Off-resonance production of ions in laser-excited sodium vapor

C. E. Burkhardt, W. P. Garver, and J. J. Leventhal
Department of Physics, University of Missouri–Saint Louis, Saint Louis, Missouri 63121
(Received 16 July 1984)

The production of Na^+ and Na_2^+ in sodium vapor irradiated by pulsed laser light in the D-line region of the spectrum has been studied by varying the laser power density and the wavelength. The data, which were acquired with an order-of-magnitude higher resolution than those in our previous experiments, support our earlier conclusion that ions formed at laser wavelengths close to, but not coincident with, the D lines result from three-photon resonance-enhanced ionization of Na_2 molecules present in the vapor.

The mechanism by which Na_2^+ ions are formed when sodium vapor is irradiated by yellow and near-yellow laser light has been a subject of considerable controversy. It is well known that cw laser light produces these ions only when the wavelength coincides with one of the D lines, and that the mechanism of formation is energy-pooling associative ionization:[1]

$$\mathrm{Na}(3p) + \mathrm{Na}(3p) \rightarrow \mathrm{Na_2}^+ e \ . \quad (1)$$

However, when a pulsed laser with inherently higher power density is employed Na_2^+ may be observed at all wavelengths in the approximate range[2–4] 5800–6200 Å. It has been proposed that some type of "laser-induced" process involving two ground-state sodium atoms is responsible for the formation of these ions.[2,3] However, on the basis of experiments performed in our laboratory[4] we suggested that the observation of Na_2^+ at off-resonance wavelengths, that is, *atomic* resonance, can be explained without the necessity of invoking these somewhat exotic processes. We inferred from our data that resonance-enhanced three-photon ionization of the unavoidably present Na_2 component of the vapor leads to the observed Na_2^+ ions. At approximately the same time, Wu and co-workers[5] reported that they had reached a similar conclusion. Very recently, Keller and Weiner[6] reported that reexamination of their data led them to conclude that indeed the neutral dimers were the precursors of Na_2^+. Thus, the three laboratories are now in essential agreement on the origin of these ions, but the precise multiphoton ionization mechanism is still uncertain. The data reported here, together with spectroscopic studies of the sodium dimer molecule,[7] suggest that this mechanism is *double*-resonance-enhanced three-photon ionization.

The apparatus is similar to that used previously.[4] Sodium vapor effuses into a cylindrical collision cell from an oven operated at 500 K; the atom density in the cell was determined to be 2×10^{12} cm^{-3} using a technique described previously.[8] The dimer concentration calculated using equilibrium thermodynamics is $\sim1\%$ of the atomic concentration. The cell is irradiated along the axis by light from a Nd:YAG (yttrium-aluminum-garnet) laser-pumped grazing-incidence dye laser operated with rhodamine-6G; the duration of the laser pulse, 7 nsec, is very nearly the same as that in our earlier work.[4] A major difference between the data reported here and those previously reported is that the new data were acquired with a much narrower laser bandwidth, 0.1 rather than 1 Å. The laser power density was varied with a combination of focusing lenses and neutral-density filters. Ions were extracted from the reaction cell with an improved electrostatic lens system, mass analyzed with a quadrupole mass spectrometer, and detected using a Cu-Be particle multiplier, the output of which was measured with a gated integrator. D-line fluorescence was also monitored. The laser wavelength λ was scanned using a computer-controlled stepping motor. Spectra were acquired at fixed laser power density by setting the mass filter to pass either Na^+ or Na_2^+ and scanning the laser wavelength. After a preset number of laser pulses at a given wavelength setting the signal from the gated integrator was read by and stored in the computer, producing an Na^+ vs λ or Na_2^+ vs λ spectrum, we concentrated on a wavelength range ~10 Å, which included the D lines as convenient markers.

Figure 1 shows a scan of the fluorescence and the Na_2^+ signal over the D_2 line at low laser power density. At this power density Na_2^+ were observed only at D-line wavelengths so that these data are essentially the same as those acquired with a cw laser. Since the Doppler width of this line is ~2 GHz (0.025 Å) the fluorescence data show the laser bandwidth which is 0.1 Å. However, the line shape of the Na_2^+ signal is essentially the square of the fluorescence shape establishing energy pooling associative ionization, reaction (1), as the source of these ions.

Figure 2 shows a sequence of Na_2^+ spectra, all taken over the same wavelength range. As discussed above, Na_2^+ at the lowest power density are formed only at the D-line wavelengths. As the power density is increased Na_2^+ are observed over the entire range. In contrast to our earlier data[4] the spectral features are sharp; furthermore, they persist through changes of power density until, at the highest power density, the D-line features are obscured. This occurs at power densities near those employed by us in our previous study and in essence reproduces the earlier data, but with higher resolution.

