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KINETIC ASPECTS OF GAS PHASE METAL ATOM OXIDATION REACTIONS. (U)
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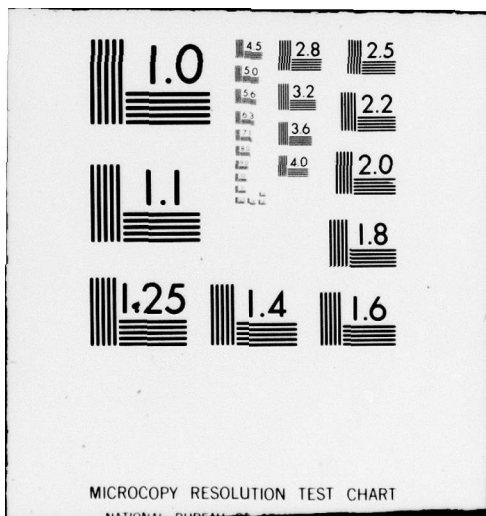
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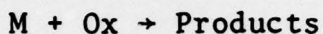
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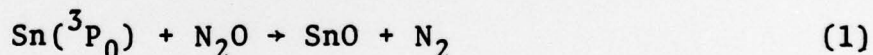
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The research program funded by the AFOSR was initiated in response to questions raised concerning the feasibility of constructing a visible chemical laser based on the oxidation of metal atoms, particularly of Group IV. Such processes



were found to lead to chemiluminescence in flames¹ and were considered likely candidates for achieving at least partial population inversions and consequent stimulated emission.

A particularly promising reaction to be studied was that of Sn atoms with N₂O. High temperature flow experiments demonstrated¹ that the SnO produced in this elementary bimolecular reaction



was formed primarily in electronically excited states.

If such a reaction were to be used to create an inverted population of electronic states for use in a laser, the following criteria would need to be met:

- 1) The reaction should be rapid in order to maintain an inversion in the presence of spontaneous emission and deactivation;
- 2) Collisional quenching of the excited state would have to be relatively inefficient;
- 3) Some reasonably convenient means of uniform mixing of reagents would have to be achieved.

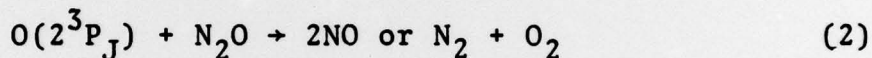
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The oxidation of Ge and Sn by various gases including N₂O, has been studied by flash photolysis at room temperature and the kinetics determined. The rate of Sn + N₂O is probably too slow to permit construction of a chemical laser based on this reaction. A new set of techniques involving laser pumping of alkaline earth atoms is also described which will permit the study of the kinetic behavior of their low-lying excited levels in bimolecular collisions.		

The primary goal of this research, therefore, was the determination of the rate constant for (1) and related reactions. In addition, further studies were carried out to develop new techniques for examining the chemistry of electronically excited atoms and molecules of relevance to laser design and construction.

Early on in the course of this research, it was recognized that the reactivity of electronically excited species could best be discussed in terms of the electronic structure of the collision complex mediating the interaction between reagents and products. Such arguments have proved useful when cast in the format of the so-called adiabatic correlation rules first proposed by Shuler² and then expanded upon by Husain and co-workers³⁻⁴. Essentially, the nature of the state manifold of the collision complex may be deduced by taking the direct product of the symmetry species of the reagents reduced in nuclear symmetry to that characterizing the complex. Similarly, the electronic states arising from an adiabatic interaction of reagents via a particular collision complex may also be elucidated. Questions of the nature of the momentum conservation, viz, can the collision complex best be described by ℓ, s or j, Ω coupling, must also be addressed, as they bear directly on the prediction of probable product species formed.

