Efficient Laser Production of a Na^+ Ground-State Plasma Column: Absorption Spectroscopy and Photoionization Measurement of Na^+†

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We report the first observation of ionization of dense Na vapor by laser radiation. A 1-MW pulsed laser at 589.6 nm produced almost complete ionization of a 10-Torr-cm column of Na. Measurements of the Na^+ photoionization cross section, the neonlike series $2s^22p^6 \rightarrow 2s^22p^5ns$ and nd, and several autoionizing resonances of the type $2s^22p_6^6 \rightarrow 2s2p^6np$ were obtained using a spark source to provide the continuum background for absorption spectroscopy of the ion.

The advent of high-power tunable lasers has recently made possible experiments in which large numbers of selectively excited atoms are produced and studied. Such laser-pumped excitation has been used to observe the absorption spectrum including autoionizing features and photoionization from $4s4p\,^3P$ levels of Ca,[1] the $3s3p\,^1P$ level of Mg,[2] and the $6s5d\,^3D$ levels of Ba.[3] The experiment reported here demonstrates that the high spectral intensity of a 1-MW pulsed laser tuned to an atomic resonance line can also efficiently ionize a large number of atoms, a result which is quite surprising at the laser beam intensities used. We have utilized the dense low-temperature plasma created by the laser in a new spectroscopic technique for the study of singly ionized sodium. We first present the spectral observations made on Na^+ and then some discussion of the possible ionization mechanisms based on these observations.

In the present experiment a determinable fraction (which can be made close to 100%) of a known amount of sodium contained in a heat-pipe oven is transferred from the neutral ground state to the ion ground state by the laser, thus providing an ion source highly suitable for quantitative absorption spectroscopy. Absorption spectroscopy of ions has been performed in the past using shock tubes,[4] flash photolysis,[5] Z-pinch plasmas,[6] laser-produced plasmas,[7] and spark-produced plasmas[8] as sources of ions. These sources generally do not produce sufficient density to allow observation of photoionization continua, and only the shock tube and Z-pinch sources offer the possibility of quantifying the number of absorbing ions. The only previous absolute measurement of continuum photoabsorption, the measurement of a single point in the spectrum of Xe^+, was made with a shock tube and was not extended to observations of the extended spectrum.[9] Most of these ion sources are hot plasmas with large emission intensities requiring extraordinary efforts to obtain absorption spectra.

The output of a flashlamp-pumped dye laser tuned to the $\lambda = 589.6$-nm, $3^2S_{1/2} \rightarrow 3^2P_{1/2}$ transition was made to traverse a sodium heat-pipe oven containing about 10 cm of sodium vapor between two plugs of helium buffer gas, all at about 1 Torr pressure (see Fig. 1). In order to observe the vacuum uv absorption spectrum of the laser-irradiated sodium, the oven was mounted directly in front of a 3-m grazing-incidence spectrograph. The vacuum uv continuum from a Ballofet-Romand-Vodar (BRV) type vacuum spark[10] was reflected by a toroidal focusing mirror and transmitted through a set of capillary-array windows[11] separating the vacuum of the spark chamber from the heat-pipe oven. A small dielectric mirror mounted adjacent to the slit allowed almost collinear illumination of the sodium by both the laser and the vacuum uv.

Spectrograms of the region from 15 to 42 nm were taken under the same heat-pipe-oven operating conditions both with and without the laser. Figure 2(a) shows a typical densitometer trace of the neutral-sodium absorption (i.e., laser off) between 26 and 34 nm. The previously determined absolute photoionization cross section shows a rapid increase near the sodium $L_{2,3}$ edge at 32.23 nm, going from approximately 0.5 to 8.5 Mb.[12]

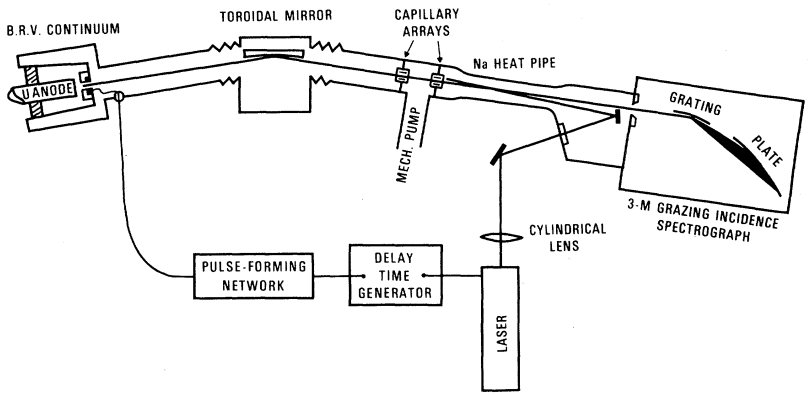

FIG. 1. Experimental layout.

