PHYSICAL REVIEW A VOLUME 34, NUMBER 1 JULY 1986

Ionization of Rydberg atoms

C. E. Burkhardt, R. L. Corey, W. P. Garver, and J. J. Leventhal
Department of Physics, University of Missouri—St. Louis, St. Louis, Missouri 63121

M. Allegrini and L. Moi
Istituto di Fisica Atomica e Molecolare del Consiglio Nazionale delle Richerche, I-56100 Pisa, Italy

(Received 1 May 1985; revised manuscript received 21 February 1986)

Ion formation in sodium vapor ($\sim 10^{11}$ cm^{-3}) containing Rydberg atoms ($18 \leq n \leq 35$) was investigated. Both atomic ions and diatomic molecular ions resulting from collisions between highly excited sodium, Na**, and Na(3s) were observed. However, the predominant production mechanism was found to be photoionization of Na** by blackbody radiation, the rate of which was measured at 500 K and found to be $\simeq 5.7\times 10^{3}$ sec^{-1} for $n=18$, in good agreement with theory. The Na^{+} signal from blackbody photoionization is observed to be independent of n, which we interpret as implying rapid and nearly complete self-l-mixing, mixing by collisions with Na(3s) atoms, for both s and d states. It is probable, however, that the s states are mixed to the adjacent, $n-1$, manifold of l states. It was also found that the heavy-body collision cross sections for Na^{+} and Na$_2{}^{+}$ formation, while roughly three orders of magnitude lower than our estimate of the self-l-mixing cross section, are appreciable, of order 100 Å^2.

I. INTRODUCTION

Although a great deal of effort has been devoted to the study of interactions involving highly excited (Rydberg) atoms, the details of certain types of reactive processes, such as those leading to ion formation, have been largely ignored.[1] In order to fill this void we have initiated a series of experiments designed to study Rydberg-atom reactivity. Preliminary results of our experiments involving sodium Rydberg atoms, Na**, have been reported.[2] In those experiments we observed the following ionization processes:

$$\mathrm{Na}^{**}+\mathrm{Na}\rightarrow\mathrm{Na}^{+}+\mathrm{Na}+e\ , \tag{1}$$

$$\mathrm{Na}^{**}+\mathrm{Na}\rightarrow\mathrm{Na}_2{}^{+}+e\ , \tag{2}$$

$$\mathrm{Na}^{**}+\mathrm{Na}^{**}\rightarrow\mathrm{Na}^{+}+\mathrm{Na}+e\ . \tag{3}$$

It was found, however, that at low atom densities the predominant ion-formation mechanism was photoionization of Rydberg atoms by blackbody radiation,

$$\mathrm{Na}^{**}+\hbar\omega_{\mathrm{BB}}\rightarrow\mathrm{Na}^{+}+e\ . \tag{4}$$

In this earlier work we observed a very strong dependence of the associative ionization cross section, reaction (2), on principal quantum number n. We also estimated the absolute cross sections for both reactions (1) and (2) by comparing the observed Na$_2{}^{+}$ signal to that for Na$_2{}^{+}$ formation in Na(3p)-Na(3p) collisions. However, the relatively wide range of cross sections for Na(3p)-Na(3p) associative ionization in the literature led us to report a concomitantly wide range for the Na**-Na processes.

In this paper we report the results of experiments in which more detailed data were obtained. We concentrated on the low-density regime in order to minimize the effects of superradiance and Na**-Na** interactions. These new data show, contrary to one of the conclusions in our preliminary report, that, in the range $18 \leq n \leq 35$, l mixing in Na**-Na collisions is very rapid, competing favorably with radiative decay of the laser-produced Na(nd) or Na(ns). Furthermore, since the blackbody-radiation-induced transfer rate to neighboring n levels has been shown to be quite high, further destruction of the initial state selectivity can occur.[3,4] Since the measured rates for heavy-body collisional processes that lead to Na^{+} and Na$_2{}^{+}$ formation are much lower than the rates for these state-changing processes, the reactant Rydberg atoms that produce the observed ions in Na**-Na(3s) collisions have a distribution of states clustered about the laser-produced state. Thus, the cross sections that we report for these processes must be understood to be associated with such a distribution of states of the reactant Rydberg atoms.

II. EXPERIMENTAL PROCEDURE

A schematic diagram of the apparatus is shown in Fig. 1. Sodium vapor was produced in an oven operated at ~ 500 K and located beneath a cylindrical stainless-steel collision cell; the density of ground-state sodium atoms, N, was determined by a method previously developed in this laboratory.[5] Two antiparallel laser beams, one yellow and one blue, entered the cell along its axis and produced Na(ns) or Na(nd) atoms by two-step excitation, $3s\rightarrow 3p\rightarrow nl$. Both lasers, the wavelengths of which we designate λ_Y and λ_B, were pumped by the frequency doubled and tripled outputs of the same Nd:YAG laser (where YAG denotes yttrium-aluminum-garnet).