The energetics of the potential hypersurfaces correlating with reactants and products are also significant. The usual mechanism by which the correlation rules are applied is the

correlation diagram. It was shown in the early stages of this research program⁵ that such diagrams may be modified by consideration of the diabatic correlations arising from interaction of the reagent species, the result being a simple technique for predicting qualitatively the energetics of reagent interaction along the reaction coordinate. This concept was then applied to the examination of the reaction



in which the diabatic correlation to highly excited states of O_2 arising from $O(2^3P_J) + O(2^1D_2)$ was shown to result in the formation of a substantial barrier to reaction (2). This was extended to a comparison of the reactions of $O(2^1D_2)$ with N_2O and CO_2 , where the former results in chemical abstraction while the latter yields deactivation only. This was ascribed to the presence of low-lying electronically excited states of N_2O which are not present in CO_2 .

The initial experimental studies⁶ in this program involved a determination of rate of (1) over the temperature range 341-377°K. The overall reaction is very slow in this region and a major cause for experimental concern is even a trace quantity of O_2 in the N_2O . The experimental results suggested an activation energy of ca. 4 kcal/mole in excellent agreement with high temperature flow experiments.⁷ Although more sophisticated data analysis yields a somewhat lower estimate of E_a ,

the inescapable conclusion is that (1) is probably too slow to be a promising pump reaction for a chemical laser. The presence of a substantial barrier in the reaction coordinate of (1) was again ascribed to the effect of a diabatic correlation with highly excited states of the product, SnO^* . In this case, however, the situation is not as clear as in (2), because the various spin-orbit levels of the 3P_J ground state are expected to undergo reactions with N_2O via different potential hypersurfaces. The fact that the apparent E_a is about equal to the $J=1 \longleftrightarrow J=0$ splitting is suggestive of a reaction mechanism involving such an excitation. To date, no clearcut experimental study of this possibility has been reported.

The reactivity of Ge and Sn upon collisions with the oxidizing gases Cl_2 , O_2 , NO_2 , COS and NO were then examined. The rates at 295°K are given in Table 1. In general, these are quite rapid and when taken in conjunction with data obtained in a molecular beam study⁸ of $\text{Sn} + \text{O}_2$, suggest a significant role for long-lived collision complexes. The oxidation reactions of Ge are faster than those of Sn, the enhancement factor being as much as an order of magnitude. This is in accord with the higher exothermicity of abstraction processes involving Ge.

During the past year, our attention has, in the main, been directed toward the development of new techniques which will enhance our ability to study the gas phase reactivity of

electronically excited atoms and molecules. Of special interest has been the use of tunable lasers to excite selectively metastable states of alkaline earth atoms. These have been chosen due to the extensive experimentation which has been carried out on their ground electronic state, n^1S_0 .

Two schemes have been envisaged and successfully tested. The first involves the direct pumping of metastables (DPM) by excitation of a transition which is only formally forbidden under the electric dipole selection rules, e.g., $\Delta S=0$. Such is the case for $\text{Ca}(^3P_1) \leftarrow \text{Ca}(^1S_0)$ which is weakly allowed ($\tau_{\text{optical}} = 0.4 \text{ mS}$ for 3P_1) and may be excited using 657.2 nm radiation. We have utilized a flashlamp pumped dye laser to excite this transition and have observed the $^3P_{0,1,2}$ multiplet, apparently in thermal equilibrium at a helium buffer gas pressure of 50 torr. By using a cell of unitized construction with heated windows, we hope to lower the required cell pressure in order to study this intramultiplet relaxation process following DPM excitation. Also, we plan to use this technique to probe energy transfer from electronically excited alkaline earths to alkali metals and alkaline earths by observation of the resonance emission of atomic states produced via E-E processes.

