Effects of Orbital Alignment on Inelastic Collisions of Ca($4s5p\ ^1P_1$) with Helium

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(Received 10 September 1984)

The relative cross section for the process $Ca(4s5p\ ^1P_1) + He \rightarrow Ca(4s5p\ ^3P_j) + He + \Delta E = 177\ cm^{-1}$ is determined as a function of initial alignment of the $Ca(4s5p\ ^1P_1)$ state. The experiment is carried out with pulsed laser excitation in a crossed beam. An initial $^1P_1$ state aligned perpendicular to the relative collision velocity vector produces 50% more ^3P_j product-state emission than a $^1P_1$ state aligned parallel. These results are discussed in terms of physical models of the curve-crossing interaction.

PACS numbers: 34.50.Hc, 34.50.Lf

Recent experiments with atoms aligned by polarized lasers in molecular beams[1-6] or in bulk gases[7] have revealed a great deal of information about the characteristics of the potential-energy curves involved in scattering or reactive events. In the present experiment the effect of alignment of the initially excited $Ca(4s5p\ ^1P_1)$ state on the electronic energy-transfer process

$$Ca(4s5p\ ^1P_1) + He \rightarrow Ca(4s5p\ ^3P_j) + He + \Delta E = 177\ cm^{-1}$$

is studied. This process provides a clear and interesting model case for a near-resonant electronic energy-transfer process which occurs at thermal energy and involves a curve-crossing mechanism. The $^1P_1$ state can be completely aligned with a polarized laser, the total cross section is large (25 Å^2),[8] and fluorescence from both the ^1P and ^3P states is easily isolated experimentally. The present experiment is also the first example of the feasibility of carrying out such alignment studies with pulsed lasers.

The calcium atom is initially aligned with respect to the collision frame. The initial alignment is partially preserved when the calcium and rare-gas atoms first form molecular wave functions. At smaller distances than this, the curve-crossing region is reached. Different initial alignments can thus give rise to different cross sections for energy transfer. We find that calcium aligned perpendicular to the center-of-mass axis (Π state) favors ^3P_j production by 50% over calcium aligned parallel to the center-of-mass axis. This is a substantial effect, considering that the experiment measures an average over impact parameter, azimuthal angle, and relative velocity.

The experimental apparatus consists of crossed beams of Ca and He, which provide the relative velocity vector definition, a pulsed laser for excitation and alignment of the Ca ($4s5p\ ^1P_1$) state, and a photomultiplier tube to detect ^1P and ^3P emission. The calcium source is an effusive beam from an oven operated at 823 K, which has a 0.1-cm-diam nozzle held at 923 K. The calcium beam is skimmed 0.75 cm after the orifice to produce a 0.15-cm-diam beam at a distance of 1.5 cm after the nozzle. The calcium density at the crossing is $\sim 6\times10^{10}$ atoms cm^{-3} with an average velocity of $\sim 8.2\times10^4$ cm s^{-1} and a velocity spread of $\sim 100\%$. The rare-gas beam is at right angles to the calcium beam and is a continous supersonic expansion from a 100-μm orifice located 1 cm below the skimmed calcium beam. With 1-atm backing pressure, the helium density at the beam crossing is $\sim 1.5\times10^{14}$ atoms cm^{-3} and the average velocity is 1.9×10^5 cm s^{-1} with a velocity spread of $\sim 20\%$. Thus, the relative velocity vector is inclined at an angle of $\alpha_{c.m.} = 66 \pm 14°$ with respect to the Ca beam and has an average velocity of $(2.0 \pm 0.5)\times10^5$ cm s^{-1}.

The pulsed laser beam intersects both the helium and calcium beams at right angles. The polarization of the laser light is rotated with a Fresnel-rhomb half-wave retarder.[9] Irises are used before and after the beam chamber to realign the laser to intersect the crossing region if the laser beam is displaced by rotation of the Fresnel-rhomb retarder.

