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Ion formation in sodium vapor containing Rydberg atoms

C. E. Burkhardt, W. P. Garver, V. S. Kushawaha, and J. J. Leventhal
Department of Physics, University of Missouri, St. Louis, 8001 Natural Bridge Road, St. Louis, Missouri 63121
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The formation of Na^+ and Na_2^+ in sodium vapor ($\sim 10^{11}$–10^{13} cm^{-3}) containing laser-selected Rydberg atoms ($15 \leq n \leq 35$) has been studied. At low atom densities photoionization, collisional ionization, and associative ionization dominate, but more-complicated mechanisms contribute to the ion yield at higher densities.

Recent interest in the study of highly excited atoms[1–3] has focused on both the intrinsic properties of these Rydberg atoms and their interactions with other species. Most of the collisional studies have dealt with the mixing of states,[4,5] electron transfer,[6] or electron detachment.[7] However, Rydberg states provide ready access to the continuum so that ion formation, although difficult to study experimentally,[8] should also be very important. Of the few experiments that have been performed, most observed only gross effects. In this paper we describe our experimental work on the subject. We have studied the formation of both atomic and molecular ions and have quantitatively examined their origins by systematically varying the experimental conditions. We believe this to be the first such detailed study.

Excited atoms were produced in a stainless-steel cell in which the sodium vapor concentration N could be adjusted to values as high as $\sim 10^{13}$ cm^{-3}; N was determined by a method previously[9] described. Holes in the ends of the cell permitted introduction of two laser beams: one yellow and tuned to a D line, the other blue to effect the $3p \rightarrow ns$ or $3p \rightarrow nd$ transitions. A set of electrostatic lenses was used to extract ions from a 2-mm-diam hole in the side of the cell. These ions were mass selected with a quadrupole mass filter and detected with a CuBe particle multiplier. The dye lasers were pumped with the frequency doubled and tripled outputs of a Nd:YAG laser. The yellow laser was operated with Rh-6G dye and the blue laser with LD 425. Maximum powers were 5 and 1 kW for the yellow and blue lasers; the bandwidths were 13 and 25 GHz, respectively.

Ion spectra were acquired with the yellow wavelength fixed at D_2 and the mass filter set at 23 or 46 amu, while the blue wavelength λ_B was scanned from 4100 to 4300 Å by a computer controlled stepping motor. Experiments were also performed using D_1; except for slightly lower signal levels the results were similar to those obtained using D_2. The spectral power output of the blue laser varied by only about 10%. At each λ_B the output of the multiplier was fed into a gated integrator and, after a preset number of pulses, usually 50, the accumulated charge was digitized and stored in the computer. Figure 1 shows two spectra and illustrates the dramatic increase in ion formation when the lasers are tuned to a Rydberg state.

The most probable sources of Na^+ are collisional ionization and photoionization by blackbody radiation.[10–12] Their relative importance was investigated by examining the Na^+ signal as a function of the laser power densities and N. Figure 2(a) shows the Na^+ variation with blue power density at two different values of N. The data taken with $N = 2 \times 10^{11}$ cm^{-3} have unit slope, indicative of a process requiring one blue photon, and hence one Rydberg atom. Since the yellow laser power dependence is also linear the collisional process leading to Na^+ is likely

$$Na^{**} + Na(3s) \rightarrow Na^+ + Na(3s) + e \ , \qquad (1)$$

where the double asterisk signifies a Rydberg state. While

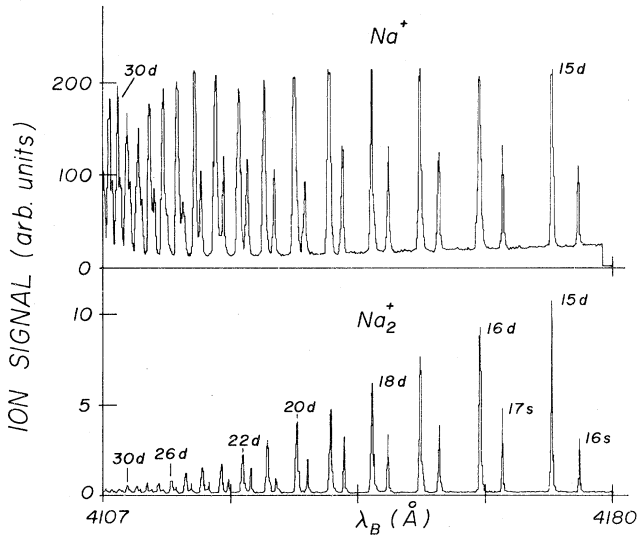

FIG. 1. Na^+ and Na_2^+ signals as functions of blue laser wavelength λ_B. The Na($3s$) density N was 4×10^{11} cm^{-3}.