Another laser excitation technique developed in this laboratory has been three-level optical pumping (TOP) which is best illustrated for the case of barium (Figure 1). A sample of Ba was maintained at elevated temperatures around 773°K in a quartz cell (225 mm x 23 mm ID). The central 150 mm

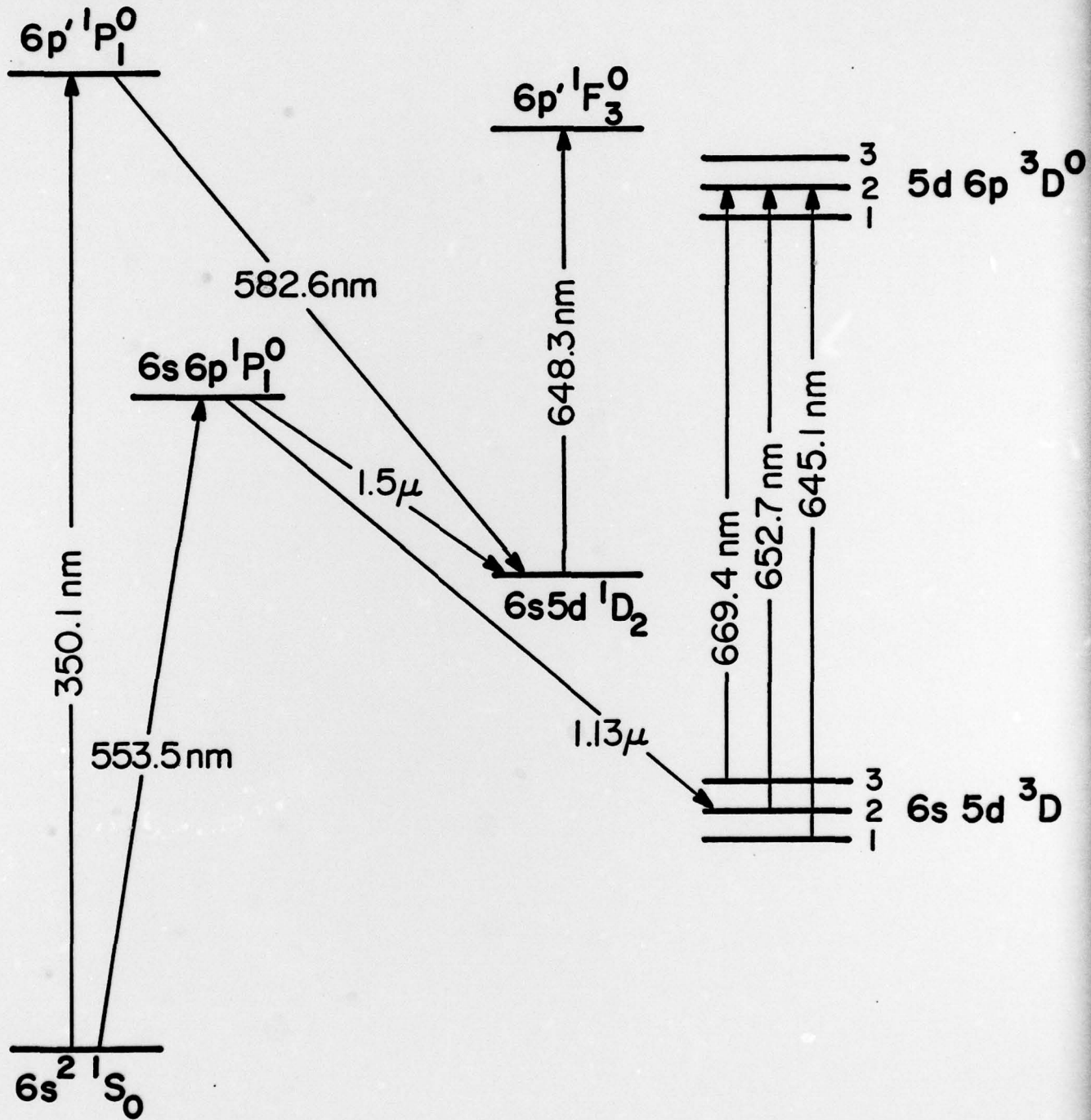


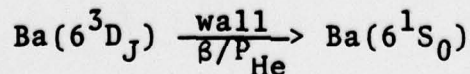
Figure 1. Low-lying energy levels of barium.

of this cell was heated to produce the Ba vapor while the presence of He buffer gas minimized diffusion of the metal to the cell end windows.

