Alignment Spectra of Two-Photon, Magnesium-Rare-Gas-Atom Fractional Collisions

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Observations of a new dynamical process, absorption of two optical photons during a binary collision, have been made. Measurements on magnesium-rare-gas collisions display a rich phenomenology associated with the collisions, the relative linear polarization directions of the exciting light beams, and their separate detunings from atomic Mg $3s\,^1S_0 \rightarrow 3p\,^1P_1 \rightarrow 5s\,^1S_0$ stepwise resonance. Polarization spectra for Mg-Ne and Mg-Ar fractional collisions are reported, and are seen to contain information on short-range collision dynamics and on evolution of alignment produced in the process.

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Significant experimental developments over the past decade have led to detailed investigations of electronic and interparticle dynamics occurring in photodissociation [1], heavy particle inelastic scattering [2], chemical reactions [3], and collisional redistribution of light [4]. A common feature of these processes is strong correlation of dynamical variables of the system [5], which may be quite evident in photofragmentation studies [6]. In many studies the focus has been on interplay of electronic multipoles and collision dynamics, particularly in electronically inelastic collisions [7]. Other experiments have determined time-dependent interparticle dynamics on a femtosecond time scale [8]. Several investigators have proposed that more detailed information about dynamical correlations in atomic collisions may be found by interrogation of a system during the fragmentation process itself [9–11]. The most recent theoretical studies have considered the role of electronic degeneracy, and thus possible effects of atomic or molecular polarization, on the collision dynamics.

Reported here are experimental studies of correlated multipole and interparticle dynamics: two-color, two-photon absorption during a single binary collision. As only a portion of the full collision trajectory is probed in the method, the process may be considered to be a fractional or incomplete collision. To our knowledge, results given here represent the first experimental studies of this fractional collision process. The data obtained depend strongly on the average electronic alignment [6] produced in the first or pumping step of the two-step radiative excitation process. Dynamical evolution of the alignment is probed in a second step by absorption of linearly polarized light during the same collision. Varying separately the frequencies of the pump and probe light sources effectively accesses the range of interparticle separations important in the collision process. Measurement of the differential absorption with the probe linear polarization direction along and perpendicular to the average alignment axis generates a frequency-dependent polarization spectrum. The spectra obtained are a frequency domain analog of the time evolution of alignment within the molecular complex. They thus contain more detailed information on the collision dynamics than either full-collision [2] or one-photon optical collision [4] studies, where the resulting spectra are an average of the dynamics over the entire trajectory from the region of excitation to asymptotic atomic products. In the remainder of this Letter we present an overview of the basic physical processes, and give a description of the experimental apparatus and technique. Results of measurements on Mg-Ne and Mg-Ar two-photon polarization spectra are presented and discussed.

The overall process may be understood with reference to Fig. 1, which shows interatomic potentials [12,13] for pertinent states of Mg-Ar. Solid vertical lines indicate interatomic separations (R) where the energy difference between the molecular states is made up by light of energy hf_1 and hf_2. Detunings from the two atomic Mg resonances, $3s\,^1S_0 \rightarrow 3p\,^1P_1$ at hf_{10} and $3p\,^1P_1 \rightarrow 5s\,^1S_0$ at

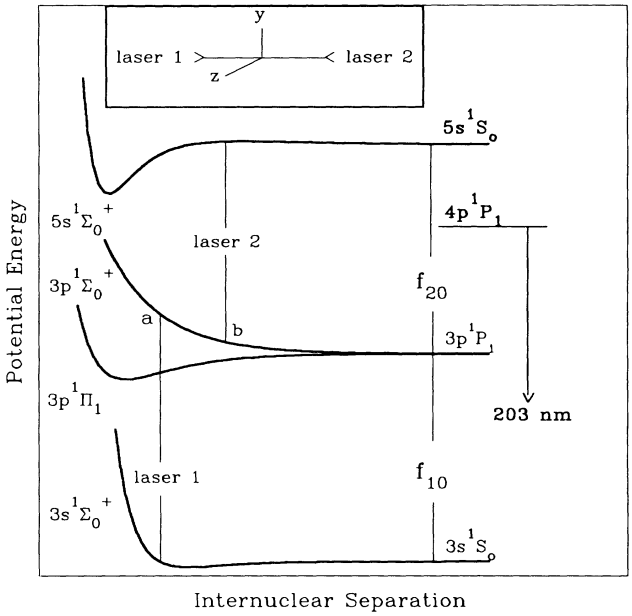

FIG. 1. Schematic potentials for Mg rare gas. Inset: Experimental geometry.