This cross section difference is indicated on the figure as the distance between the dashed line, which represents the continuum absorption of the helium buffer gas, and the peak Na absorption occurring near 32.21 nm. The spectrogram represented in Fig. 2(b) was taken with the laser firing about 500 nsec before the BRV continuum, with an energy of about 300 mJ in a 500-nsec pulse. The neutral-sodium absorption features at 32.2 nm are barely observable above the photographic grain noise. The column density of neutral sodium of about 10^{17} cm^{-2} in Fig. 2(a) is reduced to less than 15% of that amount in Fig. 2(b). The residual neutral absorption features in Fig. 2(b) may stem from the occasional laser misfirings occurring among the 100 shots needed for an exposure, while the real percentage ionization right after a properly fired laser pulse is close to 100%.

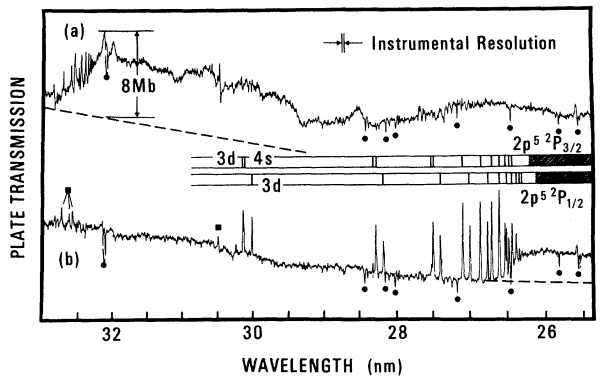

FIG. 2. (a) Absorption of neutral sodium. Emission features marked with solid dots are from the BRV source. Dashed line is background He absorption. (b) Absorption of laser-irradiated sodium. Solid squares mark persisting netural-Na features. Bar graph above Na^+ absorption lines designates series members and limits.

The sharp absorption lines seen in Fig. 2(b) beginning at 30.143 nm and extending to the Na^{++} $2p^5\,^2P_{3/2,\,1/2}$ limits are members of the $2p^5ns$ and $2p^5ns$ and $2p^5nd$ series in Na^+. Table I lists the wavelength values for the higher-lying lines observed in the present experiment compared with a previous experiment in which an emission spectrum was observed.[13] Considerable Stark broadening by the plasma is observed in the lines above $n = 6$, giving the lines a larger equivalent width and contributing to their apparent increase in strength.

The onset of the Na^+ continuum at the $2p^5\,^2P_{3/2,1/2}$ limits may be clearly seen in Fig. 2(b). To derive a measurement of the near-threshold photoionization cross section, $\sigma(Na^+ \rightarrow Na^{++})$, from this photographic data, we used a technique which exploited the previously measured Na photoabsorption[12] and the He autoionizing resonance profile[14] to calibrate the photographic plates and to determine the He and neutral-Na column densities. The value of $\sigma(Na^+ \rightarrow Na^{++})$ was then derived by assuming that the laser-created plasma contained 90% Na^+ and by comparing the photographic density change near the $2p^5\,^2P$ limits with that in the vicinity of the He 20.621-nm resonance. The result is $\sigma(Na^+ \rightarrow Na^{++}) = 5.5 \pm 2.5$ Mb, which compares well with the recent calculations of Reilman, Msezane, and Manson, who obtain a value of 7.3 Mb.[15]

Before using the assumption that all of the decrease in the ground-state neutral population was transferred into the Na^+ ground state, we carefully checked several plates in the range 44 → 13 nm for absorption features of Na* or Na_2^+. The only other features observed were the Na^+ $2s2p^6np$ resonances listed in Table II. We did not observe any Na* $3p\,^2P$ absorption, which is expected to have some strong resonance features around 38.5

TABLE I. Na^+ $2p^6 \rightarrow 2p^5 ns, nd$ series higher members.

