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Brief Reports

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Formation of Na 5*s* and Na 4*d* in Na 3*p* — Na 3*p* energy-pooling collisions

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We report our measurements of the rate constants for formation of Na 4*d* and Na 5*s* in Na 3*p* — Na 3*p* collisions. The magnitudes of these rate constants indicate that Na 4*d* and Na 5*s* are the preponderant excited atomic products formed; however, the rate constant for 3*p* — 3*p* associative ionization, with product $\mathrm{Na_2}^+$, is about one-hundred times greater.

Energy pooling in collisions between two excited sodium atoms has been a subject of considerable interest over the last few years.[1–7] Most of the experimental work has centered on associative ionization, with product $\mathrm{Na_2}^+$, but studies have also been carried out on 3*p* — 3*p* reactions of the type[2,3,6,8]

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

where the excited Na *nl* products were detected by observation of radiation. Previously, we reported[6] the rate constants for formation of both Na 4*p* and Na 5*p*. These products, if directly formed, represent exothermic (0.45-eV) and endothermic (0.14-eV) reactions, respectively. The rate constant determinations in our earlier work were based on the $4p\rightarrow 3s$ (330-nm) and $5p\rightarrow 3s$ (285-nm) emissions. However, because the 4*d* and 5*s* levels, each of which lie very close to twice the Na 3*p* energy (4.2 eV), radiate to the 4*p* level, cascading could be responsible for the 330-nm radiation, at least in part.

We have recently modified our apparatus so that a direct determination of the rate constants for formation of the 4*d* and 5*s* levels could be made. We report here the results of these measurements. Based on the usual curve-crossing models it is expected that, since the 3*p* — 3*p* asymptotic potential energy is very close to the 3*s* — 4*d* and 3*s* — 5*s* asymptotic potential energies, reactions of the type given by Eq. (1), having products Na 4*d* or Na 5*s*, would predominate. In fact, that is the observation we report here.

The experiments were carried out in apparatus similar to that previously described.[6] A single-frequency cw dye laser tuned to a *D* line illuminated a cell containing sodium atoms at $\sim 10^{13}\ \mathrm{cm}^{-3}$. Radiation from the decay of excited species formed in the cell was dispersed and detected with an optical system consisting of a 0.25-m scanning monochromator and a cooled photomultiplier tube operated in the counting mode. Narrow pass filters were used to isolate the 569-nm ($4d\rightarrow 3p$) and 616-nm ($5s\rightarrow 3p$) fluorescence. The rate constants were then determined using the relation

$$k_{nl}=I_{nl}\Big/\int[n^*(r)]^2dV\ , \qquad (2)$$

where I_{nl} is the fluorescence signal corrected for the detection solid angle, optical efficiency, and the branching ratio; $n^*(r)$ is the Na 3*p* density in atom/cm^3 as a function of *r*, the radial coordinate of the collision cell. As before,[6] we assume that the excited atom density in the cell is uniform over the cylinder defined by the laser beam so that the denominator reduces to the product of the square of the density and the volume of the "laser cylinder." The excited atom density was determined by direct observation of the 589-nm $3p\rightarrow 3s$ flourescence signal corrected for radiation trapping, optical efficiency, and solid angle of detection. Log-log plots of the 569- and 616-nm signals as functions of the laser power density were straight lines having slopes of 2, establishing that two photons from the laser beam were required to produce these signals, consistent with 3*p* — 3*p* energy pool-

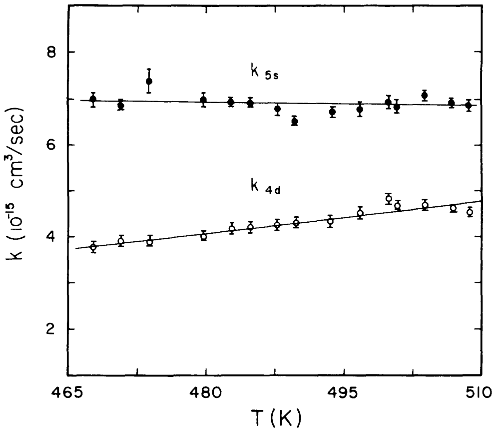

FIG. 1. Measured rate constants, k_{4d} and k_{5s}, as functions of temperature.

ing collisions being the source of the signals. We also detected weak 285-nm emissions from the 5p level,[3-6] the only state lying higher than the 4d and 5s states that was observed. Thus the 569- and 616-nm signals could not result from cascading, and represent primary formation of the 4d and 5s levels.

Figure 1 shows the measured values of the rate constants k_{4d} and k_{5s} as functions of temperatures. When proper account of branching from the 4d and 5s states is taken, it is clear that most of the 330-nm radiation, from which k_{4p} was calculated, is due to cascading from the 4d and 5s levels. In addition, nonradiative loss mechanisms such as $3s-4d$ and $3s-5s$ associative ionization[9] also occur, so that, within experimental error, it may be concluded that virtually none of the observed 330-nm radiation is due to primary formation of Na 4p in $3p-3p$ collisions.

While formation of Na 5s in $3p-3p$ collisions is slightly exothermic ($\sim$0.09 eV), Na 4d production must occur in an endothermic process ($\sim$0.08 eV). The different nature of these processes is reflected in the constancy of k_{5s} as a function of temperature, and the slight increase in k_{4d} as the temperature is increased. An Arrhenius plot of ln (k_{4d}) vs $1/T$ yields an activation energy for 4d production of 0.12 eV, in reasonable agreement with the thermochemical value 0.08 eV.

In a theoretical treatment of $3p-3p$ energy-pooling collisions, Kowalczyk[10] predicted a cross section for formation of Na 4d of $\sim 2\times 10^{-16}$ cm^2. This is about 3 orders of magnitude higher than the cross section calculated from our measured rate constant. We cannot account for this discrepancy, but it should be noted that in Kowalczyk's calculations both the 5s-3s exit channel and the efficient associative ionization exit channel[6,11] were ignored.

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