Ions formed in the cell were extracted with a set of electrostatic focusing lenses, mass analyzed by a quadrupole mass filter, and detected with a CuBe particle multiplier. A tungsten filament (not shown in the figure) could be lowered to a position near one of the laser-beam apertures;

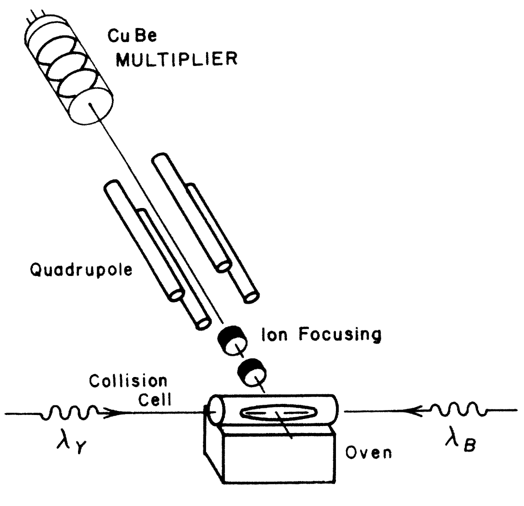

FIG. 1. Schematic diagram of the apparatus.

this filament could be directly heated to provide electrons which, when focused into the collision cell, produced ions, thus permitting the use of conventional mass spectrometry to detect "contaminants" in the collision cell. In this way it was determined that the Na_2 concentration in the vapor was roughly that calculated on the basis of equilibrium thermodynamics, about 0.75% at 500 K. This low concentration virtually insures that Na^{**}-Na_2 collisions are not contributing to the observed ion signals. Under normal operation data were, of course, acquired with the filament retracted, permitting both laser beams to enter the cell.

The output signal of the CuBe detector was fed into a gated integrator, and, after a preset number of pulses, ~50–500, the accumulated charge was digitized and stored in a computer. The wavelength settings of the dye lasers and mass settings of the quadrupole mass filter were adjusted and varied with the computer. Several different modes of data acquisition were employed.

In one mode of operation λ_Y was fixed at a D-line wavelength and production of a particular ion studied as a function of λ_B. In another mode relative abundances of the ionic products were studied at different values of N by fixing the laser wavelengths and scanning the mass spectrometer. In yet another mode of operation the collision cell and electrostatic lenses were replaced by an enclosure consisting of parallel plates, one of which was stainless-steel mesh through which ions could pass before being detected with a calibrated single-stage microchannel plate. This arrangement permitted collection of all ions formed in the interaction region and was used in our measurement of the blackbody photoionization rate. In addition, application of an appropriate voltage to one of the plates could be used to field ionize the Rydberg atoms, thus permitting determination of the number of initially formed Rydberg atoms. It was found that at $n=18$ the Rydberg atom concentration was roughly 1/200 that of Na(3s). This measurement is consistent with the fraction calculated from the $3p \rightarrow nd$ absorption cross section.

III. RESULTS AND DISCUSSION

At values of N that are low enough to preclude Na^{**}-Na^{**} interactions, atomic ions may be produced by collisional ionization, reaction (1), and by photoionization by blackbody radiation, reaction (4). At the lowest values of N, however, photoionization dominates. For example, in our preliminary report[2] it was shown that at $N=4\times10^{11}$ cm^{-3} only about 17% of the Na^+ yield was due to collisional ionization, the remainder resulting from photoionization by blackbody radiation. At still lower densities reaction (1) contributes a much smaller fraction so that at $N=10^{11}$ cm^{-3} virtually the entire Na^+ signal may be presumed to arise from photoionization. We therefore first discuss Na^+ formation by blackbody photoionization together with the consequences and implications of our data.

Figure 2 shows the Na^+ signal as a function of λ_B with λ_Y set at the D_2 wavelength; the Na(3s) density was 10^{11} cm^{-3}. As n increases the separation between adjacent resonances becomes sufficiently small so that the bandwidth of the blue laser, ~1 Å, is too broad to permit resolution of individual peaks. Ultimately λ_B reaches the threshold for photoionization of Na(3p), at which point the ion-detection system is barely saturated. Perhaps the most striking feature of the data in Fig. 2 is the near constancy of the Na^+ signal levels over most of the range of principal quantum numbers. Since at this atom density virtually all of the Na^+ signal results from photoionization by blackbody radiation, the signal from this process is essentially independent of n in this range. This leads to the important conclusion that Na^{**}-Na(3s) l mixing, self-l-mixing, is so rapid that it partially destroys the state selectivity provided by laser production of Rydberg atoms. Below we outline the analysis that leads to this conclusion, a conclusion that is consistent with the heavy-body collisional data to be discussed later in this paper.