In our previous experiments, using a laser with 80-GHz bandwidth, the Na_2^+ spectra were virtually featureless. In fact, enhancements of the Na_2^+ signal at the D lines due to $\mathrm{Na}(3p)/\mathrm{Na}(3p)$ associative ionization were not even observed. It was suggested that the Na_2^+ produced by resonance enhanced three-photon ionization of Na_2 obscured these signals. The data in Fig. 2 clearly demonstrate the transition from the cw-like low-power regime through intermediate powers at which the ion spectra are quite rich to the high-power condition that prevailed in our previous experiment with a pulsed laser.[4] Power dependences show that the $\mathrm{Na}(3s) \rightarrow \mathrm{Na}(3p)$ atomic transistions are saturated at

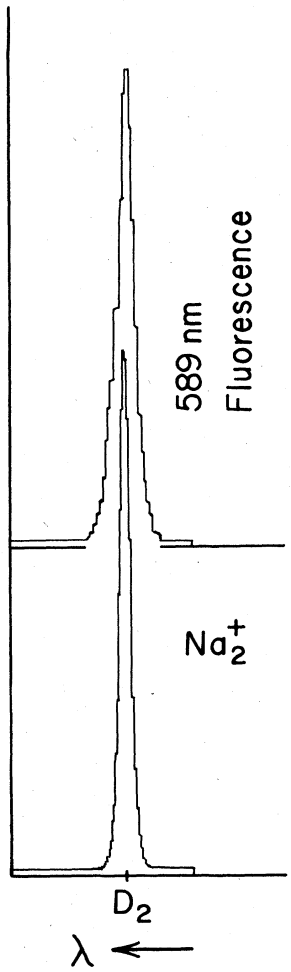

FIG. 1. Na_2^+ and D-line fluorescence signals as functions of laser wavelength taken at the lowest laser power density (1 kW/cm^2). The fact that the ion line shape is the square of the fluorescence line shape demonstrates that Na($3p$)/Na($3p$) energy pooling associative ionization is responsible for the production of Na_2^+ at this low laser power density.

all but the lowest power densities shown in Fig. 2. Thus, the growth of off-resonance signals with increasing laser power densities eventually engulfs the ion signal at the D lines. This occurs because, while a particular vibrational-rotational transition in the molecule can be saturated, additional transitions that fall within the laser bandwidth make contributions as the power is increased. In effect, then the closely spaced molecular levels magnify the dimer concentration relative to the atomic concentration. In the present experiment the narrower laser bandwidth permits resolution of many spectral features that could not be detected in the earlier work. These features are more closely spaced than the 1-Å bandwidth of the laser used for that experiment; however, at higher powers, many of the individual molecular transitions saturate and the spectrum tends toward a continuum. This effect illustrates the uncertainty that can result from laser power dependence data involving *molecular* transitions.

Figure 3 shows Na_2^+ and Na^+ spectra taken at the same power density together with a D-line fluorescence spectrum

