

Collisional deactivation of the 5s and 4p states of Na by N<sub>2</sub>

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The collisional deactivation of the Na 5s and 4p states by collisions with N<sub>2</sub> molecules has been studied using the method of laser-induced fluorescence. The total cross sections for the depopulation of the 5s and 4p states are 86(8) and 43(4) Å<sup>2</sup>, respectively. The cross sections for the specific collisional transfers 5s → 4p, 5s → 3d, and 4p → 3d are 32(8), 10(2), and 19(3) Å<sup>2</sup>, respectively.

## I. INTRODUCTION

The study of deexcitation or quenching of excited atoms has been pursued vigorously since the turn of the century.<sup>1</sup> Until very recently, though, this research was limited to states which could easily be populated with resonance lamps. The tunable dye laser has opened a broad new area of research by making it possible to study all the excited states of at least the alkali atoms. In fact, using laser excitation the collisional properties of Na, K, Rb, and Cs in states of principal quantum number up to 20 have recently been studied in some detail.<sup>2-5</sup>

In studies of the collisional deexcitation of Na we have found that even for  $n$  as high as 10 the cross sections for  $n$ -changing collisions are  $<1$  Å<sup>2</sup> for rare-gas collision partners.<sup>2</sup> On the other hand, the cross sections for deactivation of the Na 3p state by molecular gases are  $\sim 30$  Å<sup>2</sup>.<sup>6</sup> These larger cross sections are presumably due to the presence of internally accessible internal degrees of freedom of the molecular gases, vibration, and rotation.

The deexcitation of excited Na by N<sub>2</sub> has been studied experimentally in some detail. The Na 3p state has been studied by many workers (see, for example, the work of Demtröder<sup>7</sup>), and the deexcitation of the higher Na states has been recently investigated by Czajkowski *et al.*<sup>8</sup> A theory for the deexcitation of the excited states of Na by N<sub>2</sub> has been developed by Bauer *et al.*,<sup>9</sup> which predicts with reasonable accuracy the deexcitation cross section for the Na 3p state. This model may be extended in a straightforward way to predict the deexcitation cross sections for higher states of Na, although the results of this extension are in serious disagreement with the experimental results of Czajkowski *et al.*

Recently, we have begun a systematic study of the collisions of N<sub>2</sub> with the excited states of Na. In this paper we report the first part of this work, a detailed study of the collisions of N<sub>2</sub> with Na atoms in the 5s and 4p states. These particular

levels were chosen for these studies because they offer a unique opportunity (in Na) to investigate in an unambiguous fashion the final states of excited-state collision processes. The dependence of the deexcitation cross section on the principal quantum number  $n$  is currently under investigation.

## II. EXPERIMENTAL METHOD

In these experiments we use a laser-induced fluorescence approach. The relevant levels of Na are shown in Fig. 1. Using two pulsed tunable dye lasers we pump the Na atoms from the 3s state to the 3p state and then from the 3p state to the 5s

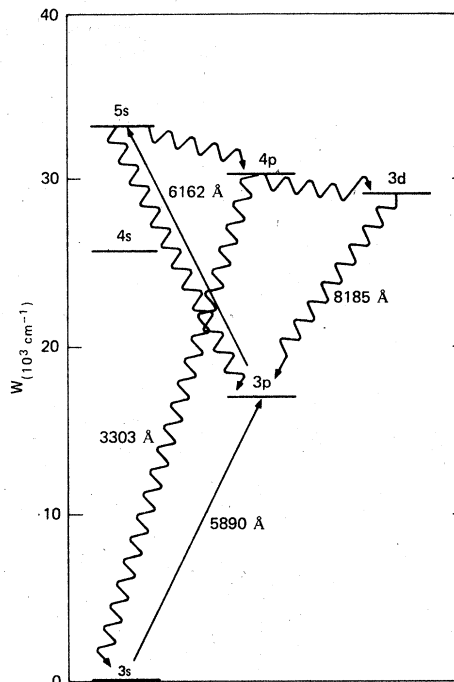


FIG. 1. Na energy-level diagram showing the relevant atomic levels. The straight arrows pointing up indicate the laser pumping steps and the wavy arrows pointing down indicate the observed fluorescence.

state as shown by the straight arrows up in Fig. 1. We monitor the populations in the 5s, 4p, and 3d states by observing the time-resolved fluorescence from these states, as shown in Fig. 1.

