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Polarization of collisionally redistributed light from the far wings of strontium—rare-gas systems

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We have made systematic measurements of the polarization of fluorescence from Sr—rare-gas systems excited off resonance by linearly polarized light. Measurements of this type give information about the evolution during a collision after the absorption of a photon. This information is important in obtaining and verifying aspects of the interaction potential that cannot be studied using conventional line-broadening experiments. We have also measured the collisional-alignment decay rates for Sr—rare-gas systems by observing the perturber-pressure dependence of the polarization of the fluorescence. To the best of our knowledge this is a new technique for measuring these decay rates.

INTRODUCTION

Atom-atom interactions are of great importance in many areas of physics and chemistry. Though these interactions have been studied theoretically and experimentally for many years, there are aspects of many relatively simple systems that are still not well understood. Far-wing line-broadening experiments have been useful in obtaining information about intermolecular potential curves. Simple absorption experiments yield difference potentials,[1] while more difficult temperature-dependent absorption experiments can, under some circumstances, yield the actual potential curves.[2] Recent experiments[3,4] have suggested, not surprisingly, that far-wing *scattering* experiments contain detailed information on the evolution of the atom-atom interaction as well as the collisional redistribution process. On the theoretical side much has been done to extend generalized line-broadening theory to the case of redistribution when the finite time duration of collisions is important.[5] Burnett and Cooper[6] (with Ballagh and Smith), in particular, have considered the explicit effects of degeneracy on the problem, and it is their formalism that we shall exploit here. (Recent work by Nienhuis[7] also considers the effects of degeneracy on the problem.)

The scattering experiment considered here follows the pioneering work of Carlsten *et al.*[8] Light with frequency ω_L and polarization $\hat{\epsilon}_1$ (near resonance with a transition of frequency ω_0) is used to excite atoms while they are colliding with perturbers. Fluorescence, $(\omega_F,\hat{\epsilon}_2)$, centered about ω_0 and emitted after the collision is then observed. In contrast to normal absorption-emission experiments the polarization of the fluorescence is important. This polarization will naturally depend on the excited m_J-state distribution. Therefore, a scattering experiment of this type is concerned with the probability of absorbing a photon $(\omega_L,\hat{\epsilon}_1)$ *and* finishing up in a particular m_J state. This clearly requires knowledge of the time evolution of the excited state from the point of absorption to the point of emission.[6] Thus, one would expect a scattering experiment of this type to depend heavily on the intermolecular potentials and their nonadiabatic mixing. Such an experiment, therefore, provides a sensitive test of potentials arrived at through other means.

EXPERIMENT

The experiment reported here is an improved version of the experiment performed by Thomann *et al.*[3] Linearly polarized light from a dye laser tuned near resonance with a Sr-atom transition (4607 Å, $J=0$ to $J=1$) is used to excite Sr being perturbed by rare-gas atoms. The spectrum of the Sr atoms consists of a Rayleigh peak at the laser frequency and a fluorescence peak at 4607 Å. The integrated fluorescence peak is observed at right angles to the incident propagation direction. Specifically, the components of the fluorescence polarized parallel $(I_{\parallel})$ and perpendicular $(I_{\perp})$ to the incident polarization direction are measured. This allows determination of the polarization P,

$$P=\frac{I_{\parallel}-I_{\perp}}{I_{\parallel}+I_{\perp}}. \tag{1}$$

The polarization dependence on incident-light frequency is the desired information.

The experimetal setup has been discussed in detail elsewhere[9] and is similar to that used by Thomann *et al.*[3] An Ar^+ laser is used to pump a dye laser which has a linearly polarized output (we can also use the visible Ar^+ laser lines directly). This light is sent into a heated cell with Sr vapor ($\sim 10^{13}\ \mathrm{cm}^{-3}$) and rare-gas perturbers (~ 3 Torr). After being sent through an analyzer the integrated fluorescence, at frequency ω_0, is spectrally resolved from the laser frequency ω_L, by a monochromator. The analyzer, a linear polarizer, remains fixed while the laser polarization is controlled with a Pockels cell. The signal is detected by a computer-controlled photon-counting system. By varying the laser wavelength the polarization dependence on detuning, $\Delta\omega = \omega_0 - \omega_L$, is obtained. A heated sapphire window is placed in the interaction region to reduce the fluorescence vapor path length to approximately 150 μm. Observations of the polarization dependence on Sr density are made to check that multiple scattering as well as resonance broadening are negligible under the conditions of the actual experiment.

PRESSURE DEPENDENCE

The polarization is observed experimentally with a finite perturber pressure. This means there is a finite probability of a depolarizing collision occurring during the natural lifetime of the excited state after the initial absorption process. The interesting physics is contained in the polarization one would obtain in the absence of depolarizing collisions. The finite-pressure results can be extrapolated to this "zero-pressure" limit if the pressure dependence of the polarization is known.

