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Citation: *The Journal of Chemical Physics* **90**, 7605 (1989); doi: 10.1063/1.456195

View online: <http://dx.doi.org/10.1063/1.456195>

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Alignment effects in Ca-He (5^1P_1 – 5^3P_J) energy transfer half-collisions

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(Received 28 February 1989; accepted 8 March 1989)

Report studies of the spin changing energy transfer process $\text{Ca}^*(5^1P_1^0) + \text{He} \rightarrow \text{Ca}^*(5^3P_J^0) + \text{He} + \Delta E$, using far wing laser scattering techniques. This report closely parallels previously published work¹ but extends those measurements to larger-frequency shifts and hence smaller internuclear separations of the collision complex. The purpose of this work is to investigate the dynamical pathway for the energy transfer process. In particular we aim to (1) determine the validity of the proposed $^1\Pi - ^3\Sigma^+$ curve crossing model which has been used to explain the orbital alignment preference observed for this process in polarized crossed beam studies^{2,3}; (2) assess the significance of long-range nonadiabatic $^1\Pi - ^1\Sigma^+$ mixing which tends to confuse the interpretation of such polarized crossed beam studies by allowing orbital scrambling.⁴

Our approach is to study the “half-collision” dynamics by exciting the Ca-He collision complex directly and monitoring the subsequent branching into the 5^3P and 5^1P exit channels. Based on crude but reasonable arguments concerning the expected shapes of the potential curves,¹ we expect that far red wing absorption corresponds predominantly to excitation of the attractive $^1\Pi$ molecular state, whereas blue wing absorption corresponds predominately to excitation of the repulsive $^1\Sigma^+$ molecular state. The orbital alignment or polarization effect should then be apparent in a red wing/blue wing asymmetry for the $(5^3P)/(5^1P)$ branching ratio. Since the excitations occur at relatively short range, the result may be less affected by long-range nonadiabatic mixing and may lead to an enhanced polarization.

The experimental setup is described in detail in Ref. 1. The major modifications here were (a) the use of Courmarin 540 A laser dye, and (b) replacement of the monochromator with 10 nm bandpass filters to improve atomic fluorescence collection efficiency.

We have measured the population branching ratio, $R = N(^3P)/[N(^1P) + N(^3P)]$, as a function of helium pressure and as a function of detuning. Here $N(^3P)/[N(^1P) + N(^3P)]$ is the population of the $5P$ triplet (singlet) level. These populations are determined through measurements of the fluorescence intensities $I(^3P)$ and $I(^1P)$ on the $\text{Ca}^*(5^3P_J - 3^3D_J)$ and the $\text{Ca}^*(5^1P_1 - 3^1D_2)$ transitions, respectively. The fluorescence measurements are scaled to the population ratios by a factor that depends on

the radiative branching, detection system efficiencies, etc. This factor can be estimated by measuring the intensity ratio at high pressures (> 100 Torr) where collisional mixing leads to an approximate Boltzmann equilibrium in the populations, $N(^3P)/N(^1P) = g(^3P)/g(^1P) e^{-\Delta E/kT} \approx 4$. The measurement is made difficult by an unfortunate accidental fluorescence coincidence of the $\text{Ca}^*(5^3S_1 \rightarrow 4^3P_J)$ multiplet, which falls within our detection bandpass and which must be subtracted out in the calibration.

The population branching ratios, R , are strong functions of pressure; at high pressures collisional mixing leads to a value of $R \sim 0.8$. At low pressures R can be extrapolated to the zero pressure limit to obtain the nascent branching ratio R_0 . This extrapolation is carried out by fitting to the solution of a simple two-state rate equation model which allows for collisional mixing between the (5^1P) and (5^3P) levels.¹ Figure 1 shows R_0 as a function of detuning and clearly exhibits the expected red wing/blue wing asymmetry. The qualitative shape of the branching ratio profiles agree with previously published results at lower-frequency detunings¹ but the absolute scale of the branching ratios differs by roughly a factor of 2. This is due to the use of an incorrect scaling factor in the previous measurements; the influence of the additional $5^3S \rightarrow 4^3P$ fluorescence channel was not properly taken into account.

As in Ref. 1, if we correlate far wing absorption with excitation to a specific molecular state, we may relate the line profile asymmetry to the polarization by

$$P = \frac{R_0(\text{red}) - R_0(\text{blue})}{R_0(\text{red}) + R_0(\text{blue})} = \frac{\sigma_{11}(\Delta) - \sigma_{22}(\Delta)}{\sigma_{11}(\Delta) + \sigma_{22}(\Delta)}.$$

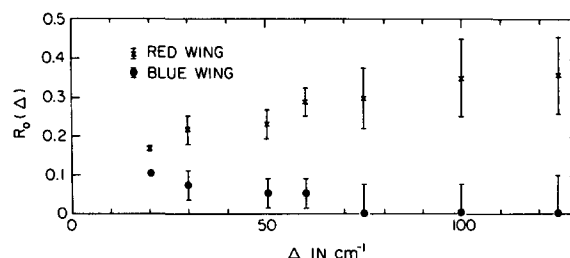


FIG. 1. Extrapolated zero pressure triplet branching ratio as a function of detuning.