Since the experimental apparatus has been described elsewhere, we only describe it briefly here. The two dye lasers are pumped by the same N<sub>2</sub> laser and have pulse widths of ~4 ns, a time much shorter than the radiative lifetime of any of the states under study. The two dye laser beams cross at a small angle in the Na cell. The cell is a cylindrical Pyrex cell which is heated to 155 °C producing a Na pressure of  $7 \times 10^{-6}$  torr. The cell is connected to a vacuum system by a magnetically activated ground glass seal through which we introduce the N<sub>2</sub>, the pressure of which is measured with a Baratron pressure gauge. We detect the fluorescence with a photomultiplier-filter combination. Since the wavelengths of the 5s-3p, 4p-3s, and 3d-3p transitions are 6162, 3303, and 8185 Å, respectively, it is easy to discriminate between them with a filter. We used an analog boxcar integrator for signal averaging. Typically, we averaged the fluorescent decays from 2000 laser pulses to obtain each decay curve. A computer is used both to control the boxcar averager and to analyze the data.

### III. THREE-LEVEL MODEL

To analyze the results of our experiment we only need to consider the 5s, 4p, and 3d states. In this analysis we ignore collisions which induce transitions from lower energy states to higher energy states (such as 4p → 5s). This is justifiable since the energy separations of the states involved are in all cases much larger than thermal energies. With these assumptions, the populations of the 5s, 4p, and 3d states are related by the coupled equations:

$$\dot{n}_s = -K_s n_s, \quad (1a)$$

$$\dot{n}_p = -K_p n_p + k_{ps} n_s, \quad (1b)$$

$$\dot{n}_d = -K_d n_d + k_{dp} n_p + k_{ds} n_s, \quad (1c)$$

where  $K_l$  represents the total decay rate of the  $l$  state and  $k_{l,l'}$  represents the rate at which the  $l'$  state directly populates the  $l$  state either radiatively or by collisions. The  $K$ 's and  $k$ 's are related to the collisional-transfer cross sections by

$$K_l = \tau_l^{-1} + n\sigma_l v, \quad (2a)$$

$$k_{l,l'} = A_{l,l'} + n\sigma_{l,l'} v, \quad (2b)$$

where  $\tau_l$  is the radiative lifetime of state  $l$ ,  $A_{l,l'}$  is the Einstein  $A$  coefficient for the  $l'-l$  transition,  $n$  is the nitrogen density,  $v$  is the rms collisions velocity,  $\sigma_l$  is the total cross section for depopula-

tion of state  $l$ , and  $\sigma_{l,l'}$  is the cross section for excitation transfer from state  $l'$  to state  $l$ .

It is a straightforward matter to work out the solutions to Eqs. (1). If we let  $n_s = 1$  at  $t = 0$ , the solutions are given by

$$n_s = e^{-K_s t}, \quad (3a)$$

$$n_p = [k_{ps}/(K_s - K_p)](e^{-K_p t} - e^{-K_s t}), \quad (3b)$$

and

$$\begin{aligned} n_d = & \frac{k_{ds}}{K_d - K_s} (e^{-K_s t} - e^{-K_d t}) \\ & - \frac{k_{dp} k_{ps}}{K_s - K_p} \left( \frac{1}{K_d - K_s} \right) (e^{-K_s t} - e^{-K_p t} - e^{-K_d t}) \\ & + \frac{k_{dp} k_{ps}}{K_s - K_p} \left( \frac{1}{K_d - K_p} \right) (e^{-K_p t} - e^{-K_d t}). \end{aligned} \quad (3c)$$

From Eqs. (3a) and (3b) it is apparent that the 5s-state population is represented by one decaying exponential and that the 4p-state population is represented by the difference of two decaying exponentials. In Eq. (3c) the first term, which is proportional to  $k_{ds}$ , represents the population transferred directly to the 3d state from the 5s state. The second and third terms, which are proportional to the product  $k_{dp} k_{ps}$ , reflect the population in the 3d state which has come through the 4p state.