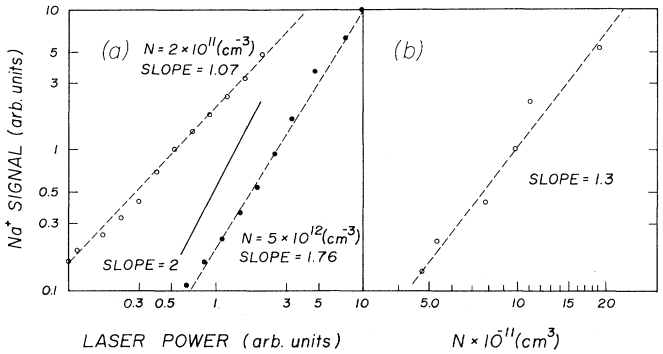

FIG. 2. (a) Na^+ signal as a function of blue-laser power density for two different values of N. The data were taken with λ_B set to produce Na($18d$). The dashed lines are least-squares fits to the data; the solid line of slope 2 is for reference. (b) Na^+ signal as a function of N; λ_B is set as in (a).

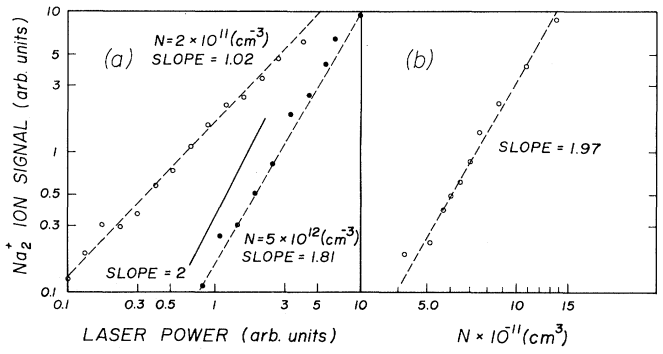

FIG. 3. (a) Na_2^+ signal as a function of blue-laser power density for two different values of N. The data were taken with λ_B set to produce Na($18d$). The dashed lines are least-squares fits to the data; the solid line of slope 2 is for reference. (b) Na_2^+ signal as a function of N; λ_B is set as in (a).

the Na^+ yields from both photoionization and reaction (1) must increase linearly with laser power, the N dependencies would be linear and quadratic, respectively. Figure 2(b) shows the Na^+ variation with N at fixed laser power; the range of N is limited to those values for which the blue power dependencies are linear. The fact that the signal increase is greater than linear, but less than quadratic implies that both collisional ionization and photoionization are occurring. Fitting these data to a parabola shows that only about 17% of the Na^+ are formed by collisional ionization. Therefore, since the Na^+ peaks are roughly equal, the photoionization yield is, as expected,[11,12] not a strong function of n. In fact, this result implies that at low N, l mixing prior to photoionization is insignificant. The number of ions produced is proportional to $N_R\tau'$ where N_R is the initial Rydberg atom concentration $\sim n^{-3}$, and τ' is a characteristic "lifetime." If spontaneous decay dominates then $\tau'=\tau$, the radiative lifetime, and $\sim n^3$. If, however, l mixing occurs[8] then $\tau'\sim n^{4.5}$. The fact that the data are independent of n indicates that indeed $\tau'\sim n^3$ and l mixing is not appreciable. Furthermore, radiative decay does dominate.

At the higher value of N, 5×10^{12} cm^{-3}, the increase of Na^+ with blue power is steeper than linear, indicating that additional mechanisms occur. Olson has studied Na^{**}/Na^{**} collisional ionization theoretically,[13] his results indicating that the cross section is an order of magnitude larger than geometric, which is consistent with our measurement. However, three-body collisions such as $Na^{**}/Na^{**}/Na(3s)$ cannot be unequivocally ruled out.

The production of Na_2^+ was also studied; Fig. 3 shows data analogous to those in Fig. 2. The blue power dependence at low N is linear, but in this case the Na_2^+ signal varies as N^2. Thus, Na^{**}/Na collisions are the primary source of Na_2^+. Again the yellow power dependence shows that only one D-line photon is required so that associative ionization

$$Na^{**}+Na(3s)\rightarrow Na_2^+ + e \qquad (2)$$

is the source of these ions. Similar results were reported by Worden, Paisner, and Conway[14] who studied ionization of Rydberg strontium atoms. Because the energy of states higher than $8d$ exceeds the ionization potential of Na_2 (4.9 eV) it is possible that Penning ionization of Na_2 produces Na_2^+; however, the dimer fraction at $N=2\times10^{11}$ cm^{-3} is only about 0.04%, making it unlikely that this is important. In addition, the quadratic N dependence favors associative ionization.