We wish to examine the n dependence of Q_{nl}, total number of ions from blackbody photoionization, which is given by

$$Q_{nl}=\int_0^{t_0} K R_{nl} N_n^{**}(t) V(t)\,dt \ , \qquad (5)$$

where K is the collection efficiency of the ion-detection system, R_{nl} is the blackbody photoionization rate, $N_n^{**}(t)$ is the Rydberg-atom density as a function of time, $V(t)$ is the volume that they occupy, and t_0 is the effective

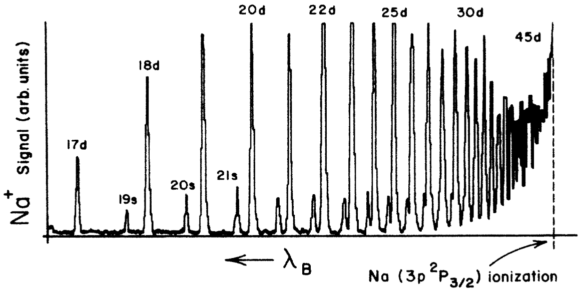

FIG. 2. Na^+ signal as a function of blue laser wavelength λ_B. The yellow laser wavelength λ_Y was fixed at that of the sodium D_2 line. The Na(3s) density was 10^{11} cm^{-3}.

residence time of the reactant Rydberg atoms in the volume from which ions are collected. $V(t)$ is taken to be time dependent to account for the possibility of diffusion. Notice that the quantity $N_n^{**}(t)V(t)$ is the total number of Rydberg atoms present at a given time, that is, the Rydberg-atom population. If it is assumed that the Rydberg-atom population is given by a single exponential, that the photoionization rate is low compared to the radiative rate,[6–8] and that $t_0 \sim \infty$, then Eq. (5) reduces to

$$Q_{nl} = KR_{nl}N_{0n}^{**}V\tau_n \ , \tag{6}$$

where N_{0n}^{**} is the initial concentration of Rydberg atoms, V is $V(0)$ the volume of the "laser cylinder," and τ_n is the effective lifetime. The validity of the above assumptions will be discussed below.

Now R_{nl}, N_{0n}^{**}, and τ_n all depend on principal quantum number, and, as noted above, the data indicate that these dependences conspire in such a way that photoionization yields are independent of n in the approximate range $18 \le n \le 30$. R_{nl}, the blackbody photoionization rate, has been the subject of recent investigations, both experimental[6] and theoretical.[7,8] It may be expressed as[6]

$$R_{nl} = \frac{c}{4}\int_0^\infty \sigma_{nl}(\nu)\rho(\nu)d\nu \ , \tag{7}$$

where $\sigma_{nl}(\nu)$ is the blackbody photoionization cross section as a function of frequency of ionizing radiation, $\rho(\nu)$ is the blackbody radiation energy density in photons/cm^3 Hz and c is the speed of light. $\rho(\nu)$ is given by the Planck formula

$$\rho(\nu) = \frac{8\pi\nu^2}{c^3}\left\{1\Bigg/\left[\exp\left[\frac{h\nu}{kT}\right]-1\right]\right\} , \tag{8}$$

where k is the Boltzmann constant. Since photoionization cross sections usually peak at threshold and fall off rapidly with increasing ν, Eq. (7) may be simplified. If E_{nl} is the ionization energy of a Rydberg state and is less than kT then the cross section is appreciable only in the low-energy "tail" of the Planck distribution where the energy density is slowly varying. Under these conditions R_{nl} becomes[6]

$$R_{nl} = \frac{c}{4}\left[\frac{8\pi}{c^3}\left[\frac{E_{nl}}{h}\right]^2\right] \times \left\{1\Bigg/\left[\exp\left[\frac{E_{nl}}{kT}\right]-1\right]\right\}\int_0^\infty \sigma_{nl}(\nu)d\nu \ . \tag{9}$$

The integral in Eq. (9) is proportional to the total oscillator strength to the continuum[9] which may be calculated from the bound-state oscillator strengths using the "partial sum rules" in Ref. 9, p. 256. We have extended Table 14 in Ref. 9, which gives hydrogen oscillator strengths, to principal quantum numbers as high as 30. We find that the total continuum oscillator strengths do not depend strongly on n so that the area under $\sigma_{nl}(\nu)$ does not depend strongly on n. Therefore, we may write

$$R_{nl} \approx \text{const} \times (E_{nl})^2 \Bigg/ \left[\exp\left[\frac{E_{nl}}{kT}\right]-1\right] . \tag{10}$$

Figure 3 shows the dependence of R_{nl} on principal quantum number for $T = 513$ K. For $20 \le n \le 30$ the log-log plot shows that

$$R_{nl} \sim n^{-1.4} \ , \tag{11}$$

which we take to be the n dependence of R_{nl} in Eq. (6).

