Distinct Alignment Effects for $Y_{2,0}$ vs $Y_{2,\pm1}$ Angular Wave Functions Observed in Collisions of an Atomic Ca D State

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Two different angular wave functions of the $Ca(4p^2\,{}^1D_2)$ state are prepared via a two-step laser excitation with parallel and perpendicular configurations of the two linear polarizations. These wave functions exhibit dramatically different alignment effects for the electronic-energy-transfer process $Ca(4p^2\,{}^1D_2)+Ne \rightarrow Ca(3d4p\,{}^1F_3)+Ne$. Relative cross sections for individual Ca ${}^1D_2$ magnetic sublevels are obtained from these measurements using the rotation properties of the two wave functions.

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There are numerous investigations of alignment effects in experimental atomic inelastic scattering events in which the aligned state is prepared via a single linearly polarized laser.[1-15] Most of these studies consider the alignment of atomic P states and demonstrate a $\cos(2/\beta)$ dependence of the cross sections on the alignment angle, β, between the average relative velocity vector and the laser polarization. A higher-order angular dependence has been observed for atomic states with total angular momentum, J, of 3.[15] Here, we report the use of two linearly polarized lasers to prepare two different angular wave functions of the same $4p^2\,{}^1D_2$ state of atomic Ca ($J=2$). By fixing the laser polarizations parallel to each other, the state with an angular wave function $Y_{2,0}$ is prepared. By fixing the polarizations of the two lasers perpendicular to each other, the state with an angular wave function of $(Y_{2,-1}-Y_{2,1})/\sqrt{2}$ is prepared. These two states show very different alignment dependences for the probability of near-resonant collisional energy transfer in the process

$$Ca(4p^2\,{}^1D_2)+Ne \rightarrow Ca(3d4p\,{}^1F_3)+Ne\,.$$

The pertinent Ca-atom energy levels are shown in Fig. 1. The $4p^2\,{}^1D_2$ state is excited in two steps via the $4s4p\,{}^1P_1$ state using two collinearly propagating, pulsed dye-laser beams. The linear polarization of both lasers is refined using Glan laser prisms and the polarization of one laser is rotated 90°, when necessary, using a half-wave plate. The polarizations are thus fixed to be either parallel or perpendicular relative to each other. At this fixed relative angle, the two polarizations are rotated simultaneously using a double Fresnel rhomb, and measurements of the energy-transfer process are made every 10°.

The Ca and Ne collisions occur in a crossed-beam apparatus. The Ca effuses out of a $1\times2\text{-mm}^2$ slit from a 650 °C oven; the rare-gas source is a pulsed supersonic free jet with a 40–160-kPa backing pressure. The lasers propagate perpendicularly to the plane defined by the two atomic beams and the laser polarizations rotate in this plane. Collisions with Ne atoms cause a small fraction ($\leq 1\%$) of the population of the $Ca({}^1D_2)$ state to transfer to the nearby $Ca(3d4p\,{}^1F_3)$ state. Total fluorescence (all polarizations) from this state is collected at 534.9 nm with a fiber-optic bundle which is positioned so as to maximize the solid angle of collection; this purposely minimizes the chance that any anisotropy which occurs in the ${}^1F_3$ final-state fluorescence will be observed. A small 10% residual modulation is observed in the ${}^1D_2$ initial-state fluorescence. However, since the maximum polarization of a ${}^1F_3$-${}^1D_2$ transition is less than a ${}^1D_2$-${}^1P_1$ transition, since the retention of polarization is likely to be small, and since the atoms are scat-

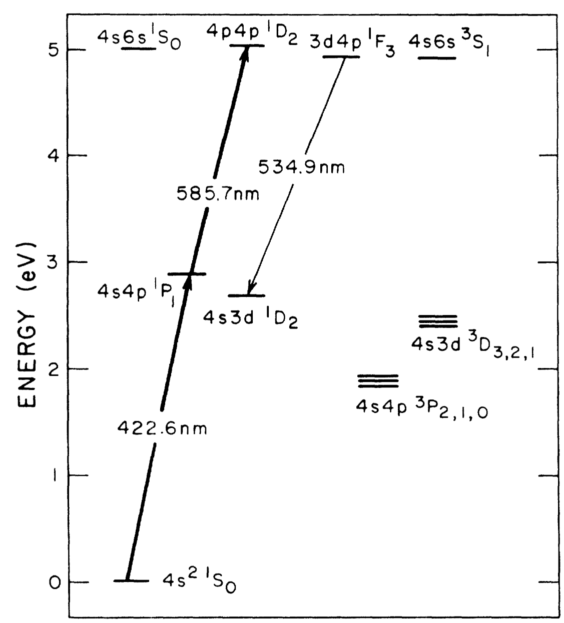

FIG. 1. Pertinent energy levels in the calcium atom. Several states exist in the 4–5-eV range and are omitted for clarity.