hf_{20}, are defined as $\Delta_1 = hf_1 - hf_{10}$ and $\Delta_2 = hf_2 - hf_{20}$. For weak field excitation in the absence of collisions, the Mg $5s\ ^1S_0$ level may be populated only when $\Delta_1 + \Delta_2 = 0$, corresponding to two-color, two-photon excitation of that level. The linear polarization degree of these atomic two-photon resonances is 100% within the range of Δ_1 and Δ_2 accessed in the experiments reported here [14]. When collisions are considered, additional absorption takes place within the molecular complex formed during the collision [11]. Absorption occurs in the vicinity of Condon points, where the energy defects Δ_1 and Δ_2 are compensated for by the potentials. For the Condon point R_a indicated by a in Fig. 1, this limits the maximum impact parameter in the initial excitation to R_a, and the maximum angular momentum available in the complex to $\mu v R_a/\hbar$. The limit pertains to fractional collisions as well. The relative collision velocity is v and μ is the reduced mass. For example, consider $\Delta_2 = 0$. As Δ_1 is varied the molecular $3p\ ^1\Sigma_0^+$ and $3p\ ^1\Pi_1$ states shown in Fig. 1 may be excited. Dissociation products generated in the Mg $3p\ ^1P_1$ level are probed with the resonant probe laser 2. The linear polarization degree in this case is significantly less than 100%, and depends on Δ_1 and the integrated effect of the dynamics from the region of excitation to large R. Here we consider the situation where both Δ_1 and Δ_2 are nonzero. If Δ_1 is fixed at some nonzero value, the spectrum consists of atomic resonances when $\Delta_1 + \Delta_2 = 0$ and when $\Delta_2 = 0$. In addition, excitation with laser 1 produces molecular population and alignment which may be probed by laser 2 when Δ_2 is not zero. In Fig. 1, this corresponds to laser 1 transitions at the Condon point R_a being probed on the Mg-rare-gas $3p\ ^1\Sigma_0^+ \rightarrow 5s\ ^1\Sigma_0^+$ transition (indicated by b) with laser 2. Polarization and absorption spectra generated as Δ_2 is varied provide information on evolution of those quantities from the inner Condon point at a to the outer one at b. Variation of Δ_1 and Δ_2 generate polarization and intensity surfaces describing the full dynamics within the intermediate states, and the radiative coupling of these to the lower $3s\ ^1\Sigma_0^+$ and upper $5s\ ^1\Sigma_0^+$ states.

In addition to stepwise excitation processes, direct two-photon molecular transitions [11] are possible. In this case, intermediate contributing states would be bound and continuum states associated with the $3p\ ^1\Sigma_0^+$ and $3p\ ^1\Pi_1$ molecular states. Condon points for direct transitions occur when the sum of detunings $\Delta_1 + \Delta_2$ is made up by the difference between the $3s\ ^1\Sigma_0^+$ and $5s\ ^1\Sigma_0^+$ potentials. The polarization of the transitions depends on the mixture of contributing intermediate states for each detuning, but should not depend directly on the dynamics within the intermediate states. For directly populated bound intermediate levels, the polarization should depend sensitively on the size of the lambda doubling and on the effective lifetime of each level.

The experimental geometry is shown schematically in the inset of Fig. 1. In the setup, two laser beams propagate collinearly along the $\pm x$ axis, and pass through a Pyrex cell (at $x = 0$) mounted with quartz windows. As described elsewhere [15], an internally heated boat is supported on a quartz rod inside the cell, and produces a Mg density of about 10^{10} cm^{-3} in the interaction region of the cell. Research-grade rare gases are admitted to the cell through an oil-free, vacuum-gas-handling system (base pressure $\sim 10^{-6}$ Torr). The linearly polarized laser beams are derived from neodymium yttrium aluminum garnet (Nd:YAG) pumped, grazing incidence dye-laser oscillators, each with a bandwidth ~ 3 GHz. Frequency doubling the output of one of the dye lasers in an angle-tuned potassium dihydrogen phosphate (KDP) crystal generates radiation in the vicinity of the Mg $3s\ ^1S_0 \rightarrow 3p\ ^1P_1$ transition at 285.2 nm. The pulse energies are about 20 μJ in an ~ 3-ns temporal width. The second laser output around 571.2 nm consists of ~ 1-mJ pulses in ~ 6-ns pulse widths. This beam is passed through a Babinet-Soleil compensator which scrambles the polarization over the beam cross section. A rotatable linear polarizer following the scrambler is used to vary the angle Θ between the linear polarization directions of two lasers. Population produced in the Mg $5s\ ^1S_0$ level is monitored by cascade fluorescence on the $4p\ ^1P_1 \rightarrow 3s\ ^1S_0$ transition at 202.6 nm. Fluorescence is collected and focused by quartz optics at 90° from the laser beams and detected by a photomultiplier tube (PMT) mounted with interference filters which eliminate all visible and nearly all 285.2-nm resonance radiation, while transmitting about 2.5% of the desired light. The integrated PMT output collected within a 350-ns gate opened at the end of the laser pulse is digitized and stored in a laboratory computer.