The initial concentration of Rydberg atoms, N_{0n}^{**}, also depends on the value of the principal quantum number for a given value of N. This dependence is that of the $3p \rightarrow nl$ oscillator strength, which is proportional[9] to n^{-3}. Of course N_{0n}^{**} also depends on the spectral power output of the blue laser, but, since this was measured and found to vary by less than 10% in the range $18 \le n \le 35$, this dependence may be ignored in this calculation.

The final quantity in Eq. (6) that depends on n is τ_n, the characteristic lifetime of the Rydberg-atom population. If the initially produced laser-excited ns or nd state is the only one that comprises the Rydberg-atom population then $\tau_n \sim n^3$. Such a dependence, when combined with the $n^{-1.4}$ dependence of R_{nl} and n^{-3} dependence of N_{0n}^{**} would lead to an $n^{-1.4}$ dependence of the Na$^+$ signal. But this is in contrast to the observed constancy of this signal with n. The independence of the Na$^+$ signal on n therefore implies that $\tau_n \sim n^{4.4}$, which is very close to the $n^{4.5}$ dependence of the lifetime of a given n state (for the hydrogen atom) averaged over all angular momentum states.[9–12] Thus, we conclude that, under the assumptions stated above, at $N = 10^{11}$ cm^{-3} l mixing in Na**-Na collisions is occurring at a rate comparable to radiative decay of the initially prepared level, and that the state selectivity provided by laser excitation is partially destroyed.

The simplicity of the above analysis depends on the approximations that $t_0 \sim \infty$ and that $N_n^{**}(t)$ is given by a single exponential. This last approximation will be valid

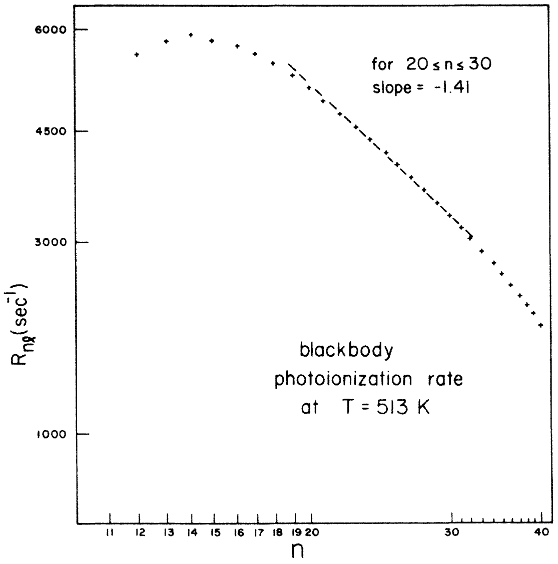

FIG. 3. Graph of Eq. (10), R_{nl} vs n. The least-squares fit to a straight line in the region $20 \le n \le 30$ shows that $R_{nl} \sim n^{-1.4}$ with correlation coefficient 0.997. The ordinate scale was normalized to the calculation in Ref. 7.

if the l-mixing cross section is very small so that radiative transitions to the $3p$ state dominate. It will also be valid if the l-mixing cross section is very large in which case radiative decay to $3p$ terminates quickly, after which $N_n^{**}(t)$ is essentially the single-exponential characteristic of an l-mixed population.[10] The cross section for self-l-mixing[13-15] of Rb($20f$) has been measured to be $\sim 10^5$ Å^2 suggesting that similarly large values are reasonable for sodium so that the second case is appropriate.

In order to assess the approximation $t_0 \sim \infty$ we may examine two limiting cases. First, if it is assumed that the initially excited volume is very small compared to the volume from which ions are collected, photoions from Rydberg atoms that migrate out of the collection volume prior to photoionization will not be detected. Since the average migration time is comparable to τ_n the assumption that $t_0 \sim \infty$ may not be justified, especially if the Rydberg atoms are destroyed upon impact with the cell walls. In this case $t_0 \ll \tau_n$ and, applying this criterion to the definite integral in Eq. (5), we see that there is no contribution to the n dependence of Q_{nl} from $N_n^{**}(t)$. We are left, therefore, with the product of the dependences of N_{0n}^{**} and R_{nl}, $\sim n^{-4.4}$. Since the data show that there is no n dependence of Q_{nl} we conclude that either the $t_0 \sim \infty$ approximation is valid so that $\tau_n \sim n^{4.4}$, or that the assumed n dependences of N_{0n}^{**} and R_{nl} are incorrect. Since the production rate is known to be proportional to the $3p \rightarrow ns$ and $3p \rightarrow nd$ oscillator strengths ($\sim n^{-3}$) and the calculation of R_{nl} is reliable we conclude that the $t_0 \sim \infty$ approximation is valid. This conclusion is further supported by the fact that the n dependence of τ_n that is required for Q_{nl} to be independent of n, $n^{4.4}$, is very nearly the same as physically interpretable n dependence, namely the $n^{4.5}$ characteristic of a mixed population of l states.[9,10] In other words we believe that it is significant that we obtain a physically meaningful n dependence.