Classification	λ(nm) Ref. 13	λ(nm) ± 0.005 this work	n^{*a}
$^2P_{3/2}$ 5d[1/2]$_1$	27.5218	27.524	4.93
$^2P_{3/2}$ 5d[3/2]$_1$	27.5003	27.501[d]	4.97
$^2P_{3/2}$ 6s[3/2]$_1$	27.4931		4.98
$^2P_{1/2}$ 5d[3/2]$_1$	27.4023	27.402[d]	4.96
$^2P_{1/2}$ 6s[1/2]$_1$	27.3940		4.98
$^2P_{3/2}$ 6d[1/2]$_1$	27.1373	----	5.83
$^2P_{3/2}$ 6d[3/2]$_1$[b]	27.0947	27.096	5.97
$^2P_{1/2}$ 6d[3/2]$_1$[c]	26.9993	26.997	5.95
$^2P_{3/2}$ 7d[3/2]$_1$[b]		26.888	6.96
$^2P_{1/2}$ 7d[3/2]$_1$[c]		26.761	6.95
$^2P_{3/2}$ 8d[3/2]$_1$[b]		26.706	7.95
$^2P_{1/2}$ 8d[3/2]$_1$[c]		26.606	7.98
$^2P_{3/2}$ 9d[3/2]$_1$[b]			8.91
$^2P_{1/2}$10d[3/2]$_1$[b]		26.530	9.92
$^2P_{3/2}$ 9d[3/2]$_1$[c]		26.508	8.93
$^2P_{3/2}$11d[3/2]$_1$[b]		26.476	10.93
$^2P_{3/2}$12d[3/2]$_1$[b]		26.434	11.92
$^2P_{1/2}$10d[3/2]$_1$[c]			9.93
$^2P_{1/2}$11d[3/2]$_1$[c]		26.381	10.90
$^2P_{1/2}$12d[3/2]$_1$[c]		26.339	11.92
$^2P_{1/2}$13d[3/2]$_1$[c]		26.306	12.96

[a] These effective quantum numbers are calculated assuming the limits $2p^5\,^2P_{3/2}$ at 381 390 cm^{-1} and $2p^5\,^2P_{1/2}$ at 382 754 cm^{-1} as given in Ref. 13.

[b] The classification given represents the stronger component of a blend of $^2P_{3/2}nd[\frac{3}{2}]_1$ and $^2P_{3/2}(n+1)s[\frac{3}{2}]_1$.

[c] The stronger component of a blend of $^2P_{1/2}nd[\frac{3}{2}]_1$ and $^2P_{1/2}(n+1)s[\frac{1}{2}]_1$

[d] Unresolved blend of bracketed lines.

TABLE. II. Lowest-lying autoionizing resonances involving excitations of the L electron in Na^+.

λ ± 0.005 (nm) Expt.	$h\nu$ (eV)	Classification	n^{*a}	λ (nm) Theory[b]
17.724	69.95	$2s2p^6\,3p\,^1P$	2.32	17.69
16.492	75.18	$2s2p^6\,4p\,^1P$	3.33	16.49
16.066	77.17	$2s2p^6\,5p\,^1P$	4.32	•••
15.867	78.14	$2s2p^6\,6p\,^1P$	5.28	•••
15.755	78.70	$2s2p^6\,7p\,^1P$	6.24	•••
15.688	79.04	$2s2p^6\,8p\,^1P$	7.17	•••

[a] These effective quantum numbers are calculated assuming the limit $2s2p^6\,^2S_{1/2}$ at 645 977 cm^{-1} as given in Ref. 16.

[b] Calculation by A. Weiss, private communication.

nm, or any Na_2^+ inner-shell excitation which should occur in the wavelength range scrutinized.

The mechanism for production of the ions is presently not understood. At approximately 1 MW/cm^2, the intensity used in the experiment, the vapor transmission of the 589.6-nm (bandwidth 0.05 nm) radiation is about 10%. The low-intensity optical thickness of the sodium vapor is 10^5 in line center and 10^3 in the wings of the laser line so that 10% transmission indicates either saturation of the $3s \rightarrow 3p$ transition or almost complete depletion of the neutral-sodium ground state. Since the predicted strong absorption lines from $Na^*(3p)$ were entirely absent from the spectra, the transmission is probably an indication of complete ionization. One possibility is that the laser is producing two-photon photoionization from large numbers of laser-pumped $3p\,^2P$ levels. (One λ = 589.6-nm photon does not have enough energy to ionize from the $3p\,^2P$ levels.) However, an experiment which looked for such resonant three-photon, two-step ionization in an atomic sodium beam showed that the process has much too low a production rate at the 1-MW/cm^2 intensity level to explain our results.[17] A more likely possibility is the promotion of atoms from the $3p$ to $4p$ level by stimulated Raman scattering[18] and subsequent single-photon ionization out of the $4p$ or $4s$ states. The gain for such a process assuming a single dominant intermediate level ($4d\,^2D$) is given by the formula

