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Energy pooling in Na $3p$-Na $3p$ collisions

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The formation of Na (nl) and $Na_2{}^+$ in sodium vapor ($\sim 10^{13}$ cm^{-3}) irradiated by a single-frequency (20-MHz bandwidth) cw dye laser tuned to one of the D lines has been studied. The dependence of product signal on laser power density suggests that Na $3p$-Na $3p$ energy pooling collisions are responsible for these species. Rate constants for specific reaction channels and temperature dependences of rate constants are also reported.

I. INTRODUCTION

Within the past few years a number of interesting effects have been observed when alkali-metal vapors were illuminated with laser light tuned to excite an atomic transition.[1-7] Some of these effects involved multiphoton processes and required the high laser power densities attainable only with a pulsed laser. Others were observed with cw laser irradiation and were for the most part the result of atomic collisions involving excited species. The effects observed in this laboratory, and reported earlier[4] in preliminary form, were initiated by a cw laser beam tuned to one of the sodium D lines and directed into a cell containing sodium atoms at density $\sim 10^{13}$ cm^{-3}. Three observations were reported:

(1) Radiation from Na states lying higher than Na $3p$.
(2) Formation of $Na_2{}^+$ ions.
(3) Formation of Na^+ ions.

Both the radiation and the $Na_2{}^+$ ions were deduced to be the products of different reaction channels involving the same reactants, two Na $3p$ atoms. These energy pooling processes are excitation transfer,

$$\mathrm{Na}\,3p + \mathrm{Na}\,3p \rightarrow \mathrm{Na}(nl) + \mathrm{Na}\,3s\,, \tag{1}$$

and associative ionization,

$$\mathrm{Na}\,3p + \mathrm{Na}\,3p \rightarrow \mathrm{Na}_2{}^+ + e\,. \tag{2}$$

It was concluded that the Na^+ ions resulted from photodissociation of nascent $Na_2{}^+$.

These results were germane to the interpretation of other experiments. For example, in two separate experiments McIlrath and Lucatorto[1] observed nearly complete ionization of Na and Li vapors using a 1-MW pulsed laser tuned to the appropriate resonance line. It has been concluded that this ionization results from electron impact on Na $3p$ or Li $2p$ where the necessary electron energy is supplied by e-Na $3p$ or e-Li $2p$ superelastic collisions.[1,6,8] Each ionization, of course, adds another electron to the mixture so that a cascade process leads to complete ionization. The process that supplies the initial seed electrons is not firmly established[4]; if the cross section is high enough, associative ionization [Eq. (2)] could serve this purpose.

Since our initial report on energy pooling processes, we have extensively modified our apparatus. The purpose of these modifications was to obtain more quantitative information on the reactions. The number of laser photons required for the reactions to proceed may now be determined by precise variation of the laser power density. In addition, modifications were made that permit the determination of rate constants, and hence effective cross sections, for these reactions. Finally, the role of kinetic energy transfer in some of the excitation transfer energy pooling processes has also been studied.

II. EXPERIMENTAL

A schematic diagram of the apparatus used in these experiments is shown in Fig. 1. A Spectra-Physics Model 580 single-frequency dye laser pumped by a 5-W Ar^+ laser and tuned to either the sodium D_1 or D_2 line was used to excite sodium atoms. The bandwidth was 20 MHz and the laser

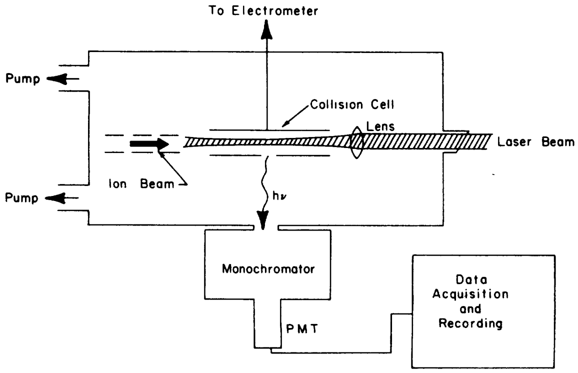

FIG. 1. Schematic diagram of the apparatus.

power at the D lines was about 100 mW. A small fraction of the laser beam was directed into a 2-GHz free spectral range (FSR), 13-MHz bandwidth confocal interferometer (Spectra-Physics Model 470-3) and displayed on an oscilloscope to monitor frequency stability. The main laser beam was focused into the collision cell using a 12.7-cm focal length lens; the laser spot size within the collision cell was $\simeq 0.07$ cm. The laser power density was varied with a set of calibrated neutral-density filters.