The above discussion does not unequivocally prove the validity of the approximation that $t_0 \sim \infty$. Furthermore, the reason for any such validity is not intuitively obvious. Additional insight might be gained by examining the second of the two limiting cases. In this limit the volume from which ions are efficiently collected in our apparatus is assumed small compared to the initial excitation volume. For this case, migration of Rydberg atoms out of the collection volume is compensated by migration of Rydberg atoms produced outside this volume into it. Here again it is difficult to assess validity by intuition, however, we did observe that Q_{nl} saturated at very low ion extractor voltage, less than 5 V, suggesting that this case may be realistic. If so then the approximation $t_0 \sim \infty$ is appropriate.

Although the evidence is not unequivocal, we, based on the above analysis and discussion, conclude that self-l-mixing is indeed rapid and that the state selectivity provided by laser excitation is partially destroyed. Because both the s and d-state Na$^+$ signals are independent of n in the range studied, this conclusion pertains to both nd and ns states. Previous experiments[10,12] at lower principal quantum numbers have shown that initially produced nd states are mixed to all nl states, $l \geq 2$, by foreign perturbers, but, because of the relatively large energy differences between s states and other angular momentum states of the same n manifold, initially produced ns states were not appreciably mixed. At higher n, however, the energy differences ΔE between s, p, and d states of both the n and $n-1$ manifolds are considerably smaller than kT and Hugon *et al.*[13,14] found that state-changing cross sections for both Rb(ns) and Rb(nd) collisions with xenon are large, greater than 10^4 Å^2.

Our experiments at principal quantum numbers greater than 18 lead to the conclusion that both ns and nd states of sodium are efficiently l mixed. This is consistent with previous results for foreign perturbers, although our results pertain to self-l-mixing; self-l-mixing for alkali-metal-atom Rydberg states is known to be even more efficient than l mixing by xenon atoms.[15] In fact, Hugon *et al.*[14] showed that state-changing cross sections for collisions of both Rb(ns) and Rb(nd) with ground-state rubidium atoms are essentially the geometric cross section of the Rydberg atom even for relatively high values of ΔE. For example, they measured 10^4 Å^2 for Rb($9s$) and ΔE is greater than 100 cm^{-1} to the nearest state. These state-changing processes could include l mixing within the n manifold of states as well as l mixing to neighboring manifolds. Recently[16] it was shown that Na(ns) and Na(np) are efficiently converted to Na($n-1, l \leq 2$) by collisions with xenon atoms. Of course, such a state-changing process would be indistinguishable in our experiments from l mixing within the n manifold because of the small (unity) change in n.

Although the n dependence of the lifetime of the mixed population is deduced to be very close to that of a statistical distribution of l states, complete l mixing is not necessary. Examination of the rate equations shows that the rate of transfer to high l states is favored because of their higher degeneracies and longer lifetimes. Thus, while the mixing may not be complete, the importance of the high l states, especially of course the circular states, leads to an effective lifetime that, in our experiment, would be indistinguishable from that associated with a statistical distribution.

In addition to collisional processes n changing can occur by superradiance or by interaction with blackbody radiation. The transfer rates for both of these effects are, however, maximum to nearby levels[3,4] (lower levels for the case of superradiance) so that although the state selectivity can be further destroyed, Rydberg atoms are still present. These transfer rates to nearby levels can be quite high, of the same order of magnitude as the radiative rates. Furthermore, since the initially produced angular momentum states are mixed we may expect that essentially all l states of $n-1$ and $n+1$ will also be populated by the processes. Since these blackbody-induced transfer rates are comparable to the radiative rates we anticipate that "state selectivity" for $N \simeq 10^{11}$ cm^{-3} and $T \simeq 500$ K refers to a roughly statistical population of all l states of principal quantum numbers $n-1$ and $n+1$ as well as n. Transfer to these neighboring n states would not severely affect the apparent lifetime of the Rydberg-atom population because only small changes in principal quantum number are involved. This distribution of states could be further altered if superradiance occurs, but our data suggest that this is not important under the conditions of these experiments.[2]

Since l mixing competes with radiative decay we may estimate the order of magnitude of the cross section by equating the rate to that for radiative decay,[9] $\sim 10^5\ \mathrm{sec}^{-1}$ for $n=20$. Thus

$$k_l N \approx 10^5\ \mathrm{sec}^{-1}\ , \tag{12}$$

where k_l is the rate coefficient for Na^{**}-Na l mixing and $N=10^{11}\ \mathrm{cm}^{-3}$. This leads to an estimate of $k_l=10^{-6}$ $\mathrm{cm}^3/\mathrm{sec}$ which corresponds to an l-mixing cross section of $\sim 10^{-11}\ \mathrm{cm}^2$, the geometric cross section. This value, while huge by the standards of collisions involving ordinary atoms, is consistent with measurements of self-l-mixing cross sections of rubidium and cesium Rydberg atoms.[13-15] While we have estimated the self-l-mixing cross section to be $\sim 10^5\ \mathrm{\AA}^2$ it is not necessary, or indeed even likely, that the cross sections for mixing of *ns* and *nd* states are the same. In fact, since it is probable that at least the *ns* states are "mixed" to l states of the neighboring manifold, our use of the term self-l-mixing is understood to include this process.

