scan over the resonance, the etalon within the dye-laser cavity is rotated about a vertical axis. A dual-channel boxcar integrator averages the height of the pulses produced by the photomultiplier monitoring the sodium fluorescence and also the heights of the pulses produced by a detector monitoring the incident laser power. A network of operational amplifiers divides the average intensity of the fluorescence by the square of the average laser intensity, and the result is plotted as a function of the etalon angle.

Whenever the sum of the frequency of two etalon modes equals the frequency of a sodium transition, the fluorescence increases dramatically. After the etalon modes shift by an amount equal to half of the free spectral range, another pair will come into resonance and the spectrum repeats. This effect permits a calibration of the frequency scale in terms of the accurately known plate separation. The resulting frequency scale is not linear but displays the familiar $\Delta\nu \propto (\text{angle})^2$ dependence seen in photographic Fabry-Perot spectra.

The experimental fluorescence signals in Fig. 2(b) show the resolved hyperfine doublet with an intensity ratio of 5:3. The width of 220 MHz of the components corresponds to the attained laser frequency stability, which could be improved further. For comparison the observed Doppler-broadened line profile is shown in Fig. 2(a), when only one light beam with linear polarization is used. The resolved doublet splitting is

$$\Delta\nu = \tfrac{1}{2}(\Delta\nu_{\mathrm{hfs}}{}^{3S} - \Delta\nu_{\mathrm{hfs}}{}^{5S}) = 784 \pm 15 \text{ MHz}.$$

Since the $\Delta\nu_{\mathrm{hfs}}{}^{3S} = 1772$ MHz, we obtain for the hyperfine interaction constant

$$A_{5S} = \tfrac{1}{2}\Delta\nu_{\mathrm{hfs}}{}^{5S} = 102 \pm 15 \text{ MHz}.$$

This value is in fair agreement with extrapolations of recent experimental data for the hyperfine splitting in excited S states of alkali atoms obtained by cascade rf spectroscopy[9] and with theoretical calculations of S-state wave functions.[10]

The data presented here should be considered only as an early example of high-resolution two-photon absorption spectroscopy. The extension to other high-lying S and D states is obvious. Numerous variations suggest themselves, including the application of an external magnetic field and variations of the frequencies and states of polarizations of the two light beams. In particular, two-photon optical-pumping techniques could be used in conjunction with applied rf and microwave fields, to probe the interactions in highly excited states close to the ionization limit.

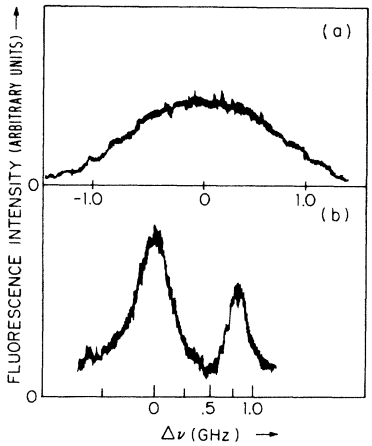

FIG. 2. (a) Doppler profile of the two-photon absorption of the sodium $3S$-$5S$ transition from one beam with linear polarization. (b) Resolved hyperfine splitting of the same transition with two counterpropagating circularly polarized beams. The nonlinear horizontal frequency scale is characteristic of tilt tuning of the Fabry-Perot interferometer.

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Note added.—The following references were brought to our attention after submission of this paper: B. Cagnac, G. Grynberg, and F. Biraben, J. Phys. (Paris) 34, 56 (1973), and Phys. Rev. Lett. 32, 643 (1974) (preceding Letter); and D. Pritchard, J. Apt, and T. W. Ducas, Phys. Rev. Lett. 32, 641 (1974) (second preceding Letter). We have also made a more accurate experimental determination for the hyperfine splitting. The new values are $\Delta\nu = 808 \pm 5$ MHz corresponding to a hyperfine interaction constant $A_{5S} = 78 \pm 5$ MHz.

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Capture of Argon K-Shell Electrons by 2.5- to 12-MeV Protons*

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Using coincidence techniques, we have measured the cross section for capture of electrons from the K shell of argon atoms by protons in the energy range from 2.5 to 12 MeV. Of the total cross section for electron capture, the contribution of capture from the argon K shell increases with proton energy from 0.5% at 2.5 MeV to 47% at 12 MeV. The contribution of electron capture to the total argon K-shell ionization cross section decreases from 0.4% at 2.5 MeV to less than 0.1% at 12 MeV.

Cross sections that have been measured in numerous experiments for the production of inner-shell vacancies in target atoms by energetic protons are found to be in good agreement with theoretical results calculated using direct ionization processes.[1] However, the transfer to the projectile of target inner-shell electrons in atomic collisions is an additional process that may contribute to the vacancy-production cross section determined experimentally. In fact, for higher-Z projectiles, elementary considerations[2] indicate that the two processes may be comparable in magnitude and that the latter process may account for charge-dependent trends recently observed in heavy-ion vacancy-production cross sections.[3] In the present work we report a measurement of the cross section for capture of electrons from a specific shell of a heavy target. Using coincidence techniques, the cross section (σ_{CK}) for electron capture of argon K-shell electrons has been determined for 2.5- to 12-MeV protons. This cross section for argon K-shell ionization by electron capture makes a small contribution to the total argon K-shell ionization cross section, and the contribution decreases monotonically with energy from 0.4% at 2.5 MeV to 0.06% at 12 MeV.

As a function of proton energy, experimental cross sections are shown in Fig. 1 for the production of vacancies in the argon K shell (σ_{VK}),[4] and for total electron capture (σ_{CT}).[5] Experimental values of σ_{CK} determined in this experiment are given by the closed circles in the figure. The theoretical contributions to σ_{CT} by specific shell for the capture of K, L, and M electrons of argon were calculated using the Brinkman-Kramers approximation by Nikolaev.[6] Although the experimental cross sections for capture of argon K-shell electrons are greater in magnitude than the calculated values by up to a factor of 2, the energy dependence of the cross section accurately follows the prediction from the Brinkman-Kramers approximation. In addition, of the total capture cross section, the fraction from K-shell capture determined in this experiment ranges from 0.5% at 2.5 MeV to 47% at 12 MeV and is only slightly in excess of the contribution of σ_{CK} to σ_{CT} calculated from the theoretical results.

The problem of electron capture by swift protons has been studied extensively by many workers and theoretical results for capture from the ground state of hydrogen, calculated in the Born approximation, are in agreement with experiment at energies above 100 keV.[7] With heavier targets, theoretical calculations have not been made in the full Born approximation, but comparison of experimental cross sections has been made with results obtained using the Brinkman-Kramers