It is also useful to obtain expressions for the integrated fluorescence yields from these states. The integrated fluorescence yield  $Y_l$  for each state  $l$  is given by

$$Y_l = \int_0^{\infty} A_l n_l dt, \quad (4)$$

where  $A_l$  is the Einstein  $A$  coefficient for the observed transition emanating from state  $l$ . Explicitly these yields are given by

$$Y_s = A_s / K_s, \quad (5a)$$

$$Y_p = k_{ps} A_p / K_s K_p, \quad (5b)$$

$$Y_d = \frac{A_d}{K_d} \left( \frac{k_{ds}}{K_s} + \frac{k_{dp} k_{ps}}{K_p K_s} \right). \quad (5c)$$

### IV. DATA ANALYSIS

The total cross sections for depopulation of the 5s and 4p states can be derived from the time-resolved 5s and 4p decay rates. As expected from Eq. (3a) the 5s decay is a simple exponential. Figure 2 shows the linear pressure dependence of the 5s decay rate vs N<sub>2</sub> pressure. Fitting the data we find that we can express  $K_s$  as

$$K_s = 11.5(7) + 16.6(15)p, \quad (6)$$

where  $K_s$  is given in MHz and  $p$  is the N<sub>2</sub> pressure in torr. Here we follow the convention of giving

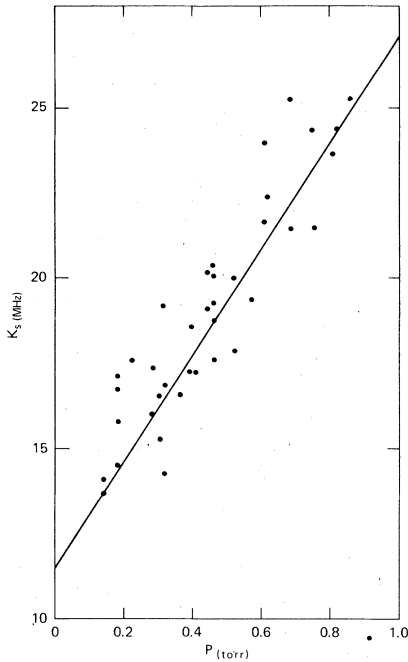


FIG. 2. 5s total decay rate  $K_s$  vs  $N_2$  pressure  $p$ . The points are the data and the line is the fit to the data.

the errors of the last digits in parentheses. Thus, 16.6(15) is equivalent to  $16.6 \pm 1.5$ . The zero-pressure point yields a radiative lifetime of 87(5) ns in good agreement with the value of 85 ns calculated by Tsekeris and Happer<sup>10</sup> using the Coulomb approximation of Bates and Damgaard.<sup>11</sup>

We fit the time-resolved 4p decays to the form of Eq. (3b) by a least-squares procedure and thus obtained both  $K_s$  and  $K_p$ . Since  $K_p < K_s$ , the long-time behavior of the 4p decay is determined primarily by  $K_p$ ; however, the values for  $K_s$ , which are less sensitive to the data, agreed within 15% with the data shown in Fig. 2. The pressure dependence of the 4p decay rate is shown in Fig. 4. We find that  $K_p$  may be expressed (in MHz) as

$$K_p = 7.4(6) + 8.4(8)p. \quad (7)$$

Again,  $p$  is the  $N_2$  pressure in torr. At zero pressure these data yield a radiative lifetime of 135(11) ns in agreement with the previous measurement of 125(12) ns.<sup>12</sup> The slope of the line in Fig. 4 is 8.4(8) MHz/torr, corresponding to a cross section of 43(4) Å<sup>2</sup>.

By the analysis of the 3d decays we are able to deduce values for some of the state specific rates  $k_{i,i'}$ , given in Eq. (2). Let us start with the time dependence of the 3d decays, the form of which is given in Eq. (3c). From the analysis of the 5s and 4p decays we already know  $K_s$  and  $K_p$ . For  $K_d$  we can use the radiative decay rate of the 3d state, 20 ns.<sup>7</sup> For our purposes it is sufficiently accu-

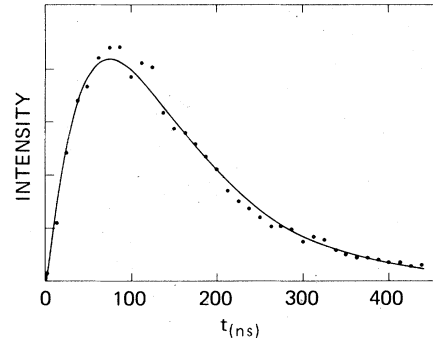


FIG. 3. 4p-3s fluorescence showing the 4p population vs time after the laser pulses. The points are the data and the solid curve is the computer fit.