Figure 1 shows a simplified energy-level diagram of the calcium system.[10] The pulsed laser is tuned to the 272.17-nm transition to excite the $4s5p\ ^1P_1$ state. Fluorescence is detected through interference filters by a fast photomultiplier tube (PMT) in the plane of the atomic beams. The Ca ($4s5p\ ^1P_1$) state is monitored by observing the $4s5p\ ^1P_1 \rightarrow 4s3d\ ^1D_2$ transition at 671.7 nm. Radiation

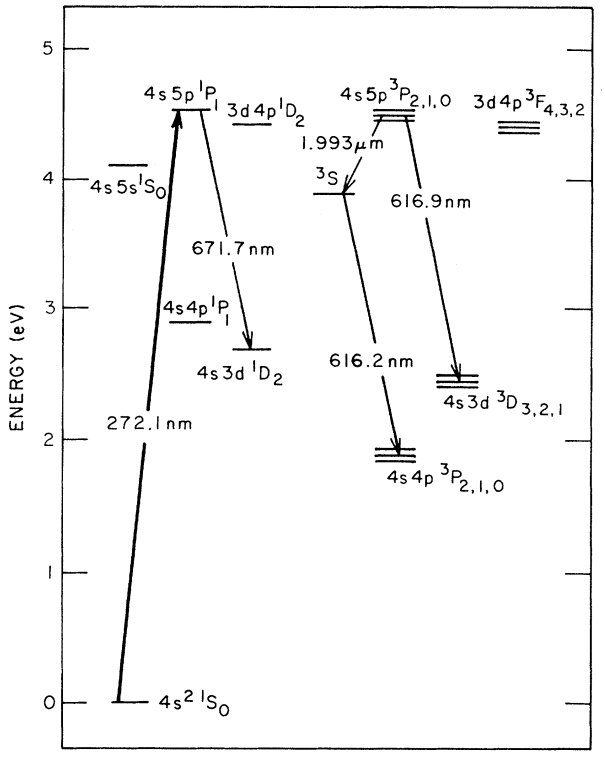

FIG. 1. Partial energy-level diagram for atomic calcium showing only the transitions used in the experiment.

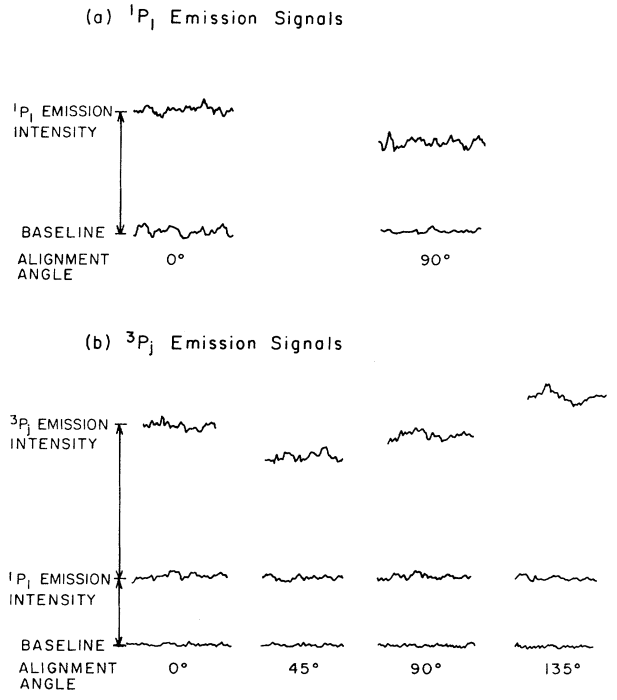

FIG. 2. (a) Initial $^1P_1$ state fluorescence signals taken at 0° and 90° alignment angle through a polarization filter. Solid angle of collection is 0.023 sr. (b) Fluorescence observed through 616.2-nm filter, with and without He present as a function of $^1P_1$ alignment angle. The upper traces are with He present, while the lower is without He. The signal without He is $^1P_1$ leakage and the signal with He is $^1P_1$ leakage plus ^3P emission. Solid angle of collection is 2.35 sr.

emitted on the the $P \rightarrow D$ transition is strongly depolarized; perfect alignment of the P state can result in a maximum value of 0.143 for the polarization $[I(0)-I(90)]/[I(0)+I(90)]$, measured in the parallel (0) and perpendicular (90) directions when observed through a polarization filter.[10] The product $4s5p\,^3P_j$ states are observed on the $4s5p\,^3P_j \rightarrow 4s5d\,^3D_j$ transitions at 616.9 nm and also on the cascade transition $4s5p\,^3S_1 \rightarrow 4s4p\,^3P_j$ at 616.2 nm without additional polarization filters in the detection system. If the product $4s5p\,^3P_j$ states would be fully aligned after the collision, an extremely unlikely occurrence because the cross sections for depolarizing collisions are large, the $4s5p\,^3P_j$ emission is not expected to vary more than a few percent with laser polarization. This is because 60% of the emission comes about by cascade through the $^3S_1$ and the remainder is on a $P \rightarrow D$ transition, both of which are strongly depolarized, and because the angle of observation is large for these signals.