In addition to the apertures for the laser beam, the collision cell has a 2 cm long × 2 mm wide slot parallel to the laser beam. Photons emanating from the collision cell that pass through the slot were dispersed with a 0.25-m scanning monochromator. A notch filter with transmission 10^{-7} at 589 nm was used to attenuate the 589-nm fluorescence from the sodium vapor; the transmitted signal was nevertheless high enough to detect. After passing through the monochromator, photons were detected with a cooled photomultiplier tube used in the counting mode. Ions formed in the laser-excited vapor were collected on an electrode inserted into the collision cell, and the ion current was measured with an electrometer. A small transverse electric field was established to ensure complete ion collection. Although both Na^+ and Na_2^+ ions are known to be formed in the laser-excited vapor, the origin of the Na^+ has been determined[4] to be photodissociation of Na_2^+ so that the total ion signal is a measure of incipient Na_2^+.

Sodium vapor was introduced into the collision cell from an oven located beneath the cell. This configuration was necessary to minimize blackbody radiation in the optical system. For this reason the reading on a thermocouple mounted in the oven could not be used to infer the sodium-atom density in the cell. Instead, the atom density n was determined by directing a mass selected N_2^+ ion beam into the cell and observing the 589-nm radiation resulting from collision-induced excitation in N_2^+-Na collisions. This signal, together with the previously measured absolute cross section for this N_2^+-Na process,[9] led to a determination of n as a function of the oven thermocouple reading. A characteristic temperature of the vapor was then assigned by comparison with the n vs T relationship given by Fairbank *et al.*[10]

III. RESULTS AND DISCUSSION

In order to determine the nature of the reaction responsible for a given product, the signal may be studied as a function of laser power density I. If m photons from the laser beam are required to produce a given signal i, then

$$i = (\text{const})I^m , \tag{3}$$

where, in these experiments, i may be either ion current or photon count rate. Taking logarithms of both sides,

$$\log i = \log(\text{const}) + m \log I , \tag{4}$$

so that a log-log plot of i vs I should yield a straight line with slope m. As an example, Fig. 2 is a plot of the 589-nm emission as a function of laser power density I, in W/cm^2. The straight line is a least-squares fit to the data for $I \leqslant 8\,\text{W cm}^2$ and has a correlation coefficient 0.99. The slope m is 1.0, as it should be for laser excitation of the Na $3s \rightarrow 3p$ transition. The leveling out of the 589-nm fluorescence signal at about 8 W cm^2 indicates saturation of the transition.

Figures 3–5 are similar plots for Na_2^+ and the 330-nm and 285-nm radiation signals, respectively. The ordinate in Fig. 3 is ion current, and, as in Fig. 2, the abscissa is laser power density. The curvature near about 8 W/cm^2 again indicates saturation of the Na $3s \rightarrow 3p$ transition. The straight line is a least-squares fit to the data for $I \leqslant 8$ W cm^2; the slope of the line is 2.0 with a correlation coefficient 0.99. The data in Fig. 3 clearly show that two laser photons are required to form a single Na_2^+ ion in support of the hypothesis[4] that associative ionization [reaction (2)] is responsible for the formation of Na_2^+. This is also consistent with the recent result of de Jong and van der Valk.[5]

The rate constant for associative ionization k_{ion} may be calculated from these data using the

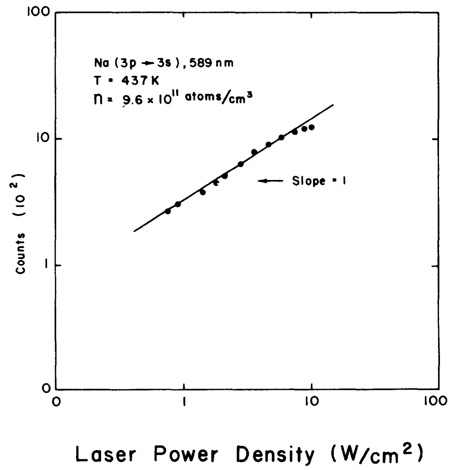

FIG. 2. Log-log plot of 589-nm fluorescence versus laser power density.