$$g = \frac{Ne^4\nu_R f_{3p4d} f_{4p4d} Il}{32\pi^3\epsilon_0{}^2 hc^2 me^2 \nu_{3p43}\nu_{4p\,4d}(\nu_{3p4d}-\nu_L)^2\Gamma_{4p}},$$

where all quantities are in mksa units, N is the atomic density, I the intensity (watts per square meter), l the length of the vapor, and Γ_{4p} the width of the $4p\,^2P$ levels. (Actually, this expression ignores the contribution from the $5s$ intermediate state which will change the value for g somewhat.) In our case the calculated value for the $3p \rightarrow 4p$ transfer by stimulated Raman scattering turns out to be 15% with sufficient uncertainty to warrant its further consideration as the first step in the mechanism observed. The second step, photoionization out of the $4p$ or $4s$ states, must have a cross section greater than 10^{-18} cm^2 in order for the proposed two-step mechanism to be a viable explanation for the observed ion production.

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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[1]T. J. McIlrath, Appl. Phys. Lett. 15, 41 (1969).

[2]D. J. Bradley, P. Ewart, J. V. Nicholas, J. R. D. Shaw, and D. G. Thompson, Phys. Rev. Lett. 31, 263 (1973); D. J. Bradley, C. H. Dugan, P. Ewart, and A. F. Purdie, Phys. Rev. A 13, 1416 (1976).

[3]J. L. Carlsten, T. M. McIlrath, and W. H. Parkinson, J. Phys. B 7, L244 (1974).

[4]G. L. Grasdalen, M. Huber, and W. H. Parkinson, Astrophys. J. 156, 1153 (1969).

[5]R. Roig, Ph.D. thesis, Harvard University, 1975 (unpublished), and to be published.

[6]J. S. Hildum and J. Cooper, J. Quant. Spectros. Radiat. Transfer 12, 1453 (1972).

[7]P. Jaegle, G. Jamelot, A. Carillon, A. Sureau, and P. Dhez, Phys. Rev. Lett. 33, 1070 (1974).

[8]G. Mehlman and J. M. Esteva, Astrophys. J. 188, 191 (1974).

[9]R. B. Cairns and G. L. Weissler, Bull. Am. Phys. Soc. 7, 129 (1962).

[10]G. Ballofet, J. Romand, and B. Vodar, C. R. Acad. Sci. 252, 4139 (1961).

[11]T. B. Lucatorto, T. J. McIlrath, and E. B. Saloman, to be published.

[12]H. W. Wolff, K. Radler, B. Sonntag, and R. Haensel, Z. Phys. 257, 353 (1972); the cross sections quoted in this were normalized to a theoretical value from E. J. McGuire, Sandia Laboratories Research Report No. SC-RR-721, 1970 (unpublished).

[13]C. M. Wu, thesis, University of British Columbia (unpublished).

[14]R. P. Madden and K. Codling, Astrophys. J. 141, 364 (1965).

[15]R. F. Reilman, A. Z. Msezane, and S. T. Manson, to be published; S. T. Manson, private communication.

[16]C. E. Moore, *Atomic Energy Levels*, U. S. National Bureau of Standards, National Standard Reference Data Systems —35 (U. S. GPO, Washington, D. C., 1971), Vol. I, p. 309.

[17]W. W. Smith, private communication.

[18]J. L. Carlsten and P. C. Dunn, Opt. Commun. 14, 8 (1975); D. Colter, D. C. Hanna, P. A. Kärkkäinen, and R. Wyatt, Opt. Commun. 15, 143 (1975).

[19]J. L. Carlsten, private communication.

[20]D. B. Lidow, R. W. Falcone, J. F. Young, and S. E. Harris, Phys. Rev. Lett. 36, 462 (1976).

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