ate to ignore the pressure dependence of the 3d state since we estimate that it would increase  $K_d$  by less than 10% at the highest pressures used, and this small variation in  $K_d$  would not affect our results. Furthermore,  $K_d$  is sufficiently fast that the fit is relatively insensitive to it. Now if we rewrite Eq. (3c) as

$$n_d = k_{ds} \left[ \frac{1}{K_d - K_s} (e^{-K_s t} - e^{-K_d t}) \right] + k_{dp} k_{ps} \left[ \frac{1}{K_s - K_p} \left( \frac{1}{K_d - K_s} (e^{-K_d t} - e^{-K_s t}) + \frac{1}{K_d - K_p} (e^{-K_p t} - e^{-K_d t}) \right) \right], \quad (8)$$

we find that all the terms in the square brackets are known. Thus if we supply the values of  $K_s$ ,  $K_p$ , and  $K_d$  and fit the time resolved 3d decays to Eq. (8) we can determine the relative amplitudes of the two terms in Eq. (8), which we define as the ratio  $R = k_{dp} k_{ps} / k_{ds}$ . Figure 5 shows the value of  $R$

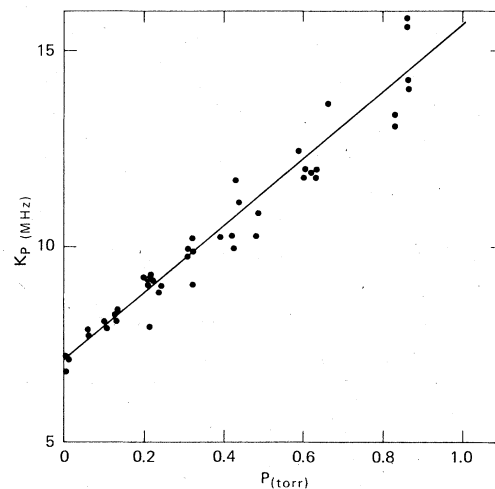


FIG. 4. 4p total decay rate  $K_p$  vs  $N_2$  pressure  $p$ . The points are the data and the line is the fit to the data.

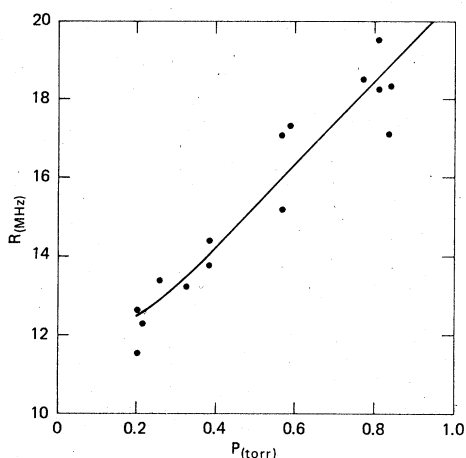


FIG. 5. Plot of  $R$  (see definition in text) vs  $N_2$  pressure  $p$  as determined from the time resolved  $3d-3p$  fluorescence.

obtained from the time-resolved  $3d$  decays. We can express the  $k_{i,i'}$  (in MHz) as

$$k_{ps} = 5.0 + \beta p, \quad k_{dp} = 0.105 + \gamma p, \quad k_{ds} = \alpha p, \quad (9)$$

where the  $p$  is the pressure of  $N_2$  in torr and  $\alpha$ ,  $\beta$ , and  $\gamma$  are given in MHz/torr, and are simply related to the  $\sigma_{i,i'}$  of Eq. (2b). Reexpressing  $R$  using Eq. (9),

$$R = (5.0 + \beta p)(0.105 + \gamma p) / \alpha p. \quad (10)$$

At high  $N_2$  pressures ( $> 0.2$  torr),  $\gamma p \gg 0.105$  and  $R$  approaches a straight line, and Eq. (10) reduces to

$$R \cong (\gamma/\alpha)(5.0 + \beta p). \quad (11)$$

That is,  $R$  has a nearly linear pressure dependence. Thus, we have used an iterative procedure to fit the data of Fig. 5 to Eq. (10), yielding the solid line of Fig. 5 and the values  $\gamma/\alpha = 1.8(2)$  and  $\beta = 6.2(15)$  MHz/torr.

