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Temperature effects in the collisional redistribution of resonance radiation in the Ba-Ar and Ba-Xe systems

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We present data on the temperature dependence of the polarization ratios of redistributed fluorescence in the Ba-Ar and Ba-Xe systems. The temperature dependence is observed to be less than 1% per 100 K, which is significantly below predicted levels.

Several recent papers have described the experimental investigation of the collisional redistribution of polarized light in the collision systems comprised of group-IIA alkaline-earth atoms, e.g., Sr or Ba and rare-gas atoms.[1-5] The basic process is described by the equation

$$M(^1S_0)+A+\hbar\omega\rightarrow M(^1P_1)+A\ , \tag{1}$$

in which M is an alkaline-earth atom and A is a rare-gas atom. Typically, the incident laser photon is detuned so far from the $^1S\rightarrow{}^1P$ atomic transition that absorption occurs only during a strong collision with a rare-gas perturber on a time scale that is short compared to the duration of the collision. Under these conditions one may view the collision as forming a transient molecule with absorption occurring via the classical Franck-Condon principle, according to which the probability for absorption can be directly related to local characteristics of the interatomic-potential-energy curves. Furthermore, the asymptotic m_j distribution in the excited state contains information about the dynamical evolution of the half-collision, from the point of absorption to the completion of the collision. Generally, this information is reported in terms of the polarization properties of the excited-state fluorescence via the polarization ratio P,

$$P=\frac{I_\parallel-I_\perp}{I_\parallel+I_\perp}\ . \tag{2}$$

Here, $I_\parallel$ and $I_\perp$ refer to the intensities of the fluorescent light polarized parallel and perpendicular to the polarization of the incident laser photon. For a $J=0$ to 1 transition, a linear polarization ratio of unity signifies that mixing of the m_j states accompanying the completion of the collision is unimportant. Conversely, a polarization ratio of zero would imply that complete mixing occurs between the asymptotically degenerate levels as the collision partners fly apart. Typical polarization ratios range between 0.1 and 0.7 (zero buffer gas pressure limit) and depend strongly on the initial excitation point of the half-collision, determined by the detuning of the incident laser photon.

A large body of theoretical treatments of the redistribution process has been developed, and has been reviewed by Burnett.[6] Recently, a comprehensive treatment based on the close-coupled approach to collisions in a radiation field has been published by Julienne and Mies.[7] They have found that the calculated polarization ratios are especially sensitive to the specific form of the interatomic-potential curves at large internuclear separations. Since this is the region where the potential curves are nearly degenerate, one would intuitively expect this to be the region where nonadiabatic mixing between the asymptotically degenerate states would be strongest. Reasonable qualitative fits to the experimental data[2] were obtained in Ref. 7 by using single relative velocity for the collisions. However, better quantitative agreement resulted at a few detunings for which the close-coupled calculations were roughly averaged over a thermal velocity distribution appropriate to the experimental conditions. This raises the question as to whether additional information about the evolution of the half-collision could be obtained from the temperature dependence of the polarization ratios. Reference 7, in fact, contains a series of curves predicted the temperature dependence of the polarization ratios at various detunings. Although little explanation is given for the predicted temperature dependence, the effects would seem to be large enough to measure experimentally. This paper reports, briefly, results of an experimental investigation into the predicted temperature dependence of the polarization data in the Ba–rare-gas system.

Although the experiments originally envisaged[6] to investigate Eq. (1) used only one laser, an alternative technique that probes the reaction products is to make use of a second laser to provide a source of polarized photons to excite the ^1P states to a further excited ^1S state. It may be shown that the total rate of emission of fluorescent photons from this high-lying state retains all the information about the molecular dynamics of the half-collision process[8] inherent in Eq. (1),[9,10] although, clearly, additional information may also be derived. The two-laser concept is easier to implement experimentally, there being no requirement for (heated) windows close to the interaction region, within a heated, diffusion-controlled, metal-vapor cell.[4] Briefly, two counterpropagating laser beams were focused into a stainless-steel cell containing buffer gas and barium vapor.[4] A standing-wave, cw Ar$^+$

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pumped dye laser operating on Rhodamine-560 (0.59 g/l) provided light close to the resonance transition in barium (554 nm). An intracavity thin étalon allowed a bandwidth of roughly 3 GHz to be obtained.[11] The barium excited states were probed on the $6s6p\ {}^1P_1 \rightarrow 6s8s\ {}^1S_0$ transition in barium (613 nm) by a standing-wave ring laser,[12] operating on Rhodamine-6G (1.2 g/l). An intracavity thin étalon was also used to narrow the probe dye-laser light. Fluorescence on the $6s8s\ {}^1S_0 \rightarrow 6s6p\ {}^3P_1$ 460-nm transition in Ba I was monitored perpendicular to the dye-laser beams via a monochromator and cooled photomultiplier. Photon-counting electronics measured the signals obtained. The data collection and polarization states of the lasers were under computer control. Care had to be taken with both stray light and condensation on the photomultiplier electrodes to reduce background dark counts to an acceptably low level. Polarization data could then be obtained for a variety of cell temperatures. All temperatures were measured via thermocouples attached to the outside of the stainless-steel cell.