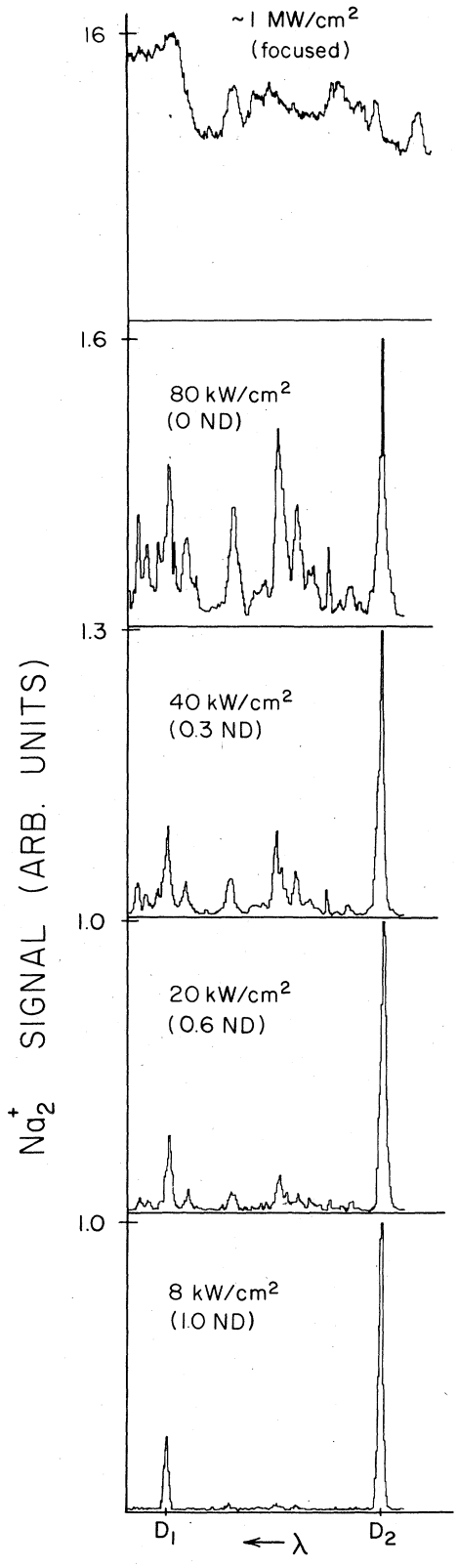

FIG. 2. Na_2^+ vs λ spectra taken under identical conditions (3×10^{12}, atoms/cm^3) except for laser power density. The top spectrum was taken with a focused laser beam and the next was taken with an unfocused beam; the remaining spectra were taken by attenuating the laser beam with various neutral-density (ND) filters.

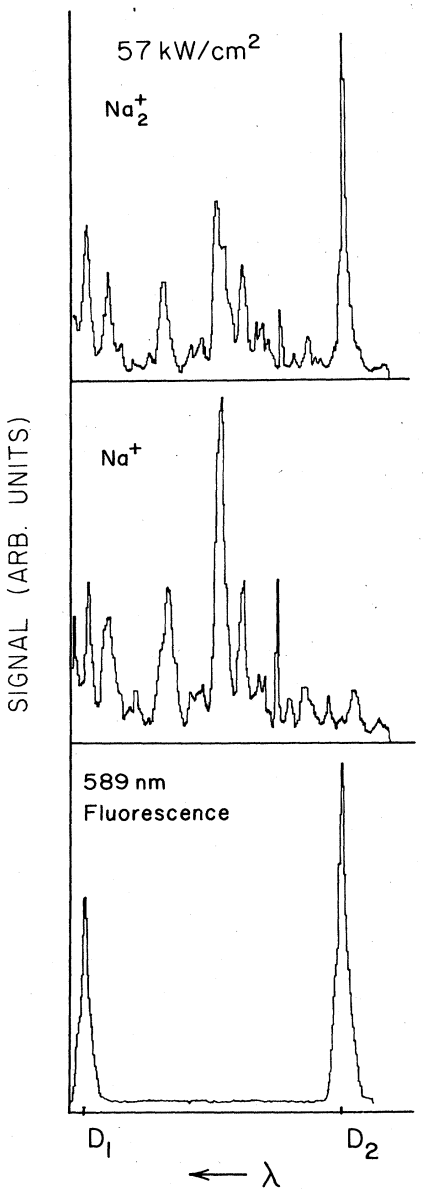

FIG. 3. Na_2^+ vs λ and Na^+ vs λ spectra taken at laser power density 57 kW/cm². Also shown is a D-line fluorescence spectrum for reference.

which serves to locate the D-line wavelengths on the abscissa. Na^+ spectra behave in much the same way as those of Na_2^+ as the power density is increased; however, no features are observed at precisely the D-line wavelengths at any power densities showing that three-photon ionization of Na($3s$) through the Na($3p$) state has, as previously observed by us,[4] a low rate.

As the laser power is increased Na^+ are observed at exactly the same off-resonance laser wavelengths as Na_2^+. Although there is a peak in the Na^+ spectrum that is near, but not coincident with, D_1, the almost total absence of Na^+ at D_2 clearly shows that excited atoms are not crucial for producing atomic ions. Furthermore, the fact that the off-resonance spectral features for both ions occur at precisely the same wavelengths strongly suggests a common origin of Na^+ and Na_2^+. This common origin must be three-photon ionization of Na_2:

$$3\hbar\omega + Na_2 \rightarrow Na_2^+ + e \quad (2)$$

$$\rightarrow Na^+ + Na + e \ . \quad (3)$$

When the laser is tuned to a D line $3p/3p$ associative ionization must be responsible for a portion of the observed Na_2^+ ions, but there is no heavy body collision process involving excited *atomic* reactants that produces Na^+. The absence of Na^+ at D_2 also shows that atomic ions are not produced to an appreciable extent by photodissociation of nascent Na_2^+ in this experiment. This is unlikely anyway because the short duration of the laser pulse (7 nsec) virtually guarantees that laser photons will not be present by the time heavy body collisions have yielded products. The latter also suggests that photoionization of *highly* excited sodium atoms produced in energy pooling $3p/3p$ collisions[9,10] does not contribute to the Na^+ signal.