tered into a wide range of laboratory angles, the maximum polarization of the final-$^1F_3$-state emission is much less than 10% and is considered negligible. The light passes through an interference filter and is detected by a photomultiplier tube (PMT). The amplified PMT current is integrated and digitized for 1000 laser pulses at each angle. The background signals due to laser scatter, stray room light, and PMT dark counts are accounted for by subtracting the signal measured through the $^1F_3$ collection optics at each angle with the rare-gas collision beam turned off. Normalization for variations in the initial $^1D_2$ population is not necessary. Magnetic fields have been reduced to less than 0.05 G in the interaction region using magnetic shielding foil. Excitation transfer may occur to several near-resonant states, as already considered in a study of the $6\,^1S_0$ state.[16] Because the radiative rates from the Ca($^1D_2$) and Ca($^1F_3$) states dominate the kinetic time dependence of the signals, the observed alignment effects may be directly attributed to the $^1D_2 \rightarrow {}^1F_3$ collisional transfer process, even though other states are also populated by collisions. Further experimental details will be given in a forthcoming publication.[17]

The first polarized laser excites the ground Ca($4s^2\,^1S_0$) state to the $4s4p\,^1P_1$ state, with the selection rule $\Delta M_{J'}=0$ for a z' axis defined along the laser polarization vector. (The "prime" is used to distinguish this axis from the z axis defined along the average relative velocity vector.) Thus, only the $M_{J'}=0$ state (a $p_{z'}$ orbital) is populated in the P state. If the second laser is polarized parallel to the first, then the two excited electrons form a D state which is also only populated in the $M_{J'}=0$ component (a $p_{z'}^2$ configuration). The angular part of this wave function is described by the $Y_{1,1,2,0}$ ($Y_{l_1,l_2,L,M_{L'}}$) coupled spherical harmonic. If the second laser is polarized perpendicular to the first, the transition takes $M_{J'}=0$ in the P state to a coherent superposition of $M_{J'}=\pm 1$ in the D state. Thus, qualitatively, the electrons occupy the $p_{z'}$ and $p_{x'}$ orbitals. The angular part of this wave function is described by a coherent superposition of coupled spherical harmonics, $(Y_{1,1,2,-1} - Y_{1,1,2,1})/\sqrt{2}$.

The observed alignment data are shown in Fig. 2 for both parallel and perpendicular laser polarizations, where the $^1F_3$ fluorescence intensity is plotted as a function of the alignment angle β. Two or more points are averaged at each angle and the average standard deviation of the mean is shown by the error bars. The angle β represents our estimate of the value of the angle between the polarization of the first laser and the center-of-mass relative velocity vector, and this angle is accurate to within $\pm 5°$. A slight lack of symmetry in the data about the angle $\beta=0$ is apparent in Fig. 2(b) and may be due to our inability to align the laser polarizations exactly perpendicularly. This was not a problem in the parallel-polarization case since the two lasers propagate

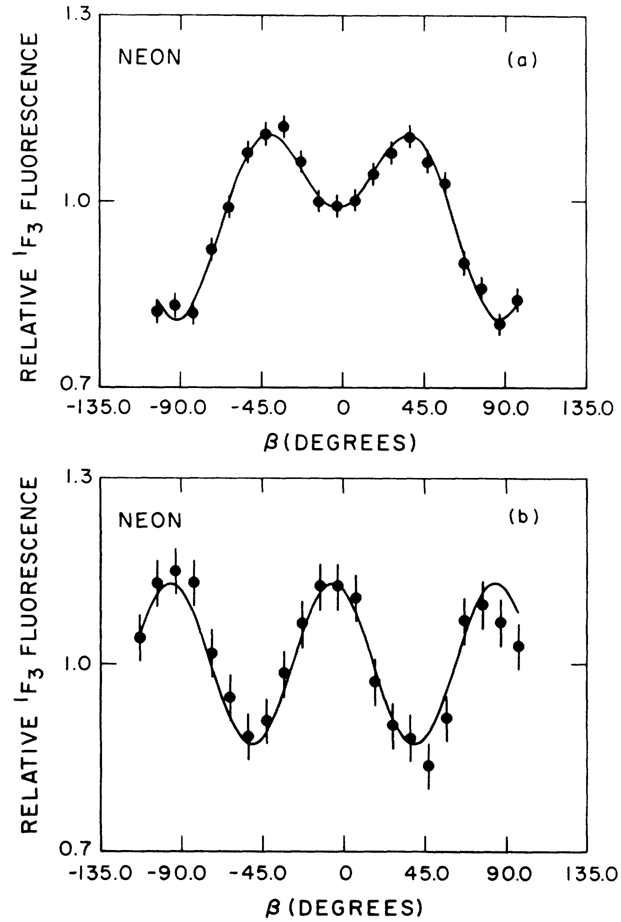

FIG. 2. Alignment data for energy transfer of Ca($4p^2\,^1D_2$) with Ne. The relative fluorescence from the $^1F_3$ state is shown as a function of the estimated angle β between the polarization of one laser and the initial Ca-Ne collision axis. (a) Laser polarizations fixed parallel to one another; (b) laser polarizations fixed perpendicular to each other.

through the same polarizing optic.