At the He density stated above and with the 60 ns lifetime of the $^1P_1$ state, only about $1/10^4$ of the initially excited calcium atoms will be transferred to the product states. The pulsed laser offers several advantages in this regard, including the use of time-gated detection which is synchronized with the emission from the state of interest, and the minimization of secondary collision effects. In addition to the product-state signal, a small fraction, approximately 10^{-4}, of the 671.7 nm light from the initial state is transmitted by the 616.2 nm filter. This signal is exploited for normalization of the product signal. This normalization signal is proportional to the initial-state population and is independent of its polarization to within 3%. The total fluorescence output of the PMT is integrated with a boxcar integrator with and without He present.

Figure 2 shows one set of emission signals $I(\theta)$ from the initial $^1P_1$ state without He and from the final ^3P_j states, with and without He, as a function of the initial polarization angle, θ, which is measured with respect to the calcium beam in the lab frame. Figure 2(a) shows the $^1P_1$ emission at 671.7 nm observed in a small angle through a polarization filter aligned parallel to the laser beam. From four different measurements, $I(0)/I(90)$ is found to be 1.28 ± 0.18 (polarization of emission is 0.12), which

gives an initial $^1P_1$ state alignment $(87 \pm 15)\%$.[11] Figure 2(b) shows the integrated 616.2-nm signal. The alignment sensitivity parameters[2] are then calculated from $S_1 = [I(0) - I(90)]/[I(0) + I(90)]$ and $S_2 = [I(45) - I(135)]/[I(45) + I(135)]$. The ^3P_j intensity varies with alignment angle, and with use of the definition $S = (S_1^2 + S_2^2)^{1/2}$, the ratio of minimum to maximum intensity is $I_{min}/I_{max} = (1 - S)/(1 + S)$ and the angle of maximum fluorescence is $\tan(2\gamma) = S_2/S_1$. Three separate determinations of S_1 and S_2 were made. The resulting intensity ratios and angles of maximum intensity are $I_{min}/I_{max} = 0.81 \pm 0.16$ and $\gamma = -42°$, $I_{min}/I_{max} = 0.68 \pm 0.10$ and $\gamma = -34°$, and $I_{min}/I_{max} = 0.53 \pm 0.20$ and $\gamma = -30°$. The weighted averages are $I_{min}/I_{max} = 0.67 \pm 0.20$ and $\gamma = -36 \pm 8°$.

Since $\alpha_{c.m.} - \gamma = 102 \pm 16°$, we see that I_{max} occurs when the $^1P_1$ state is aligned essentially perpendicular to the center-of-mass velocity vector. This corresponds to a Π molecular state. The simple curve-crossing picture of this process has been discussed previously.[8] First it is important to point out that this is not a spin-changing process since there is spin mixing between the initial and final states. Figure 3 shows hypothetical potential-energy curves depicting the region of molecular-orbital formation (R_L) and the curve crossing radius (R_c). Both the $^1P_1$ and ^3P_j states form an attractive Π state and a repulsive Σ state with helium.[12] It is believed that the main interaction arises from the slightly attractive Π state of $Ca(4s5p\ ^1P_1) + He$ which crosses with the repulsive Σ state from $Ca(^3P_j) + He$. This qualitative picture agrees well with the observed polarization dependence for the cross section.

As the excited calcium atom proceeds through the collision it undergoes a transition from initial laboratory-frame-fixed atomic orbitals to center-of-mass-fixed molecular orbitals. Assume for simplicity that this transition occurs at a fixed internuclear separation of R_L, termed the locking radius, shown in Fig. 3. We make the definition that the laboratory-fixed orbitals are $|\sigma\rangle$ or $|\pi\rangle$, when the Ca alignment is parallel or perpendicular to the relative collision velocity, respectively. The center-of-mass-fixed orbitals are denoted $|\Sigma\rangle$, $|\Pi_x\rangle$, and $|\Pi_y\rangle$, lying in and out of the plane of the collision, respectively. The $|\pi\rangle$ state corresponds essentially to I_{max} and $|\sigma\rangle$ corresponds to I_{min}. To conserve symmetry in the collision plane only the Π_x component will lead to products.