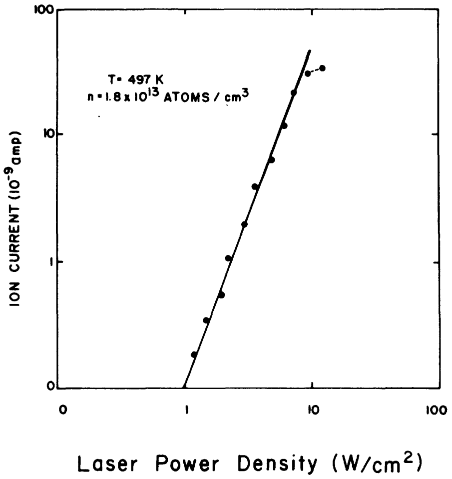

FIG. 3. Log-log plot of total ion current versus laser power density.

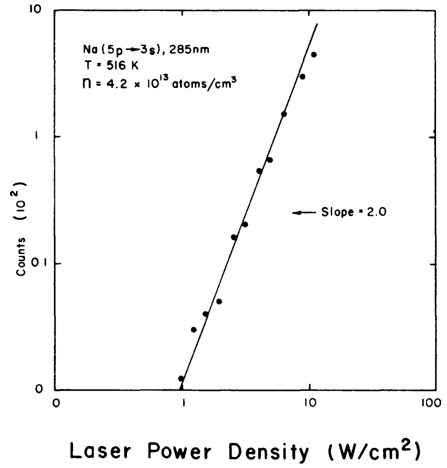

FIG. 5. Log-log plot of 285-nm fluorescence versus laser power density.

relation

$$k_{\text{ion}}=\left(\frac{i_{\text{ion}}}{1.6\times10^{-19}}\right)\Big/\int[n^*(r)]^2\,dV\ , \tag{5}$$

where i_{ion} is the total ion current and $n^*(r)$ the density of Na $3p$ as a function of r, the radial coordinate of the cylindrical collision cell. The integration is to be carried out over the entire collision cell. It is the denominator in Eq. (5) that is the greatest source of error in computing rate constants (for either associative ionization or excited-state formation) in these experiments. Because the 589-nm fluorescence from excited sodium atoms is imprisoned in the vapor at the atom densities of these experiments, $n^*(r)$ is not precisely known. However, by examining limiting cases an uncertainty may be assigned to the computed rate constants. At one extreme is the case in which the optical depth is long compared to the dimensions of the collision cell. Under these circumstances $n^*(r)$ may be approximated by

$$n^*(r)=\begin{cases}n_0^*=\text{const}, & 0<r<r_L\\ 0, & r_L<r\end{cases} \tag{6}$$

where r_L is the radius of the laser beam. On the other hand, if the optical depth is short compared to the dimensions of the collision cell, then $n^*(r)$ may be approximated by

$$n^*(r)=\begin{cases}n_0^*, & 0<r<r_L\\ n_0^*(r_L/r), & r_L<r<r_c\\ 0, & r_c<r\end{cases} \tag{7}$$

where r_c is the radius of the collision cell. For the latter case the integral in Eq. (5) becomes

$$\int[n^*(r)]^2\,dV=[n_0^*]^2V_L(1+2\ln r_c/r_L)\ , \tag{8}$$

where $V_L=\pi r_L^2 l$, the volume of the "laser cylinder" in the collision cell of length l. From Eq. (8) it may be seen that the logarithmic term arises from the imprisonment of the 589-nm radiation. As expected, imprisonment of the 589-nm radiation effectively increases the interaction volume. Because relatively wide monochromator slits (2 mm) were necessary in these experiments, the monochromator provided no discrimination against this increased interaction volume. For the dimensions of this experiment $2\ln r_c/r_L$ is very nearly 2.0, so that rate constants calculated under the assumption that the atom density is as given in Eq. (6), for long optical depth, may be