In order to extract information on the dynamics of the energy-transfer process, we use a semiclassical description to derive the following expression for the alignment dependence of the collisionally induced electronic energy cross section:[17]

$$\sigma(\beta)=\sum_M \left|\sum_{M'} p_{M'} d^L_{MM'}(\beta)\right|^2 \sigma^M , \qquad (1)$$

where M is the component of L along the relative velocity vector of the collision, M' is the component of L along the first laser polarization vector, the $d^L_{MM'}$ are rotation matrix elements which relate the quantization axes of the laser and collision frames, and the $p_{M'}$ are the probability amplitudes for being in a given M sublevel [i.e., for parallel laser polarizations, $p_{M'}=\delta_{M',0}$; for perpendicular polarizations, $p_{M'}=(\delta_{M',-1}-\delta_{M',1})/\sqrt{2}$]. The σ^M are the total cross sections for collisionally induced electron-

TABLE I. Relative energy-transfer cross sections for individual magnetic sublevels of the calcium-neon system from the energy-transfer process $4p^2\,{}^1D_2 \rightarrow 3d4p\,{}^1F_3$. (All errors listed are ± 1 standard deviations. The relative cross sections are normalized such that $\sigma^0+2\sigma^{|1|}+2\sigma^{|2|}=1.0$.)

Laser polarization	σ^0	$\sigma^{\|1\|}$	$\sigma^{\|2\|}$	$3\sigma^0+\sigma^{\|2\|}$
$\parallel$	0.202 ± 0.002	0.245 ± 0.004	0.153 ± 0.004	0.759 ± 0.008
$\perp$ [a]	···	0.245 ± 0.004	···	0.753 ± 0.016

[a]The perpendicular results are scaled to match the value of $\sigma^{|1|}$ in the parallel results.

ic energy transfer from an individual sublevel (M) of the initial Ca ${}^1D_2$ state to the ${}^1F_3$ state. These individual M-state cross sections are averaged over impact parameter and azimuthal angle, and summed over all magnetic sublevels of the final ${}^1F_3$ state.

The explicit expressions of Eq. (1) for the two cases of parallel $[\sigma_{\parallel}(\beta)]$ and perpendicular $[\sigma_{\perp}(\beta)]$ laser polarizations are found to be

$$\sigma_{\parallel}(\beta)=\tfrac{1}{64}[(22\sigma^0+24\sigma^{|1|}+18\sigma^{|2|})+(24\sigma^0-24\sigma^{|2|})\cos(2\beta)+(18\sigma^0-24\sigma^{|1|}+6\sigma^{|2|})\cos(4\beta)]\,, \quad (2)$$

$$\sigma_{\perp}(\beta)=\tfrac{1}{8}[(3\sigma^0+4\sigma^{|1|}+\sigma^{|2|})+(-3\sigma^0+4\sigma^{|1|}-\sigma^{|2|})\cos(4\beta)]\,, \quad (3)$$

where $\sigma^{|1|},\sigma^{|2|}$ are defined as the average cross sections of $\pm M'$ states:

$$\sigma^{|1|}=(\sigma^{+1}+\sigma^{-1})/2,\quad \sigma^{|2|}=(\sigma^{+2}+\sigma^{-2})/2\,.$$

Least-squares fits of Eqs. (2) and (3) to the data (i.e., alignment curves) are shown in Fig. 2 (where the fits allow for a phase shift in β). It is seen that these alignment curves relate directly to the rotation properties of the initial laser-prepared states: For the state prepared with perpendicular laser polarizations the alignment curve is sinusoidal with a period of 90°, while for the state prepared with parallel polarization the alignment curve has both $\cos(2\beta)$ and $\cos(4\beta)$ components.

Using Eq. (2), the relative cross sections for the different initial Ca ${}^1D_2$ sublevels ($|M|=0$, 1, and 2), which correlate at large internuclear distances to the individual Ca-Ne molecular states ($\Lambda=\Sigma$, Π, and Δ), are extracted from the parallel-laser-polarization alignment data and are given in Table I. These cross sections are normalized such that $\sigma^0+2\sigma^{|1|}+2\sigma^{|2|}=1$. Independent values of all three relative cross sections cannot be determined from the perpendicular-polarization alignment data. Rather, values for $\sigma^{|1|}$ and the linear combination $3\sigma^0+\sigma^{|2|}$ are obtained and given in Table I. These values provide a consistency check on the values from the parallel-polarization data; the agreement is well within experimental error. The data clearly indicate that the major pathway for energy transfer from the Ca ${}^1D_2$ state to the ${}^1F_3$ state induced by collisions with Ne is via the $|M|=1$ state, while the least efficient path is via the $|M|=2$ state.

In conclusion, two-step excitation of an atomic D state with well-defined relative polarizations of the lasers is used to prepare different symmetries in the angular wave function; these states exhibit dramatically different alignment effects in a collisional-energy-transfer process. The results are understood in terms of the rotation properties of the initial wave functions and provide insight into the relative roles of the individual Ca magnetic sublevels in the energy-transfer process. We are presently measuring energy-transfer alignment effects for the $Ca(4p^2\,{}^1D_2)$ state with other rare gases. These results, including the trends in the relative cross sections with increasing rare-gas mass, will be presented in a later publication.[17]

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