Since the spectral power output of the blue laser does not vary appreciably over the wavelength range of interest the peak heights in the Na_2^+ spectrum represent the approximate n dependence of the cross section. The observed decrease with increasing n is consistent with recent theory.[15,16] The absolute cross section for a given n may be estimated by comparing the signal to that from Na($3p$)/Na($3p$) associative ionization. Unfortunately, there is disagreement in the literature on the $3p/3p$ cross section,[17–21] the reported values ranging from ~0.05 to 1.5 Å^2. Nevertheless, it is relatively straightforward to estimate the ratio of the cross sections since a weak but measurable Na_2^+ signal is present with the blue laser beam blocked. This also leads to an estimate of the collisional ionization cross section; for $n=18$ it is about four times that for reaction (2).

The charge from $Na^{**}/Na(3s)$ associative ionization is given by

$$q_R = e\langle v\rangle \sigma_R N_R N \tau_R V \ , \qquad (3)$$

where e is the electronic charge, $\langle v\rangle$ the average atomic speed, σ_R the cross section, and V the reaction volume. An analogous equation for $3p/3p$ associative ionization may be written. Taking the ratio and making the assumptions that $N\approx N_{3p}$ and that the reaction volumes are the same we have

$$\sigma_R \cong (q_R/q_{3p})(N/N_R)(\tau_{3p}/\tau_R)\sigma_{3p} \ . \qquad (4)$$

N/N_R is estimated to be ~100 under the conditions of our experiment;[8] τ_{3p}/τ_R is 1/360 for[22] $n=18$, and q_R/q_{3p} is $\sim3\times10^3$. Therefore, $\sigma_R(n=18)$ is 50–1500 Å^2 depending on σ_{3p}. Since associative ionization is generally regarded as being due to the relatively short-range interaction of the Rydberg ion core with the ground-state atom,[23] σ_R probably lies at the lower end of this range.

At elevated N the Na_2^+ signal increase is greater than linear, but less than quadratic, with both yellow- and blue-laser powers. Therefore, additional mechanisms produce Na_2^+, possibly Na^{**}/Na^{**} and $Na^{**}/Na(3p)$ associative ionization. However, neither of these is energetically favorable if the Na_2^+ product is in the electronic ground state, and excited electronic states of the alkali dimer ions have not

been observed.[24] Thus, a more subtle mechanism seems likely. If at elevated atom densities nascent Rydberg atoms undergo n lowering to nearby levels by quenching or superradiance, then the Na_2^+ yield would indeed increase faster than linearly because of the n dependence of reaction (2). Since superradiance, when it occurs, occurs very rapidly,[10] $\sim$ 10–20 nsec after the laser pulse, it is probably more important than quenching. Furthermore, referring back to the power dependence at low n, the unit slope indicates that the threshold for superradiance had not yet been reached.

The situation at still higher N is even more complicated. Above $\sim 5\times10^{12}$ cm^{-3} a precipitous increase in Na^+ production with a concomitant drop in Na_2^+ is observed. Ion spectra show truncated Na_2^+ peaks indicating that at line center further production of Na_2^+ is inhibited. There was, however, no simultaneous truncation for Na^+. This suggests that the initially formed Rydberg atoms are ionized before they react to form Na_2^+. One mechanism for this is Na^{**}/Na^{**} collisional ionization. But, while this no doubt depletes the Na^{**} concentration, the dramatic increase in Na^+ production is suggestive of an avalanche mechanism. In their experiments Worden *et al.*[14] made similar observations and postulated that at high Rydberg atom concentrations seed electrons produced by photoionization initiated a cascade of e/Na^{**} ionization. This mechanism is consistent with our observations.

The experiments reported here demonstrate the importance of ion formation in any medium containing highly excited atoms. Ions may be formed in heavy-body collisions or by photoionization. As the concentrations of both ground-state and excited atoms increase, additional processes play a role in ion formation and Rydberg atom destruction. Still further increases lead to avalance mechanisms that rapidly destroy Rydberg atoms. Internal energy stored in these highly excited atoms can also be dissipated by superradiance.

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