The theory of Burnett and Cooper[6] can be used to obtain the following perturber-density dependence:

$$P = \frac{3\alpha^{(2)}(\omega_L)}{2 + \alpha^{(2)}(\omega_L) + \dfrac{2}{\gamma_N}\left[\dfrac{\gamma_c^{(2)}}{N_p}\right] N_p}\,, \tag{2}$$

where $1/\gamma_N$ is the natural lifetime of the excited state (4.68 nsec)[10] and N_p is the perturber density. The quantity $\gamma_c^{(2)}/N_p$ is the collisional-alignment decay rate. This decay rate must be measured since it is not known for Sr—rare-gas systems. The quantity $\alpha^{(2)}(\omega_L)$ is related to the generalized profile $f^{(2)}(\omega_L)$ of Burnett and Cooper[6]:

$$f^{(2)}(\omega_L) = \frac{1}{\pi} \frac{\alpha^{(2)}(\omega_L)\gamma_c^{(1)}(\omega_L) + \frac{1}{2}(\gamma_N + \gamma_c^{(2)})}{(\Delta\omega)^2}\,, \tag{3}$$

where $\gamma_c^{(1)}(\omega_L)$ is the frequency-dependent line-broadening coefficient. Equation (3) is valid for detunings large compared to $\gamma_c^{(1)}(\omega_L)$. It is interesting to note

$$\alpha^{(2)}(\omega_L) = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \tag{4}$$

which is called the longitudinal polarization. The perturber-density dependence given in Eq. (2) is slightly different than that given by Lewis *et al.*[11] The pressure dependence given by them is valid for the longitudinal polarization—not the polarization.

For the purpose of calculating $\gamma_c^{(2)}/N_p$ it is convenient to define a parameter β:

$$P \equiv \frac{3\beta}{2+\beta} \tag{5}$$

or

$$\frac{1}{\beta} \equiv \frac{3-P}{P} = \frac{1}{\alpha^{(2)}(\omega_L)}\left[1 + \frac{1}{\gamma_N}\left[\frac{\gamma_c^{(2)}}{N_p}\right] N_p\right]. \tag{6}$$

This predicts a straight line for a plot of $1/\beta$ versus perturber density (pressure) with a slope and "y intercept" dependent on detuning but with an "x intercept" independent of detuning. Therefore, by looking at the perturber-pressure dependence of the polarization one can obtain $\gamma_c^{(2)}/N_p$. A plot of the experimental data for $1/\beta$ versus perturber (He in this case) pressure is shown in Fig. 1. As predicted, the slope is detuning dependent but the x intercept is independent of detuning, to within the experimental error. The upper line in Fig. 1 is for a detuning of 133 cm^{-1} to the blue and the lower curve is for 238 cm^{-1} to the red. Results show this pressure dependence to be valid for all detunings, including the kT (thermal energy) wings.

The pressure dependence for all the Sr—rare-gas systems has been observed and yields the following

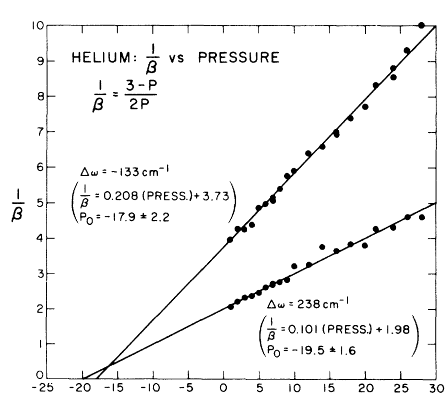

FIG. 1. $1/\beta$ vs He pressure. Fitted lines were obtained by a weighted least-squares fit. P_0 is the x intercept.

values of the collisional-alignment decay rate:

Gas	$\gamma_c^{(2)}/N_p$ (10^{-9} sec^{-1}/cm^{-3})
He	1.66 ±0.28
Ne	0.884±0.078
Ar	1.58 ±0.19
Kr	1.91 ±0.39
Xe	2.00 ±0.31.

These rates are comparable to decay rates obtained in alkali-metal—rare-gas systems.[12] Excluding He, they also show the same trend of the alkali metals of increasing $\gamma_c^{(2)}/N_p$ for increasing atomic mass of the perturber. This is, to the best of our knowledge, the first measurement of these decay rates. The technique used should have applicability to a large number of systems.

RESULTS AND DISCUSSION

Detuning-dependent polarization data were taken at a buffer gas pressure of 3 Torr and then extrapolated to the zero-pressure limit using Eq. (2) and the measured value of $\gamma_c^{(2)}/N_p$. Results for the red wings of the rare-gas perturbers are shown in Fig. 2. Values of the inverse of a collision time (τ_c^{-1}) which nominally locates the extent of the impact region are marked on the abscissa. The polarization for He shows little variation with detuning. Ne, however, shows a small dip in the polarization curve at approximately 25 cm^{-1} and this dip gets deeper as the perturber mass increases. Kr and Xe also show a shoulder in the far red wing at approximately 100—200 cm^{-1}. Satellite positions for Sr—rare-gas systems are known for He, Ar, and Xe.[1] He and Ar show diffuse satellites at 20 cm^{-1}, while Xe has a distinct satellite at 50 cm^{-1}. Thus there is a suggested correlation between the observed dips and the satellite positions.[13] Blue wing results are shown in Fig. 3. He, Ne, and Ar all show a decrease in polarization upon leaving the impact region and a leveling off of the polarization at large detunings. Kr and Xe show rapid, large drops in the polarization with a slow rise in the far wing.