From the integrated  $3d$  fluorescence yield  $Y_d$  we are able to derive separate values for  $\alpha$  and  $\gamma$ . Basically, the procedure is to compare the increase in  $3d$  fluorescence yield produced by collisions with the fluorescence yield due to the radiative cascade  $5s-4p-3d$  for which the rates are already known. The attraction of this method is that we do not need to measure the absolute yield but only its pressure dependence. At low  $N_2$  pressures we can expand Eq. (5c) using Eqs. (6), (7), and (9). The result of this expansion is

$$Y_d = C(0.070 + 1.17\gamma + 0.089)p, \quad (12)$$

where  $C$  is a numerical constant. Figure 6 is a typical plot of  $Y_d$  vs  $N_2$  pressure. Fitting the data such as those of Fig. 6 to Eq. (12) we derive a val-

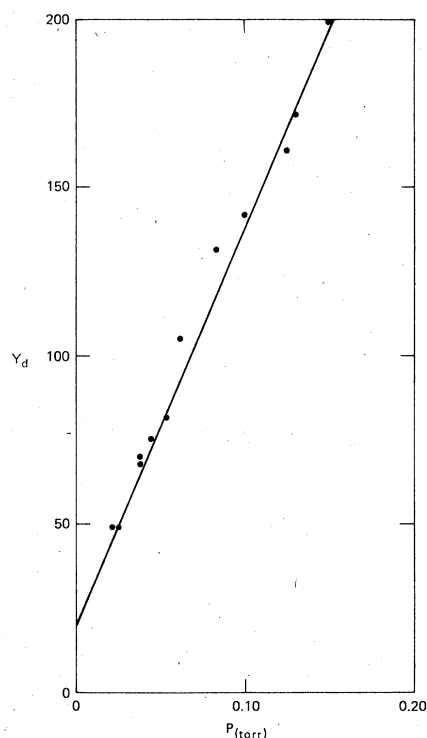


FIG. 6. Plot of the time integrated  $3d-3p$  fluorescence yield  $Y_d$  vs  $N_2$  pressure  $p$ .

ue of  $\gamma = 3.7(2)$  MHz/torr. Thus,  $\alpha = 2.0(3)$  MHz/torr.

## V. RESULTS AND DISCUSSION

For convenience, all the results are tabulated in Table I. Although the compact notation for the cross section used in Sec. III is convenient for the expression of formulas, a more complete notation is useful to tabulate the results. Accordingly, we have used a more expressive notation in Table I with the notation of Sec. III given in parenthesis.

It is interesting to compare our results with the theory of Bauer *et al.*, recently extended by Barker,<sup>13</sup> for the deactivation of excited Na by  $N_2$ . They propose a curve-crossing model based on the

TABLE I. Experimental results.

Quantity	Value
$\sigma_{5s}(\sigma_s)$	86(8) $\text{\AA}^2$
$\sigma_{4p}(\sigma_p)$	43(4) $\text{\AA}^2$
$\sigma_{3d-5s}(\sigma_{ds})$	10(2) $\text{\AA}^2$
$\sigma_{3d-4p}(\sigma_{dp})$	19(3) $\text{\AA}^2$
$\sigma_{4p-5s}(\sigma_{ps})$	32(8) $\text{\AA}^2$
$\tau_s$	87(5) ns
$\tau_p$	135(11) ns

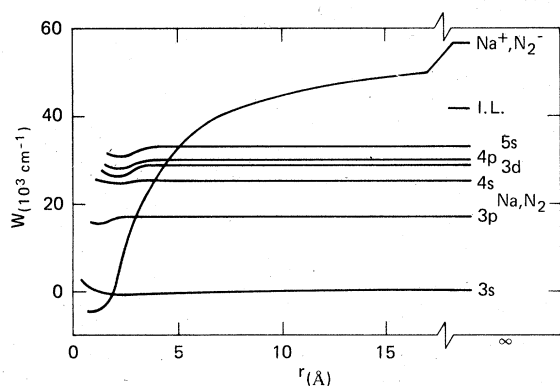


FIG. 7. Potential curves for the Na-N<sub>2</sub> system, which has both covalent Na-N<sub>2</sub>,  $v=0$  curves and the ionic Na<sup>+</sup>-N<sub>2</sub><sup>-</sup>,  $v=0$  curve.