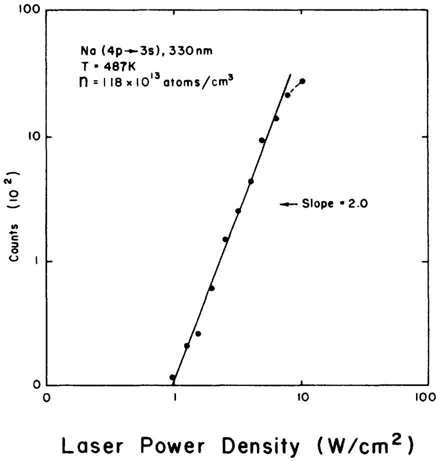

FIG. 4. Log-log plot of 330-nm fluorescence versus laser power density.

regarded as an upper limit; rate constants reported here are calculated using this form of $n^*(r)$. However, as indicated in Eq. (8), these rate constants could be lower by as much as a factor of 3. To minimize the effect, data acquired for the purpose of computing rate constants were obtained at the lowest possible temperatures at which a signal could be detected. Nevertheless, the uncertainty discussed above must be considered.

The data yield k_{ion} (497 K) $\simeq 2\times10^{-13}$ cm^3/sec. Using a beam apparatus de Jong and van der Valk[5] obtained 1.5×10^{-13} cm^3/sec, but, of course, their value cannot be compared directly to ours because of the different distribution of atomic speeds. An effective associative ionization cross section σ_{eff} may be calculated using the relation

$$k=\bar{v}\sigma_{\text{eff}}\ , \tag{9}$$

where $\bar{v}$ is the average atomic speed. Using the above rate constant the cross section for associative ionization is found to be $\sim2\times10^{-18}$ cm^2. De Jong and van der Valk found an effective associative cross section of 5×10^{-18} cm^2. Both of these values are considerably lower than the 10^{-15} cm^2 estimate contained in our preliminary report[4] of Na 3p energy pooling collisions. Nevertheless, as noted by de Jong and van der Valk, cross sections of these magnitudes are still sufficiently high to make it likely that the electron seeding mechanism in the McIlrath-Lucatorto[1(a)] experiment is associative ionization.

The formation of high-lying excited atomic sodium states was also investigated. Figure 6 is a partial Grotrian diagram showing relevant states. We have chosen to study the formation of Na 4p and Na 5p by examination of the 330-nm and 285-nm radiation signals, respectively. The 330-nm data of Fig. 4 show that, as was the case for ion formation, production of Na 4p requires two laser photons; again, saturation is apparent at about 8 W cm^2. The rate constant k_{330} may be calculated according to

$$k_{330}=\left(\frac{i_{330}}{\bar{E}(330)}\right)\left(\frac{4\pi}{\bar{\Omega}(s)}\right)\Big/\int[n^*(r)]^2dV\ , \tag{10}$$

where i_{330} is the observed 330-nm signal in photons/sec, $\bar{E}(330)$ is the absolute spectral efficiency at this wavelength, and $\bar{\Omega}(s)$ is the average solid angle subtended by the slit. The factor $[4\pi/\bar{\Omega}(s)]$ accounts for the finite solid angle sampled by the optical system[11] and is calculated under the assumption that points along the axis of the cylinder are the only sources of radiation; these sources emit photons isotropically. It is also assumed that Na 4p is not populated by cascading from higher levels.