A major limitation of the early redistribution experiments performed by Alford and co-workers[2–4] was the empirical dependence on barium density in the polarization data at metal-vapor densities greater than roughly 2×10^{11} cm^{-3}. This is attributed to the influence of radiative trapping.[13] This effect is shown dramatically in the typical linear polarization data shown in Fig. 1, at several wave numbers detuned to the red of the Ba I resonance transition. The metal-vapor cell makes use of a "cold finger" (independently heated) to control the metal-vapor density. If the vapor is controlled by the finger, the vapor density will rise as a steep monotonic function of finger temperature. Provided that the finger temperature is kept below 520 °C for all cell temperatures, we are confident that radiative trapping is of negligible depolarizing influence. In our experiments we maintained the temperature at 505 °C. Indeed, varying the cell temperature and monitoring the total signal observed at any particular detuning enabled us to observe the approach to vapor-pressure equilibrium, and hence finger control of the vapor density. We therefore believe our data to be free of vapor-pressure–dependent effects.

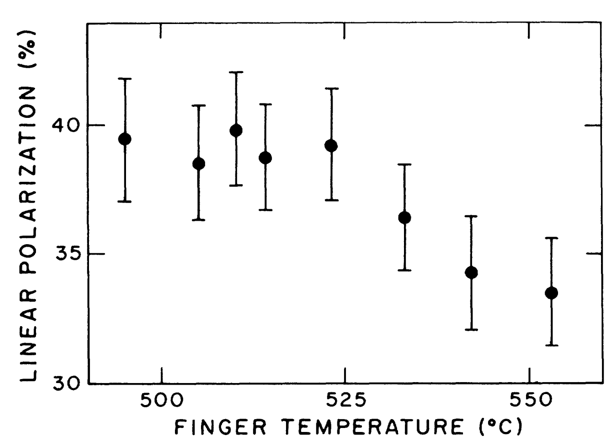

FIG. 1. Polarization data as a function of cell cold-finger temperature. The drop in polarization at high temperatures is an effect of radiative trapping in Ba vapor.

Our initial experiments were performed in Ba-Ar, using circularly polarized light and where $I_{\parallel}$ ($I_{\perp}$) in Eq. (2) now refers to probing with a helicity parallel (antiparallel) to the excitation laser helicity.[4] Data at 29.25 cm^{-1} to the red of the resonance transition and 19.5 cm^{-1} to the blue (detunings for which Ref. 7 suggests the strongest temperature dependences) are shown in Fig. 2. (Corrections due to hyperfine structure[2,3] are not significant in the determination of the temperature variation.) The data have large error bars but still show less temperature dependence than that predicted in Ref. 7. The prediction is of the order of 3% per 100 K, with the polarization ratios increasing with increasing temperature. Our data is 29.3 cm^{-1} to the red certainly seem to run counter to this trend. The difficulties associated with making accurate circular polarization measurements prompted a careful investigation of the more heavily interacting Ba-Xe system, via linear polarization ratios.

The predictions in Ref. 7 indicate that, on the blue wing of the resonance transition, there are two competing temperature effects, giving rise to small net temperature dependence. On the red wing, however, there do not appear to be competing effects and the polarization is a monotonically increasing function of temperature. Our data for various detunings to the red of the Ba I resonance transition for the Ba-Xe system are shown in Fig. 3. Again, corrections due to hyperfine structure[2,3] are unimportant for the temperature variation. Low signal levels prevented our taking accurate data at red detunings significantly beyond the Σ-Σ satellite (at $\simeq 30$ cm^{-1} to the red), and the vapor cell employed prevented cell (in contrast to finger) temperatures much below 750 K or greater than 1000 K being investigated. For all our data it is clear that a temperature dependence of less than 1%

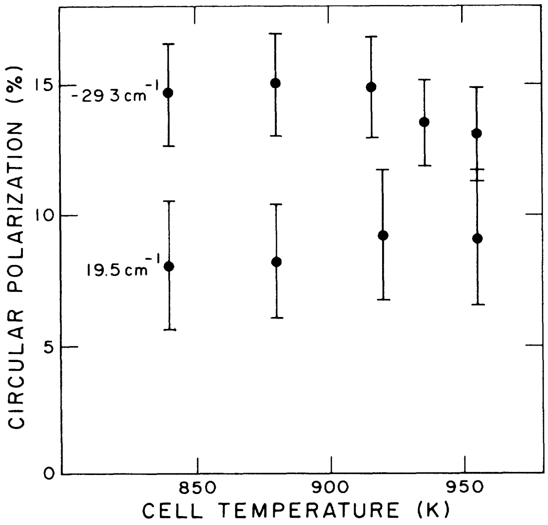

FIG. 2. Preliminary results obtained for the circular polarization ratio for 29.25 cm^{-1} (red) and 19.5 cm^{-1} (blue) as a function of cell-body temperature in the Ba-Ar complex. These data are for 4 Torr of rare gas, uncorrected for barium hyperfine structure.