Theoretical calculations of polarization curves are critically dependent on the intermolecular potential curves and their nonadiabatic mixing. Moreover, potential curves for Sr—rare-gas systems are not very well known. Semiclassical calculations, assuming straight-line trajectories, for model potentials have been done by Lewis *et al.*[11,13] and Cooper.[14] These studies qualitatively explain the drop in the polarization as being due to quasistatic excitation of the Π and/or Σ molecular states followed by rota-

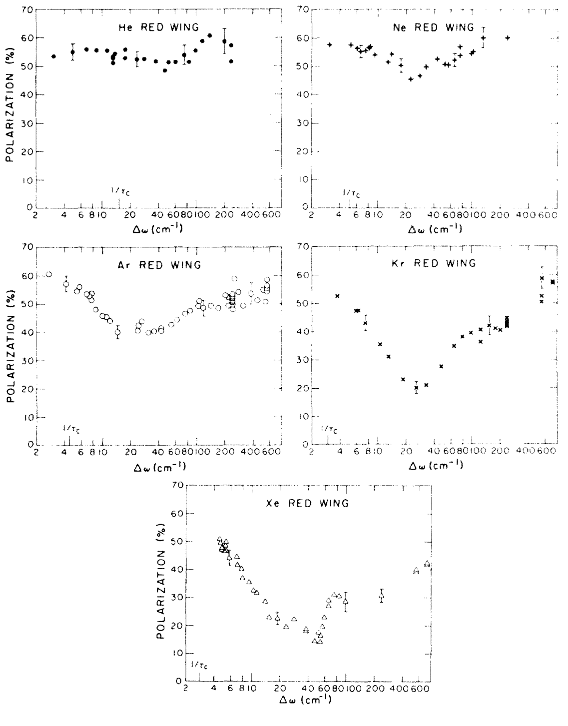

FIG. 2. Polarization data for Sr red wing. These are zero-pressure data. τ_c^{-1} is the inverse of a collision time and nominally marks the end of the impact region.

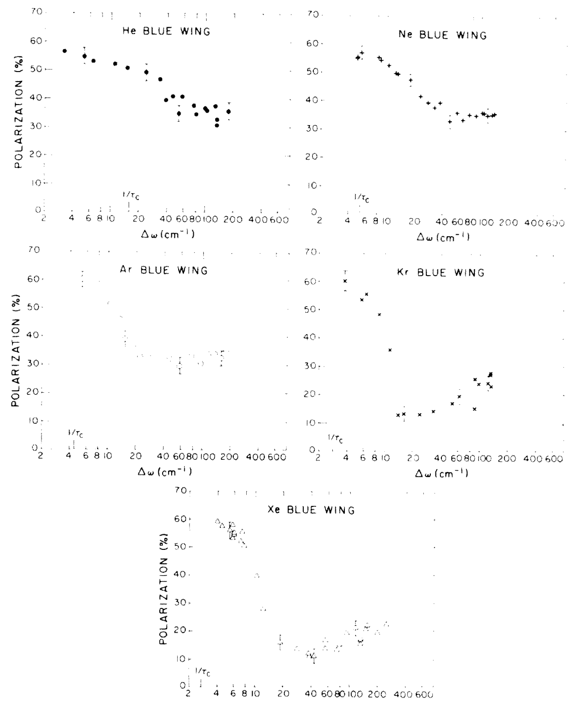

FIG. 3. Polarization data for Sr blue wing. Zero-pressure data. τ_c^{-1} is the inverse of collision time.

tion of the molecular dipole until the atom and perturber decouple (the decoupling position will be sensitive to curve shapes and possible crossings). The far-wing rise in polarization appears qualitatively to be due to "hard-sphere" collisions off the repulsive core of the interaction. This hard-sphere type of collision restricts the rotation of the molecular dipole and leads to values of the very-far-wing polarization comparable to that observed. Interference between possible channels of excitation may well be important at small $\Delta\omega(\sim\tau_c^{-1})$, and in the region of a satellite where excitation in a possible channel is being cut off.

CONCLUSION

We have presented these systematic far-wing polarization data for the various rare gases in the hope that they will provide molecular theorists with very strong constraints on the potentials. The semiclassical calculations mentioned above have shown the direction this work can take. Recent work by Julienne[15] using fully quantal methods also indicates the importance of polarization data in determining collision dynamics. Polarization data of this kind offer a stronger test of theoretical work than simple line-shape data and will, we hope, lead to a better understanding of atom-atom interactions. In addition to the polarization curves, a new method for measuring collisional multipole decay rates has been discussed. Results for collisional-alignment decay rates have been given for Sr—rare-gas systems and are comparable to those found in alkali-metal—rare-gas systems.

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