Although the l-mixing cross sections for *ns* and *nd* states are large we cannot, from our data, compute their ratio. Since the laser light is linearly polarized the initial populations of the *nd* and *ns* states should be in the ratio of the $\Delta m_j=0$ oscillator strengths. Using the radial matrix elements for sodium given by Lingard and Nielsen[17] the asymptotic value of this ratio is approximately 5. This is only coincidentally the same as the ratio of the degeneracies, as may be seen by noting that the analogous ratio of oscillator strengths for hydrogen is about 20. Since the observed ratios of the peak heights are $\sim$5:1 we conclude that they reflect only the initial number of Rydberg atoms produced, and not the ratio of the l-mixing cross sections. This also provides verification that the l-mixing rates for both *ns* and *nd* states are much greater than the blackbody photoionization rates.

In order to independently check this conclusion we used the experimental setup described in Sec. II in which total ions could be collected to measure the photoionization rate. This provides an absolute measurement of Q_{nl} in Eq. (6) so that K, the ion collection efficiency, is unity for all n. We also obtained spectra identical to that shown in Fig. 2, Na^+ versus λ_B, showing that the observed constancy of the Na^+ signal as a function of n cannot be an artifact introduced by an n-dependent ion-collection efficiency.

For $K=1$ the blackbody photoionization rate is

$$R_{nl}=\frac{Q_{nl}}{N_{0n}^{**}V}\frac{1}{\tau_n}\ , \tag{13}$$

where $N_{0n}^{**}V$ is the total number of Rydberg atoms initially produced. Thus, R_{nl} may be calculated in terms of τ_n. Our data for Na(18d) are typical: $Q_{nl}=4\times10^6$ ions/pulse and $N_{0n}^{**}V=2.5\times10^7$. This gives

$$R_{18,l}=0.16/\tau_{18} \tag{14}$$

with τ_n in seconds. If τ_{18} is taken to be the 18d lifetime,[11] $\sim$5 μsec, $R_{18,d}\simeq 3.2\times10^4\ \mathrm{sec}^{-1}$, about five times larger than the calculated value.[7,8] If, however, τ_{18} is taken to be the l-averaged hydrogenic lifetime,[9] $\sim$28 μsec, then $R_{18,l}\simeq 5.7\times10^3\ \mathrm{sec}^{-1}$, very close to the calculated value (see Fig. 3). These data therefore support our previous conclusion that the effective lifetime of the Rydberg-atom population more nearly coincides with the l-averaged lifetime than the state-specific lifetime, indicating that substantial l mixing occurs.

One of the initial goals of this work was to determine state-specific microscopic cross sections for Na^{**}/Na(3s) collisions that lead to ion formation, reactions (1) and (2). In view of our finding that self-l-mixing occurs with an enormous cross section, $\sim 10^5\ \mathrm{\AA}^2$, it is clear that at values of N sufficiently high to observe ion formation in heavy-body collisions, state selectivity provided by laser production of Na(*nd*) or Na(*ns*) will have been destroyed. While this l mixing redistributes the excited-state population among all angular momentum states of the laser-produced principal quantum number, other effects, such as superradiance or blackbody-radiation-induced transfer can efficiently populate neighboring n states. These neighboring n states will also have a wide distribution of l states. Thus, while heavy-body cross-section measurements will be presented in this section, it must be understood that these cross sections are state specific only to the extent that they have been measured using reactant Rydberg atoms that were initially state selected, but which have undergone redistribution as discussed in the preceding section. Although the collision cross section is usually defined as an intrinsic property of a particular (state-specific) set of reactants with a given relative velocity or velocity distribution, the "cross sections" measured in this work are functions of other (experimental) parameters as well, in particular the atom density N and the temperature T. The atom density determines the extent of l mixing and the temperature of course determines the nature of the blackbody radiation. It is interesting that, while blackbody-radiation-induced transfer may be virtually eliminated by cooling the reaction region,[3,11] there is little that can be done to avoid self-l-mixing. This is so because atom densities sufficiently low to preclude self-l-mixing are also low enough to preclude ion formation in heavy-body collisions.