Data were accumulated by recording the integrated signal from 2000 laser shots with laser 2 linearly polarized alternately along y (I_y) or along z (I_z). Signals required the presence of both Mg vapor and rare-gas atoms, and generally increased linearly with the rare-gas density for both rare gases. Although the signal size was not linear in the intensity of laser 2 for some narrow ranges of Δ_2, indicating the presence of bound-bound molecular transitions embedded in the continuum absorption spectrum, the polarization was not measurably dependent on the intensity of either laser for any values of Δ_1 and Δ_2. Results presented here are independent of Mg density, although a decrease in the polarization was observed at higher Mg densities.

Polarization P_L and relative total intensity I_T spectra [6] were generated by forming $P_L = (I_z - I_y)/(I_z + I_y)$ and $I_T = I_z + 2I_y$. Typically two to six measurements of P_L and I_T were made at each Δ_1 and Δ_2, ensuring a statistical uncertainty of a few percent. Best quantitative results are for P_L: Only those will be presented here. At high rare-gas pressure, the spectra obtained depended on rare-gas presure. However, as illustrated by the Mg-Ar data in Fig. 2, P_L spectra were not strongly pressure dependent, and the spectra were largely independent of pressure variations below 10 Torr. The pressure depen-

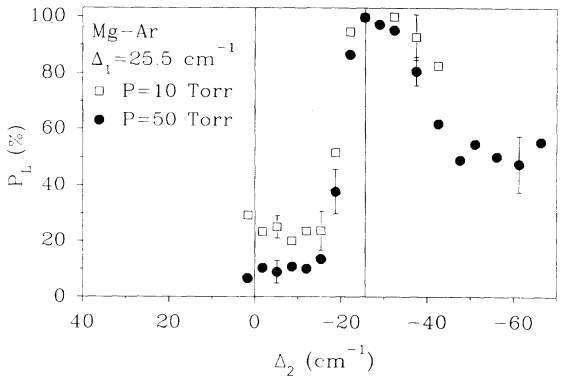

FIG. 2. Pressure dependence of Mg-Ar $P_L(\Delta_2)$ spectrum for $\Delta_1 = 25.5$ cm^{-1}.

dence of P_L is due to collisions subsequent to the initial excitation of the intermediate states by laser 1.

Low-pressure polarization spectra for several values of Δ_1 are presented in Fig. 3 for Mg-Ne. Other spectra taken for larger and smaller values of Δ_1 are similar in shape to these, and will be reported elsewhere [15]. The error bars represent statistical errors and residual uncertainty in the extrapolation to a low-pressure limit. First note the qualitative differences in the spectra for Mg-Ne and Mg-Ar, which generally arise from differences in the interatomic potentials [12,13]. Second, two features are common to all the spectra: a two-color, two-photon atomic resonance located at $\Delta_1+\Delta_2=0$, and the atomic Mg $3p\ ^1P_1 \rightarrow 5s\ ^1S_0$ transition at $\Delta_2=0$. Other features in the spectra arise from absorption of two linearly polarized photons in a single Mg-rare-gas collision. They have their origin in the dynamics of the alignment within and in the mixture of the molecular states involved in each case.