potential-energy curves of Fig. 7. As shown by Fig. 7 the covalent curves correlate with the excited states of Na at an infinite separation between the Na and N<sub>2</sub>. There is also an ionic curve corresponding to Na<sup>+</sup>, N<sub>2</sub><sup>-</sup> at  $r=\infty$ . Since the electron affinity of N<sub>2</sub><sup>-</sup> is -1.89 eV (Ref. 14) at  $r=\infty$  this curve lies above the ionization limit of Na. Above each of the covalent curves shown in Fig. 7 there is a series of potential curves corresponding to excited vibrational states of N<sub>2</sub>. Above the ionic curve there is a similar set of curves for the excited vibrational states of N<sub>2</sub><sup>-</sup>. The curves for excited vibrational states are spaced by  $\approx 2000$  cm<sup>-1</sup> in both cases (for example, there are seven vibrationally excited N<sub>2</sub> curves between the Na 3p and 4p curves shown). Thus there is a large number of potential curves in the region  $< 5$  Å as shown by Fig. 8.

During a collision the atom passes through many curve crossings. If these crossings are all traversed either wholly diabatically or adiabatically so that the system follows a unique path, then after the collision the system will be in the same state as before the collision. If however some of the crossings are traversed partially diabatically then after the collision the Na atom will have a probability of being in other electronic states. According to the Landau-Zener theory the crossings are traversed adiabatically if the coupling matrix elements are large and diabatically if the couplings are small.<sup>15</sup> The matrix elements consist of two parts, electronic and vibrational.

Since the Franck-Condon factors vary greatly for different  $\Delta v$ , the total magnitude of the matrix elements spans a large range. This trait is one of the important differences between quenching by an atom or by a molecule. In addition to having more internal degrees of freedom with which it can absorb energy, the molecule further provides a variety of curve crossings, varying in strength. Thus it is almost certain that some of the crossings will be

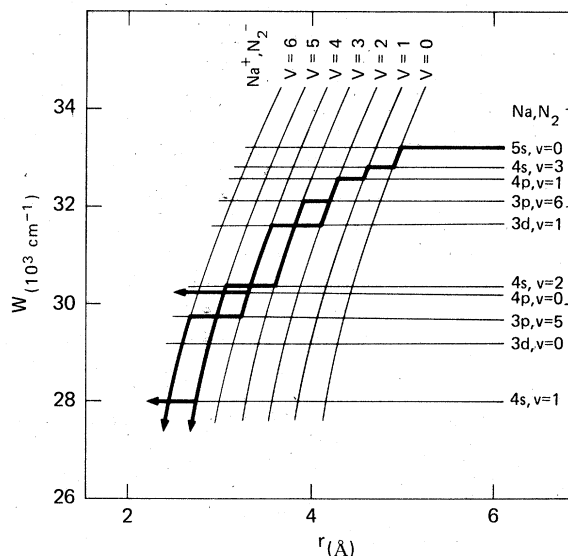


FIG. 8. Expanded view of the  $r=5$  Å,  $W=30\,000$  cm<sup>-1</sup> region of Fig. 7 with the excited vibrational curves shown as well as  $v=0$ . The bold lines indicate the branching of the path of an atom on the incoming Na 5s, N<sub>2</sub>,  $v=0$  curve.

traversed partially diabatically in contrast to the atomic case where typically strong electronic couplings result in adiabatic-curve crossings during thermal collisions.

As an example of the net result, consider an atom which enters the collision along the Na 5s, N<sub>2</sub>( $v=0$ ) curve as shown in Fig. 8. Using the method of Olson *et al.*<sup>16</sup> we can estimate the electronic coupling matrix elements at each crossing. To take into account the vibrational overlap for the matrix elements at each crossing, we have used the Franck-Condon factors for NO (the same ones used by Bauer *et al.* in Ref. 9).<sup>17</sup> Thus the system traverses the first ( $\Delta v=0$ ) crossing adiabatically and is thus pulled into a steep potential well. As it falls into the well, the atom continues following adiabatic paths for crossings of small  $\Delta v$  and diabatic paths at crossings of large  $\Delta v$ . At certain values of  $\Delta v$  ( $\Delta v=4$  in the example drawn in Fig. 8), the path is split into two as the crossing is traversed neither wholly adiabatically nor wholly diabatically. Due to this path branching, the atom has a probability of being in many different states by the time it reaches the repulsive wall at small internuclear separation. Consequently a high percentage of the Na atoms in the 5s state which come within  $r_c$ , the radius of the crossing of the  $v=0$  ionic curve with the covalent 5s curve, will be deexcited. Thus a good estimate for the deexcitation cross section is