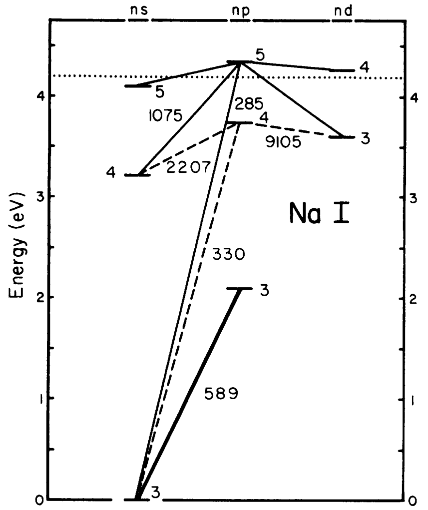

FIG. 6. Partial energy level diagram for NaI. The heavy line indicates the laser excited $3s\rightarrow3p$ transition. The dashed lines indicate the electric dipole allowed transitions from Na 4p and the solid lines from Na 5p. Wavelengths of the transitions shown are in nanometers. Only the np-3s radiation can be observed in our experiments. The dotted line is drawn at 4.2 eV, twice the Na 3p energy.

The data yield k_{330} (487 K) $=1\times10^{-16}$ cm^3/sec; however, the rate constant for formation of Na 4p is related to k_{330} by

$$k_{4p}=\frac{1}{B_r}k_{330}=3\times10^{-16}\ \text{cm}^3/\text{sec}\ , \tag{11}$$

where B_r is the branching ratio[12] for the $4p\rightarrow3s$ transition. It is possible that trapping of the 330-nm resonance line could alter the branching in favor of the $4p\rightarrow4s$ transition; however, application of Holt's[13] treatment of resonance trapping, which is appropriate in this case, shows that the correction at 487 K is negligible. This is not so as the temperature is increased, as will be discussed below.

Figure 5 shows data for production of Na 5p as a function of laser power density; clearly, it is similar to Fig. 4 for Na 4p. Notice that a temperature of 516 K was necessary in order to have a sufficient 285-nm signal. The onset of saturation is, however, not as obvious as in the preceeding figures. The slope of the least-squares straight line is again 2.0 with a correlation coefficient 0.99 showing that two laser photons are required for production of Na 5p, and, as before, suggesting that Na 3p-Na 3p energy pooling is responsible for formation of Na 5p. The rate constant k_{5p} calculated as above for k_{4p} is 7×10^{-18} cm^3/sec. There is, however, a significant difference between the energy pooling reactions leading to Na 4p

and Na $5p$. The former results from an exothermic reaction, while the latter requires conversion of 0.14 eV of kinetic energy to internal energy; that is, it is formed in an endothermic reaction. In order to assess the role of kinetic energy conversion in this process we examined the 285-nm signal as a function of temperature. The effect of trapping of this signal,[13] with concomitant modification of the branching ratio, was determined to be negligible over the entire range of temperatures studied. Increasing the temperature produces both a higher atom density and a higher average atomic speed. If kinetic energy conversion were not important for formation of Na $5p$, then the ratio of the 285-nm signal to the square of the atom density would be independent of temperature. Figure 7 is a plot of $i_{285}/[n_0^*]^2$ as a function of temperature; the use of n_0^* in the denominator carries the implicit assumption that the interaction volume remains constant as the temperature is varied. Within the limitation of this assumption the increase in the ratio $i_{285}[n_0^*]^2$ with increasing temperature indicates that indeed kinetic energy conversion is important in the formation of Na $5p$. Also plotted for comparison in Fig. 7 are analagous data for the 330-nm radiation. These data exhibit little temperature dependence, as frequently is the case for exothermic or thermoneutral processes.

If imprisonment of the 589-nm radiation were not important, the ratio $i_{285}/[n_0^*]^2$ would be proportional to the rate constant. For endothermic processes the temperature dependence of the rate constant is usually given by[14]

$$k(T)=A(T)e^{-E_T/kT}\,, \tag{12}$$

where E_T is the threshold or activation energy and k is the Boltzmann constant. $A(T)$ is a weak function of temperature and is usually taken to be a constant so that a semilog plot of $k(T)$ vs $1/T$ should yield a straight line with slope $-E_T/k$. Figure 8 is such a plot for the 285-nm radiation data of Fig. 7. The solid line is a least-squares fit with a correlation coefficient 0.96. The slope of this line yields a threshold energy E_T of 0.86 eV, which is about six times higher than the thermochemical value of 0.14 eV. Although E_T need not be the thermochemical value, our "experimentally determined" value seems excessively high. The probable cause of the discrepancy lies in the neglect of the increased interaction volume with increasing temperature due to imprisonment of the 589-nm radiation. To estimate the extent of the effect we have plotted the Arrhenius form of the rate constant, Eq. (12), with $E_T = 0.14$ eV in Fig. 8; this function was normalized at the lowest temperature data point. Thus if E_T is roughly the thermochemical value, then the effective interaction volume at the highest temperature is about three times the volume of the laser cylinder. This is very close to the value calculated using Eq. (8).