Is is unlikely that these ions are produced by three-photon resonance enhanced ionization through only the A state of Na_2 because the ion spectra do not reproduce A state absorption spectra. Rather, we believe that the three-photon ionization proceeds primarily through a set of recently studied gerade states. Schawlow and co-workers,[7] using Doppler-free spectroscopy, have shown that illumination of sodium dimers by yellow laser light produces excited Na_2 by two-photon absorption. This excitation is facilitated by near resonances with vibration-rotation levels of the intermediate $A\,^1\Sigma_u^+$ state. Figure 4 is a partial potential energy diagram for the Na_2 molecule; the $^1\Sigma_g^+(3s+5s)$ state shown schematically is representative of the gerade states that are accessible by two-photon absorptions. Because the 8-GHz bandwidth of our pulsed laser is about 400 times that of the single-frequency cw laser used by Schawlow and co-workers,

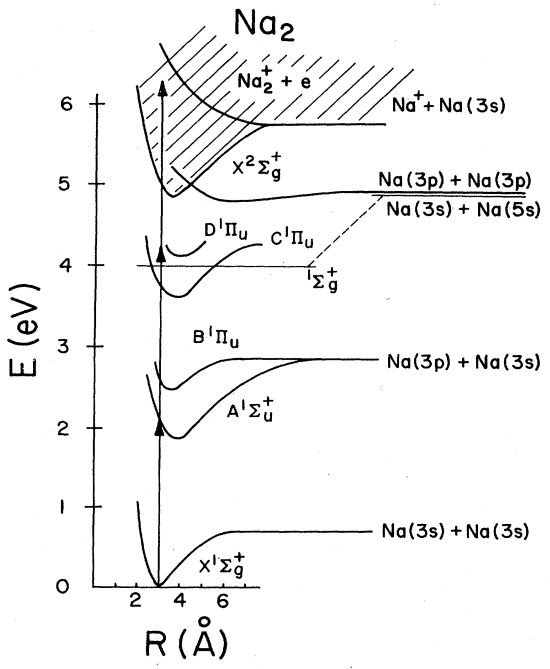

FIG. 4. Partial potential energy diagram for Na_2 and Na_2^+.

and the laser power density is, of course, substantially higher, the number of two-photon excitations that occur in our experiment can greatly exceed the number observed in the Doppler-free work. These gerade states probably serve as *real* intermediates for resonance-enhanced three-photon ionization of $Na_2(X)$ to produce Na^+ or Na_2^+. In fact, given the near resonance of the A state for the two-photon excitation to a gerade state observed in the Doppler-free work and the wider bandwidth of our laser, the production of ions, both Na^+ and Na_2^+, at off-resonant wavelengths is probably a result of *double*-resonance-enhanced, three-photon ionization. Of course, the atomic ions are formed by dissociative three-photon ionization of Na_2^+.

The authors would like to thank Dr. M. Allegrini and Dr. L. Moi for helpful discussions and the authors of Ref. 5 for making their results available to us prior to submission for publication. This work was supported by the U.S. Department of Energy, Division of Chemical Sciences, under Grant No. DE-FG02-84ER13237.

[1]See, for example, J. J. Leventhal, in *Photon-Assisted Collisions and Related Topics,* edited by N. K. Rahman and C. Guidotti (Harwood Academic, Chur, 1982).

[2]F. Roussel, B. Carre, P. Breger, and G. Spiess, J. Phys. B **14**, L313 (1981).

[3]P. Polak-Dingels, J.-F. Delpech, and J. Weiner, Phys. Rev. Lett. **44**, 1663 (1980); J. Boulmer and J. Weiner, Phys. Rev. A **27**, 2817 (1983).

[4]M. Allegrini, W. P. Garver, V. S. Kushawaha, and J. J. Leventhal, Phys. Rev. A **28**, 199 (1983).

[5]C. Y. R. Wu, D. L. Judge, F. Roussel, B. Carre, P. Breger, and G. Spiess, in *Laser Techniques for Extreme Ultraviolet Spectroscopy,* edited by T. J. McIlrath and R. R. Freeman (AIP, New York, 1982); C. Y. R. Wu, F. Roussel, B. Carre, P. Breger and G. Spiess (unpublished).

[6]J. Keller and J. Weiner, Phys. Rev. A **30**, 213 (1984).

[7]G. P. Morgan, H.-R. Xia, and A. L. Schawlow, J. Opt. Soc. Am. **72**, 315 (1982), and references cited therein.

[8]W. P. Garver, M. R. Pierce, and J. J. Leventhal, J. Chem. Phys. **77**, 1201 (1982).

[9]M. Allegrini, G. Alzetta, A. Kopystynska, L. Moi, and G. Orriols, Opt. Commun. **22**, 329 (1977).

[10]G. H. Bearman and J. J. Leventhal, Phys. Rev. Lett. **41**, 1227 (1978).