Although virtually the entire Na^+ signal is due to photoionization, collisional ionization contributing very little to the total, the (much smaller) $\mathrm{Na_2}^+$ signal observed at the Rydberg-state resonances arises exclusively from Na^{**}-Na(3s) associative ionization.[2] Figure 4 shows the $\mathrm{Na_2}^+$ signal as a function of λ_B with λ_Y fixed at D_2. The small "background" at nonresonant values of λ_B is produced by Na(3p)-Na(3p) associative ionization;[18] the yellow laser intensity was adjusted to minimize ion formation by multiphoton ionization of $\mathrm{Na_2}$ present in the vapor.[19] In our preliminary report we noted the very strong n dependence of the cross section for Na^{**}-Na(3s) associative ionization. Sharp decreases in associative ionization with increasing principal quantum numbers have also been observed in experiments with argon[20] and strontium.[21]

In our preliminary report we also estimated this cross section by comparing the $\mathrm{Na_2}^+$ signal with that observed

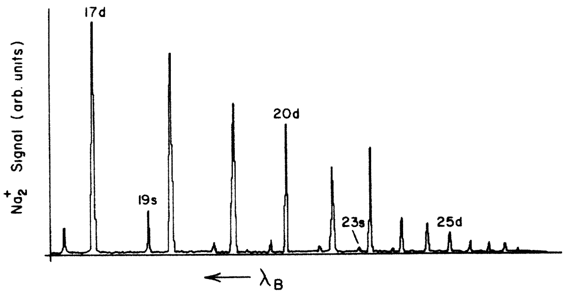

FIG. 4. $Na_3{}^+$ signal as a function of blue laser wavelength λ_B. The yellow laser wavelength λ_Y was fixed at that of the sodium D_2 line. The Na(3s) density was 10^{11} cm^{-3}.

for Na(3p)-Na(3p) associative ionization. This method was dependent upon an assumed value for the Na(3p)-Na(3p) associative ionization cross section, but our estimate necessarily reflected the relatively wide range of values in the literature. However, since the contribution of collisionally produced Na^+ to the total Na^+ signal may be ignored at low values of N, we may compute the cross section for Na**-Na(3s) associative ionization at a given n by comparing the $Na_2{}^+$ signal to that for Na^+, using the blackbody photoionization rate measured in these experiments.

The $Na_2{}^+$ signal from associative ionization is given by

$$Q_2 = KN_{0n}^{**} k_a N V' \tau_n \ , \tag{15}$$

where k_a is the rate constant for associative ionization, V' is the interaction volume and the other quantities are as previously defined. Under the assumption that all Na^+ arise from photoionization by blackbody radiation the Na^+ signal is given by Eq. (6). Dividing Eq. (6) by Eq. (15), rearranging and making the approximation that $V' \approx V$ we have

$$k_a(nl) = \frac{Q_2}{Q_1} \frac{R_{nl}}{N} \ , \tag{16}$$

where for consistency in the present context we have replaced Q_{nl} in Eq. (6) with Q_1. The $V' \approx V$ approximation represents an assumption that the volume from which ions may be collected is very nearly equal to the volume of the "laser cylinder." While migration may cause the interaction volume V' to vary with lifetime, the cross section reported below is that for a specific (initially prepared) state, namely 18d. The lifetime of this state is sufficiently short that the $V' = V$ approximation is justified. Although the validity of this approximation decreases somewhat with increasing n, the effect is well within the uncertainty of the heavy-body cross section estimates.

In Eq. (16) it is understood that the nl associated with both the photoionization rate and the rate constant designates the initially prepared Rydberg state. Notice that this expression does not include the ion-collection efficiency, the initial number of Rydberg atoms produced or the interaction volume. It includes the lifetime of the Rydberg-atom population only to the extent that it was used in the computation of the blackbody photoionization rate from the data.

Using the relationship between rate constant and cross section we may write

$$\sigma(nl;N,T) = \frac{Q_2}{Q_1} \frac{R_{nl}}{\langle v \rangle N} \ , \tag{17}$$

where $\langle v \rangle$ is the average atomic speed and we have explicitly indicated the N and T dependences of σ as discussed at the beginning of this section.

From our data and Eq. (17) we find that

$$\sigma(18d;10^{11}\ \text{cm}^{-3},513\ \text{K}) \simeq 150\ \text{Å}^2 \ . \tag{18}$$

This value, while high by standards of collisions involving ordinary (non-Rydberg) atoms, is orders of magnitude lower than the estimated self-mixing rate. This justifies our assertion that it would be very difficult to measure state-specific ion-formation cross sections. Furthermore, this value of σ indicates that Na**-Na(3s) collisions that lead to $Na_2{}^+$ formation are those having impact parameters less than ~10 Å. This is reasonable since associative ionization is due to relatively short-range interactions between the Rydberg-atom core and the ground-state atom.[22]