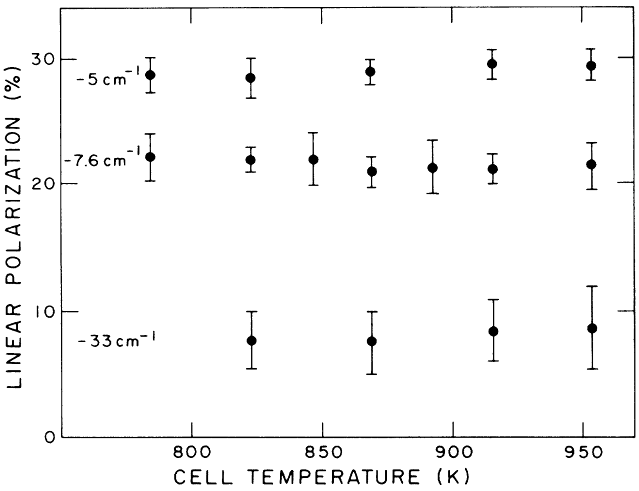

FIG. 3. Linear polarization ratios for a variety of detunings to the red of the Ba resonance transition in Ba-Xe. The data are for 3.5 Torr of rare gas, uncorrected for barium hyperfine structure.

per 100 K is observed, significantly below the expectations (again of the order of 3% per 100 K at -30 cm^{-1}) of Ref. 7. Obviously, when polarization data for the Ba-Xe system are simulated, e.g., via the techniques of Ref. 7, a predicted temperature dependence of polarization ratio (at our investigated detunings) must not be allowed to exceed that allowed by the errors bars of our data. We believe that these data provide a significant constraint on the permissible empirical adjustment of interatomic potentials.

Finally, we point out that the trend of rising degrees of polarization with rising cell temperatures predicted in Ref. 7 may be explained in terms of the simple recoupling model of Lewis *et al.*[14] Deep within a collision, a molecular [Hund's case (a)] basis is valid and the dipole moment will be strongly coupled to the rotation of the internuclear axis as the collision propagates. However, as the collision approaches the asymptotic region, an atomic [Hund's case (e)] basis is more appropriate, and the dipole moment will maintain a fixed orientation in space. Viewed from the space- (laboratory-) fixed atomic basis, much of the mixing of asymptotic states takes place during the molecular evolution. The decoupling model assumes that the transition to the atomic basis occurs at a definite internuclear separation given roughly by the point at which the energy difference between the Hund's case (a) Σ and Π potentials (asymptotically connecting to the $^1P_1$ final state) satisfies the relation

$$\Delta E(\Sigma\text{-}\Pi)\simeq \hbar v/b \ , \tag{3}$$

in which v is a typical radiator-perturber relative velocity and b is a typical impact parameter. Since ΔE is proportional to some inverse power n of the internuclear separation ($n>1$), the decoupling radius decreases with increasing temperature. The excited-state orbitals then rotates through a collision as the temperature rises. The residual polarization should thus show a positive slope as a function of temperature. This simple model ignores any nonadiabatic coupling between molecular states which cannot be described by an effective decoupling radius. It may be that the smaller (and at times negative) temperature dependencies predicted by Ref. 7 for the blue wing are due to an excited state Σ-Π curve crossing inside the effective decoupling radius. Excitation to the blue wing is known to take place via the Σ curve alone, which leads to lower polarization ratios than excitation to the Π curve (on average $\frac{1}{2}$ of the Π states have dipoles oriented perpendicular to the collision plane and therefore do not rotate with the internuclear axis through the collision). Increasing either the detuning to the blue or the temperature will effectively increase the velocity of the collision complex through the crossing, resulting in proportionately more complexes staying on the Σ curves, thereby compensating, in part, for the temperature effect on the decoupling radius.

With reference to our results, it would seem that the decoupling radius in our experimental systems is less sensitive to temperature than the simulated system of Ref. 7. This suggests that the actual Σ and Π excited-state potential curves diverge more rapidly from each other than predicted. Larger temperature dependencies can be expected in systems for which the excited-state potential curves diverge less rapidly. Investigations of the possible effects which curve crossings may have on experiments of this sort would require one going to detunings comparable to the thermal energies, so that the velocity distribution through the crossing would differ significantly from the thermal distribution.

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