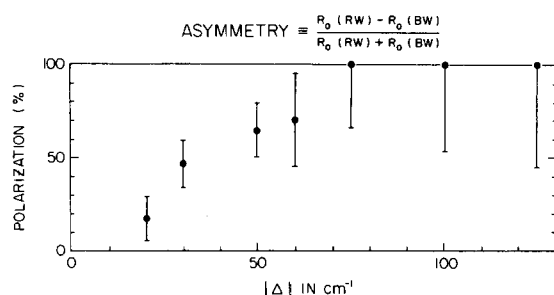


FIG. 2. The red/blue profile asymmetry or polarization as a function of detuning.

Here R_0 is the nascent branching ratio at a given detuning in the red or blue wing, and σ_{Π} (σ_{Σ}) is the cross section for the spin change to occur via the Π or Σ molecular states, respectively.

The dramatic increase in the polarization (approaching 100%) shown in Fig. 2 indicates a complete correlation between the $^1\Pi$ state excitation and the energy transfer process, in agreement with the curve crossing model. It further demonstrates that absorption in the far wings ($\gtrsim 70 \text{ cm}^{-1}$) indeed occurs in a region where nonadiabatic $^1\Pi$ - $^1\Sigma^+$ mixing can be neglected, and therefore may allow us to define the range of "orbital scrambling." In a simple van der Waals approximation, $\Delta \gtrsim 70 \text{ cm}^{-1}$ corresponds to internuclear separations $R \lesssim 6.5 \text{ \AA}$. The steady increase in polarization in

the range $\Delta = 20\text{--}70 \text{ cm}^{-1}$ might be associated with a gradual decrease in the probability for nonadiabatic $^1\Pi$ - $^1\Sigma^+$ mixing as the excitation occurs to smaller R ; however, there is an alternative explanation. At smaller detunings there may be appreciable nonclassical antistatic wing absorption⁵; the assumption that red wing/blue wing absorption can be correlated entirely with $^1\Pi$ / $^1\Sigma^+$ excitation should become more exact as the detuning increases. Thus, the value of detuning $\sim 70 \text{ cm}^{-1}$ puts only a limit on the possible range of nonadiabatic mixing. Nevertheless, these results should allow very stringent tests of molecular dynamics calculations.

This work was supported by the National Science Foundation through Grant No. CHE 86-15118. We gratefully acknowledge very helpful discussions with Professor Alan Gallagher and Professor Stephen Leone during the course of this work.

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¹K. C. Lin, P. D. Kleiber, J. X. Wang, W. C. Stwalley, and S. R. Leone, *J. Chem. Phys.* **89**, 4771 (1988).

²M. O. Hale, I. V. Hertel, and S. R. Leone, *Phys. Rev. Lett.* **53**, 2296 (1984).

³Bussert, W. D. Neuschäfer, and S. R. Leone, *J. Chem. Phys.* **87**, 3833 (1987).

⁴B. Pouilly and M. H. Alexander, *J. Chem. Phys.* **86**, 4790 (1987).

⁵J. Szudy and W. E. Baylis, *J. Quant. Spec. Radiat. Transfer* **15**, 641 (1975).

COMMENTS

Comment on: "Predissociation of the $d\ ^1\Pi_g$ Rydberg state in O_2 : Nature of the Rydberg-valence interactions"

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(Received 1 February 1989; accepted 21 February 1989)

The $d\ ^1\Pi_g$ (R) Rydberg state of molecular oxygen has been identified using a variety of experimental techniques, including electron energy loss,¹ resonance enhanced multiphoton ionization (REMPI),²⁻⁴ and translational spectroscopy.^{5,6} The rotational constants of the lowest vibrational states display an anomalous behavior. The anomalies have been attributed to the effects of $^1\Pi_g$ valence (V) states^{3,6,7} and an approximate theoretical treatment by van der Zande *et al.*⁶ has demonstrated that interactions between the $d\ ^1\Pi_g$ (R) state and the bound valence $^1\Pi_g$ (V) state separating diabatically to $\text{O}(^1D) + \text{O}(^1D)$ are responsible. We present here the results of a more rigorous theoretical analysis in which we solve the pair of coupled equations⁸ that describe the interaction of the $d\ ^1\Pi_g$ (R) and $^1\Pi_g$ (V) states.

Van der Zande *et al.*⁶ adopted for the potential energy curve of the diabatic $d\ ^1\Pi_g$ (R) state the RKR potential energy curve⁹ of the ground state of O_2^+ , lowered in energy by 3.83 eV. For the $^1\Pi_g$ (V) state, they constructed a diabatic potential energy curve using the $1\ ^1\Pi_g$ adiabatic valence potential at internuclear distances less than $2.9 a_0$ and the $2\ ^1\Pi_g$ adiabatic valence potential at internuclear distances greater than $2.9 a_0$. They assumed that the shape of the diabatic valence potential in the region of R_e was given correctly by the calculations of Saxon and Liu,¹⁰ and they shifted its position so that first order perturbation theory reproduced the predissociative widths of the upper vibrational levels $v > 3$ of the Rydberg state. By diagonalizing the diabatic interaction potential energy matrix, van der Zande *et al.*⁶ also