Figure 4 shows the exceptionally strong n dependence of the associative ionization cross section. This cross section varies roughly as n^{-6} although correction for the lifetime of the Rydberg atom population makes this dependence even stronger, $\sim n^{-7.5}$. Part of this n dependence can be attributed to the $\sim n^2$ dependence of the average value of the radial electronic coordinate. In order for associative ionization to occur the Rydberg electron must carry off enough kinetic energy to stabilize the $Na_2{}^+$ product. Therefore there must be communication between the Na^+-Na(3s) collision complex and this electron via a force, for example the quadrupole force. Of course, the distance between the Rydberg electron and this diatomic core determines the strength of the force. If the Rydberg electron is remote, then interactions will be weak, making it difficult to eject the Rydberg electron with enough kinetic energy to stabilize the $Na_2{}^+$. Furthermore, the strong n dependence, together with our conclusion that l mixing is essentially complete prior to associative ionization, suggests that the more heavily weighted higher angular momentum states are less reactive than are lower states. This is so because higher angular momentum states prohibit significant probing of the collision core by the Rydberg electron. We conclude, therefore, that electrons in high n states, *and* high l states will have minimum communication with the Na^+-Na(3s) core, causing high-n—high-l Rydberg atoms to be virtually unreactive.

Since the cross section for collisional ionization is roughly four times that for associative ionization[2] at $n = 18$, we estimate that the cross section for collisional ionization is of the order of 600 Å^2. However, because at these values of N almost all of the Na^+ signal arises from photoionization by blackbody radiation, it is difficult to extract detailed information about collisional ionization, especially the n dependence. While 600 Å^2 is a large cross section it too is considerably smaller than the estimated self-l-mixing cross section so that the term cross section has the same connotation as that reported for associative ionization. This estimated value of the collisional ionization cross section suggests that impact parameters of the order of 15 Å are sufficient for ionizing collisions. Such a long-range interaction is not unreasonable in view of the relatively large orbital distances for an electron having $n = 18$.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Division of Chemical Sciences, under Grant No. DE-FG02-84ER1327, the National Science Foundation under Grant No. INT-8318024 and by the Consiglio Nazionale delle Ricerche U.S.-Italy Cooperative Program under Grant No. 47923. The authors would like to thank Dr. J. D. Kelley of McDonnell-Douglas Research Laboratories for many valuable discussions and Dr. S. Gozzini for critically reading the manuscript.

---

[1] See, for example, *Rydberg States of Atoms and Molecules,* edited by R. F. Stebbings and F. B. Dunning (Cambridge University Press, Cambridge, 1983).

[2] C. E. Burkhardt, W. P. Garver, V. S. Kushawaha, and J. J. Leventhal, Phys. Rev. A **30**, 652 (1984).

[3] W. P. Spencer, A. G. Vaidyanathan, D. Kleppner, and T. W. Ducas, Phys. Rev. A **25**, 380 (1982).

[4] T. F. Gallagher, in Ref. 1, and references cited therein.

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

[6] W. P. Spencer, A. G. Vaidyanathan, D. Kleppner, and T. W. Ducas, Phys. Rev. A **26**, 1490 (1982).

[7] G. W. Lehman, J. Phys. B **16**, 2145 (1983).

[8] C. E. Theodosiou, Phys. Rev. A **30**, 2881 (1984).

[9] H. A. Bethe and E. E. Salpeter, *The Quantum Mechanics of One and Two Electron Atoms* (Academic, New York, 1957).

[10] T. F. Gallagher, S. A. Edelstein, and R. M. Hill, Phys. Rev. A **15**, 1945 (1977).

[11] W. P. Spencer, A. G. Vaidyanathan, D. Kleppner, and T. W. Ducas, Phys. Rev. A **24**, 2513 (1981).

[12] T. F. Gallagher, S. A. Edelstein and R. M. Hill, Phys. Rev. Lett. **35**, 644 (1975).

[13] M. Hugon, F. Counand, and P. R. Fournier, J. Phys. B **13**, L109 (1980).

[14] M. Hugon, B. Sayer, P. R. Fournier, and F. Gounand, J. Phys. B **15**, 2391 (1982).

[15] M. Hugon, F. Gounand, P. R. Fournier, and J. Berlande, J. Phys. B **12**, 2707 (1979); see also F. Gounand and J. Berlande in Ref. 1.

[16] J. P. McIntire, G. B. McMillan, K. A. Smith, F. B. Dunning, and R. F. Stebbings, Phys. Rev. A **29**, 381 (1984).

[17] A. Lingard and S. E. Nielsen, At. Data Nucl. Data Tables **19**, 534 (1977).

[18] 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).

[19] C. E. Burkhardt, W. P. Garver, and J. J. Leventhal, Phys. Rev. A **31**, 505 (1985).

[20] K. Radler and J. Berkowitz, J. Chem. Phys. **70**, 221 (1979).

[21] E. F. Worden, J. A. Paisner, and J. G. Conway, Opt. Lett. **3**, 156 (1978).

[22] A. P. Hickman, R. E. Olson, and J. Pascale, in Ref. 1.