Finally, it should be noted that the interaction volume will similarly affect the 330-nm radiation data shown in Fig. 7 so that the "true" rate constant k_{330} might be expected to decrease as the temperature is increased. However, in order to

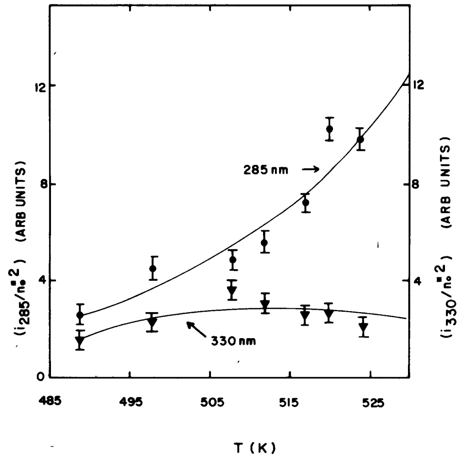

FIG. 7. Variation of $i_{285}/[n_0^*]^2$ and $i_{330}/[n_0^*]^2$ with temperature.

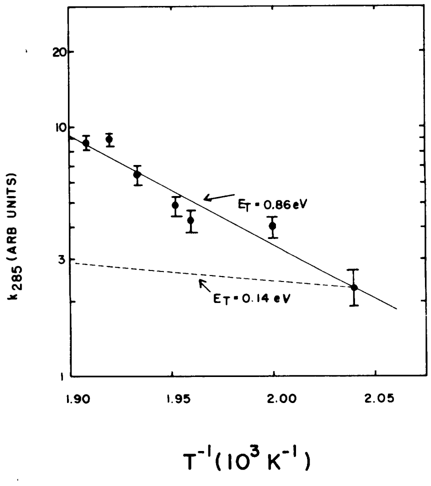

FIG. 8. Semi-log plot of $k_{285}(T)$ vs $1/T$ (data points). The solid straight line is a least-squares fit to the data. The broken line is a plot of Eq. (12) with $A(T)$ taken to be constant and $E_T = 0.14$ eV.

convert k_{330} into k_{4p} it is necessary to account properly for the branching ratio, as was done previously in the computation[13] of k_{5p} (498 K). In contrast to the situation for the 285 nm radiation, trapping of the 330-nm signal, while not important at 487 K, does introduce a slight correction as the temperature is increased toward 550 K.[13] This effect tends to compensate for the interaction volume effect discussed above so that the temperature dependence of k_{4p} is roughly that of $i_{330}/[n_0^*]^2$.

IV. SUMMARY

The formation of Na_2^+ and Na(nl) when sodium vapor is illuminated with laser light tuned to one of the D lines has been investigated in an effort to clarify production mechanisms. It was shown that Na_2^+ formation requires two laser photons. This result strengthens our previous conclusion that this species results from Na 3p-Na 3p associative ionization. The rate of formation of Na_2^+ and an electron was measured and shown to be of sufficient magnitude to make it likely that this process is the electron seeding mechanism in other experiments.

Energy pooling in collisions between two Na 3p atoms is probably also responsible for the formation of Na 4p and Na 5p as evidenced by the quadratic dependence of product signal on laser power density. While Na_2^+ and Na 4p may be formed by pooling only the excitation energy of two interacting Na 3p atoms, Na 5p formation requires an additional 0.14 eV. It was shown that this additional energy is supplied by conversion of relative kinetic energy of the two interacting Na 3p atoms. Thus, Na 5p is formed in an unusual process by pooling both internal energy from each of the two interacting atoms with the relative kinetic energy of the atoms.

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