The data presented represent an average over many variables including available collision energies, impact parameters, multiple Condon points, and contributing collision trajectories. To understand the detailed features of the results, calculations for these systems are evidently needed. However, some features may be tentatively understood by considering the molecular potentials for each case. For illustrative purposes, we discuss only the Mg-Ne data with $\Delta_1 > 0$, which corresponds to radiative excitation of the $3p\ ^1\Sigma_0^+$ molecular state. Discussion is based on the general location of the Condon points R_1 and R_2, at each Δ_1 and Δ_2, for two-step radiative transitions. For any nonzero Δ_1 there are three ranges of Δ_2 which must be considered. For each case, rotation of the molecular alignment axis during dissociation on the $3p\ ^1\Sigma_0^+$ repulsive potential leads to reduction in the average polarization in that state. Inspection of the Mg-Ne polarization spectrum in Fig. 3(a) shows this to be the case as Δ_2 is shifted away from the atomic two-photon resonance at $\Delta_2 = -\Delta_1$. When $\Delta_2 > 0$, the optical transition region is at long range, and corresponds to probing nearly dissociated Mg-Ne pairs: Only outgoing collision trajectories on the $3p\ ^1\Sigma_0^+$ potential contribute to the signal. However, both incoming and outgoing trajectories on the initial $3s\ ^1\Sigma_0^+$ potential can provide excitation amplitude into the intermediate states. The resulting polarization in this case should be that of the corresponding one-photon optical collision; the value obtained when $\Delta_2=0$. The nearly flat P_L spectrum in this region for all the data in Figs. 2 and 3 conforms with this picture. It appears generally that this value for P_L is attained for detuning Δ_2 in the vicinity of ± 5 cm^{-1}, depending on the value of Δ_1. This is a sensible result, if one considers that smaller values of the probe detuning should generally be associated with Mg-rare-gas pairs at larger R. The asymptotic atomic P_L is approached for Mg-Ne separations near a decoupling radius where the atomic alignment is no longer coupled to the rotating molecular axis. Note that for $\Delta_2 \gg 0$, the large R probe transitions may become antistatic. Then contributions from direct two-photon molecular transitions, which can have real Condon points in this spectral region, may dominate the spectrum. The relative strengths of direct and stepwise transitions are not distinguishable in the data reported here. For $\Delta_2 < 0$, the strongly repulsive $3p\ ^1\Sigma_0^+$ potential implies that large changes in the detuning give relatively small changes in R_2. Furthermore, the potentials of Hliwa and Daudey [13] predict a confluence of the Condon points R_1 and R_2 in the range $\Delta_1 > -\Delta_2 > 0$. The polarization should be

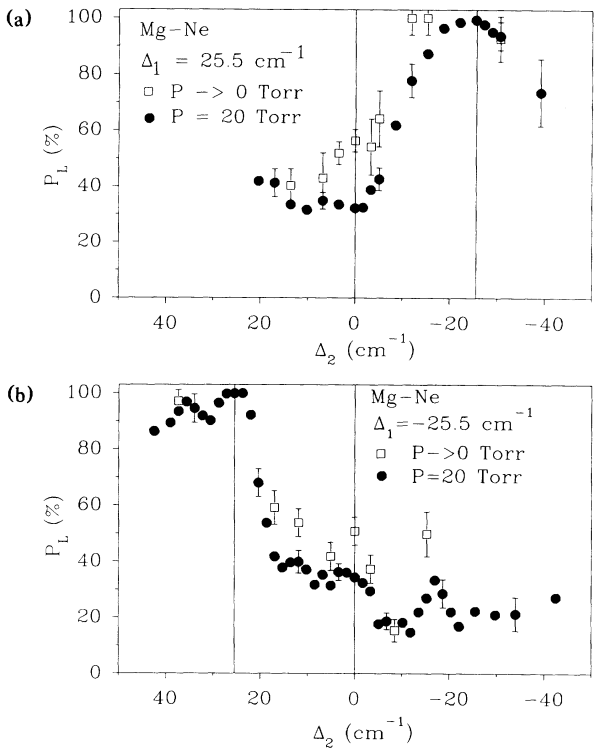

FIG. 3. Polarization spectra as a function of Δ_2 for (a) Mg-Ne, $\Delta_1 = 25.5$ cm^{-1}; (b) Mg-Ne, $\Delta_1 = -25.5$ cm^{-1}.

large in this region, and Fig. 3(a) does show a sharp increase in P_L between the two atomic resonances for Mg-Ne. This is in contrast to the Mg-Ar data of Fig. 2; Mg-Ar potentials [12] indicate that any such increase should occur only when $-\Delta_2 > \Delta_1$. Finally, when $-\Delta_2 > \Delta_1$, trajectories for which $R < R_2$ are probed, and a decreased value of P_L due to rotation of the alignment axis is expected and observed. In contrast to the case above where $\Delta_2 > 0$, only incoming trajectories on the initial $3s\ ^1\Sigma_0^+$ potential contribute excitation amplitude to the observed signal. This gives both incoming and outgoing trajectories in the intermediate state which can contribute to excitation amplitude into the final $5s\ ^1\Sigma_0^+$ state.

In summary, a new dynamical process has been observed in Mg-Ne and Mg-Ar mixtures: absorption of two optical photons during a binary collision. Experimental data illustrating features of such fractional collisions have been presented and discussed in terms of qualitative Mg-rare-gas potentials. Polarization spectra depend clearly on the relative detuning of the two light sources and on the rare gas. The spectra obtained are a frequency domain analog of femtosecond time scale pump-probe spectra. As such, they contain detailed information on evolution of the alignment within the collision complex. Investigation of the process then provides a new method of learning about multipole and collision dynamics within the molecular domain itself.

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