Since the larger impact parameters are weighted more than the small ones, assume that the process

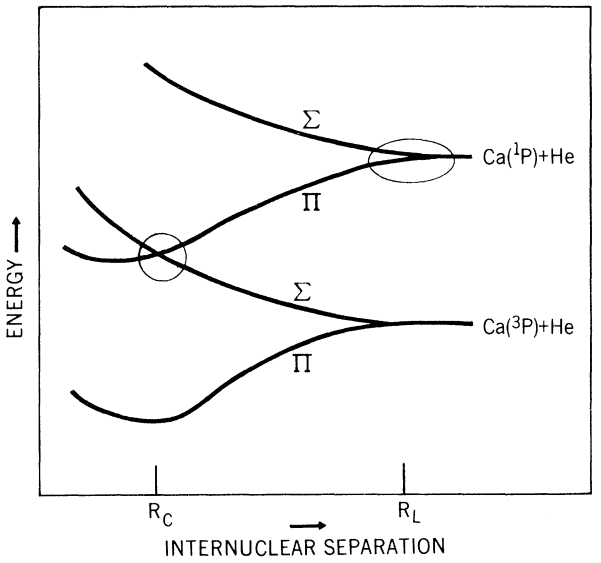

FIG. 3. Hypothetical potential-energy curves for the Ca-He collision system. The curve crossing radius, R_c, and the region of molecular orbital formation R_L, are shown.

takes place at a critical impact parameter $b_c \sim R_c$. Thus we can write $I_{min}/I_{max} = [Q_\Pi P_\Pi(\sigma) + Q_\Sigma P_\Sigma(\sigma)]/[Q_\Pi P_\Pi(\pi) + Q_\Sigma P_\Sigma(\pi)]$. Here Q_Π and Q_Σ are the cross sections for the two different potentials, and $P_\Pi(\sigma)$, $P_\Sigma(\sigma)$, $P_\Pi(\pi)$, and $P_\Sigma(\pi)$ are the probabilities determined by geometry of being on a particular potential at R_L for a given initial approach. In the extreme case that $Q_\Sigma = 0$, as implied by the experimental preference for Π geometry, $I_{min}/I_{max} = P_\Pi(\sigma)/P_\Pi(\pi) = 2R_c^2/(R_L^2 - R_c^2)$. From the experimentally measured I_{min}/I_{max} we can then estimate that $R_L/R_c \sim 2.0$. It can be shown by use of different ratios of Q_Σ/Q_Π that a minimum value for R_L/R_c is 1.6, given the observed intensity ratio. Thus, these experiments can provide information concerning the distance at which the transition occurs from atomic to molecular orbitals.

It is shown that the pulsed-laser-excitation, crossed-beam technique can provide excellent data for alignment-dependent atomic collision processes. These data give useful information about the preferred symmetry of a curve crossing and semiquantitative information about the process of forming molecular orbitals from atomic states. Further improvements in the experimental apparatus will provide much better data. It is an exciting prospect to invite more detailed theoretical investigations of these alignment-dependent collision process.

The authors gratefully acknowledge the support of this work by the National Science Foundation.

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[1]A. Bähring, I. V. Hertel, E. Meyer, W. Meyer, N. Spies, and H. Schmidt, J. Phys. B (to be published).

[2]C. T. Rettner and R. N. Zare, J. Chem. Phys. **75**, 3630 (1981), and **77**, 2417 (1982).

[3]L. Hüwel, J. Maier, R. K. B. Helbing, and H. Pauly, Chem. Phys. Lett. **74**, 459 (1980).

[4]I. V. Hertel, H. Schmidt, A. Bähring, and E. Meyer, Rep. Prog. Phys. (to be published).

[5]J. G. Kircz, R. Morgenstern, and G. Nienhuis, Phys. Rev. Lett. **48**, 610 (1982).

[6]J. M. Mestdagh, J. Berlande, P. dePujo, J. Cuvellier, and A. Binet, Z. Phys. A **304**, 3 (1982).

[7]J. Alford, N. Andersen, K. Burnett, and J. Cooper, Phys. Rev. A **30**, 2366 (1984).

[8]M. O. Hale and S. R. Leone, J. Chem. Phys. **79**, 3352 (1983).

[9]F. A. Jenkins and H. E. White, *Fundamentals of Optics* (McGraw-Hill, New York, 1976).

[10]G. Rizberg, Ark. Fys. **37**, 231 (1967).

[11]A. Fischer and I. V. Hertel, Z. Phys. A **304**, 103 (1982).

[12]A. R. Malvern, J. Phys. B **11**, 831 (1978).