$$\sigma_i = \pi r_c^2. \quad (13)$$

The results of the large values of the partial cross sections  $\sigma_{4p-5s}$  and  $\sigma_{3d-5s}$  indicate that most of deexcitation of the 5s state is to the two nearby states 4p and 3d. As shown by Fig. 8 there are only two 4p curves and two 3d curves ( $v=0$  and 1) on which the Na-N<sub>2</sub> system can be after the collision. Since half the atoms come out on these four curves, this implies that the curve crossings are partially diabatic at only one or perhaps two values of  $\Delta v$ . If the crossings were diabatic for many values of  $\Delta v$ , we would expect to find more or less equal populations in all energetically accessible final states. In this case most of the deexcitation would be to the Na ground state with many vibrational levels of N<sub>2</sub> populated. Since this does not occur, we must conclude that it is only for one or two values of  $\Delta v$  for which the curve crossings are traversed partially diabatically.

In Table II we list our observed values for  $\sigma_{5s}$  and  $\sigma_{4p}$ , the values calculated by Bauer *et al.*, and the measurements of Czajkowski *et al.* We also list the values of  $r_c$  for several Na excited states and the values of the deactivation cross sections they imply. As shown by Table II our results differ significantly from the results of Czajkowski *et al.* We attribute this difference to the fact that in their analysis of the experiments they assume that all collision processes involving excited Na leave the Na atom in its ground state, which we know now is not the case, at least for the 5s and 4p states. If in general the Na atoms are collisionally deexcited in small steps to other excited states, then more of the Na atoms initially produced in the higher Na states (for example, the 9s state) will be funnelled through the 5s state as the N<sub>2</sub> pressure is increased (by radiative processes very few of the atoms in the 9s state would decay via the 5s state). This effect would offset to some degree the decrease in fluorescence from the 5s state due to the collisional depopulation of the 5s state. Fitting their data with a model which neglects deexcitation to other excited states will thus give values of the deexcitation cross sections which are too small. It is interesting to note that for the highest Na states studied in their experiments, 8s and 9s, the exact final state of collisional deactivation is unimportant for the analysis of the data, and for these states they find much larger cross sections.

As shown by Table II the agreement between the

TABLE II. Deactivation cross sections for collisions of excited Na with N<sub>2</sub>.

State	$r_c$ (Å)	$\pi r_c^2$ (Å <sup>2</sup> )	$\sigma_I^a$ (Å <sup>2</sup> )	$\sigma_I^b$ (Å <sup>2</sup> )	$\sigma_I^c$ (Å <sup>2</sup> )
3p	2.9	26	26		41(8)
4p	4.4	61	54	43(5)	23(5)
5s	4.9	75		86(8)	27(5)
6s	5.7	102			41(8)
8s	6.6	135			94(19)
10s	7.0	152			
50s	7.6	183			

<sup>a</sup>See Ref. 9.

<sup>b</sup>This work.

<sup>c</sup>See Ref. 8.

deactivation cross section we measured for the 4p state,  $\sigma_p$ , is in reasonable agreement with both our approximate calculations and the more rigorous calculations of Bauer *et al.* In addition the approximate cross section which we calculate for the 5s state is in acceptable agreement with our measured value. The good agreement between the calculated and measured values for the deactivation cross sections suggests that the theoretical model is applicable to these deactivation collisions. Using this model we can use Eq. (13) to predict the deactivation cross sections for higher states to be only slightly larger than those of the 5s state, due to the steep slope of the ionic curve. The values calculated for the 6s, 8s, 10s, and 50s states are listed in Table II.

To our knowledge these measurements are the first unambiguous measurements of the cross sections for deactivation by N<sub>2</sub> of excited atoms to a specific final state,  $\sigma_{i,i'}$ , (aside from the obvious exceptions of the quenching of resonance radiation and intramultiplet mixing). The experiments show quite clearly that the deactivation of the Na 5s and 4p states occurs by small steps rather than one large step to the ground state. Further experiments are underway to determine the dependence of the deactivation cross section on  $n$ .

#### ACKNOWLEDGMENTS

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