Pumping the transition $6^1P_1^0 + 6^1S_0$ at 553.5 nm followed by the spontaneous emissions $6^1P_1^0 \rightarrow 6^1D_2$ ($\lambda = 1500$ nm) and $6^1P_1^0 \rightarrow 6^3D_{2,1}$ ($\lambda = 1.130$ nm) is expected to result in production of the optically metastable 6^1D_2 and 6^3D_J levels of barium. By arranging for passage of a coaxially located beam of resonance radiation emitted from a hollow cathode lamp (Figure 2) it is possible to monitor the production and removal of these electronically excited metastables.

Our initial results demonstrated quite clearly that, contrary to expectation, it was the 3D_J state which is selectively excited following TOP at 553.5 nm. This could only occur if the spontaneous transition $6^1P_1^0 \rightarrow 6^1D_2$ possessed a smaller A_{nm} than $6^1P_1^0 \rightarrow 6^3D_J$. Interestingly, it has been observed⁹ in a barium discharge pumped laser that the singlet-triplet transition does, in fact, reach threshold first, in sensible accord with our result.

Further experiments involved a study of the diffusion of Ba(6^3D_J) through helium. Here, the rate of removal of Ba(6^3D_J) was shown to be dominated by diffusion of the atoms through the buffer gas (Figure 3) via the first-order process,



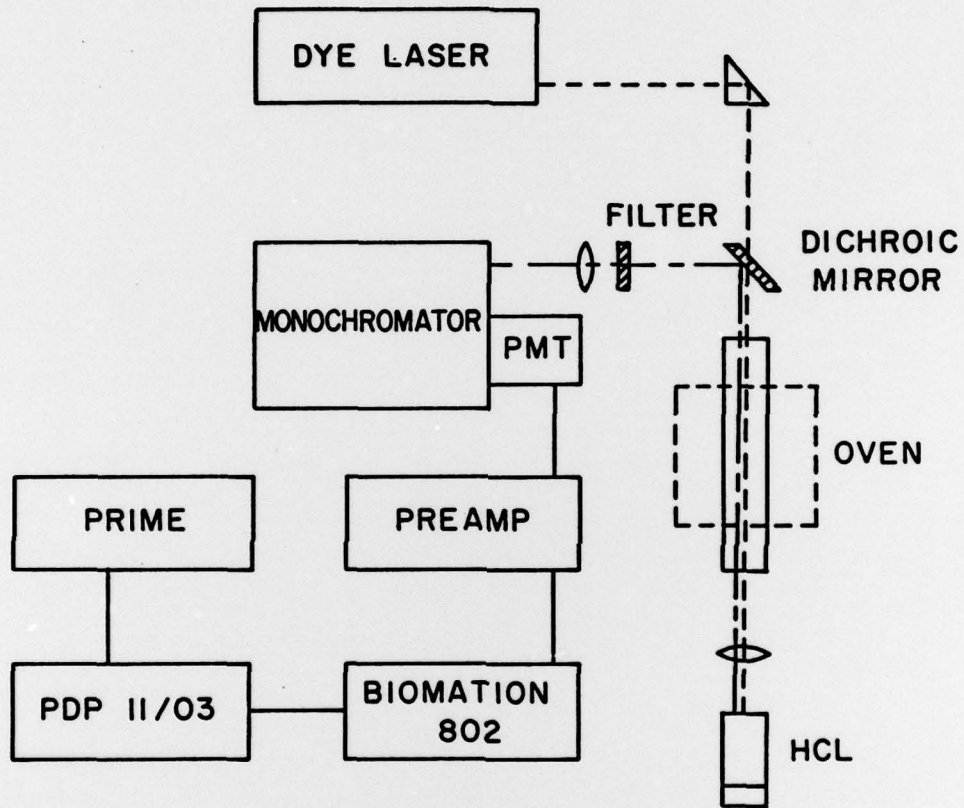


Figure 2. Experimental apparatus.

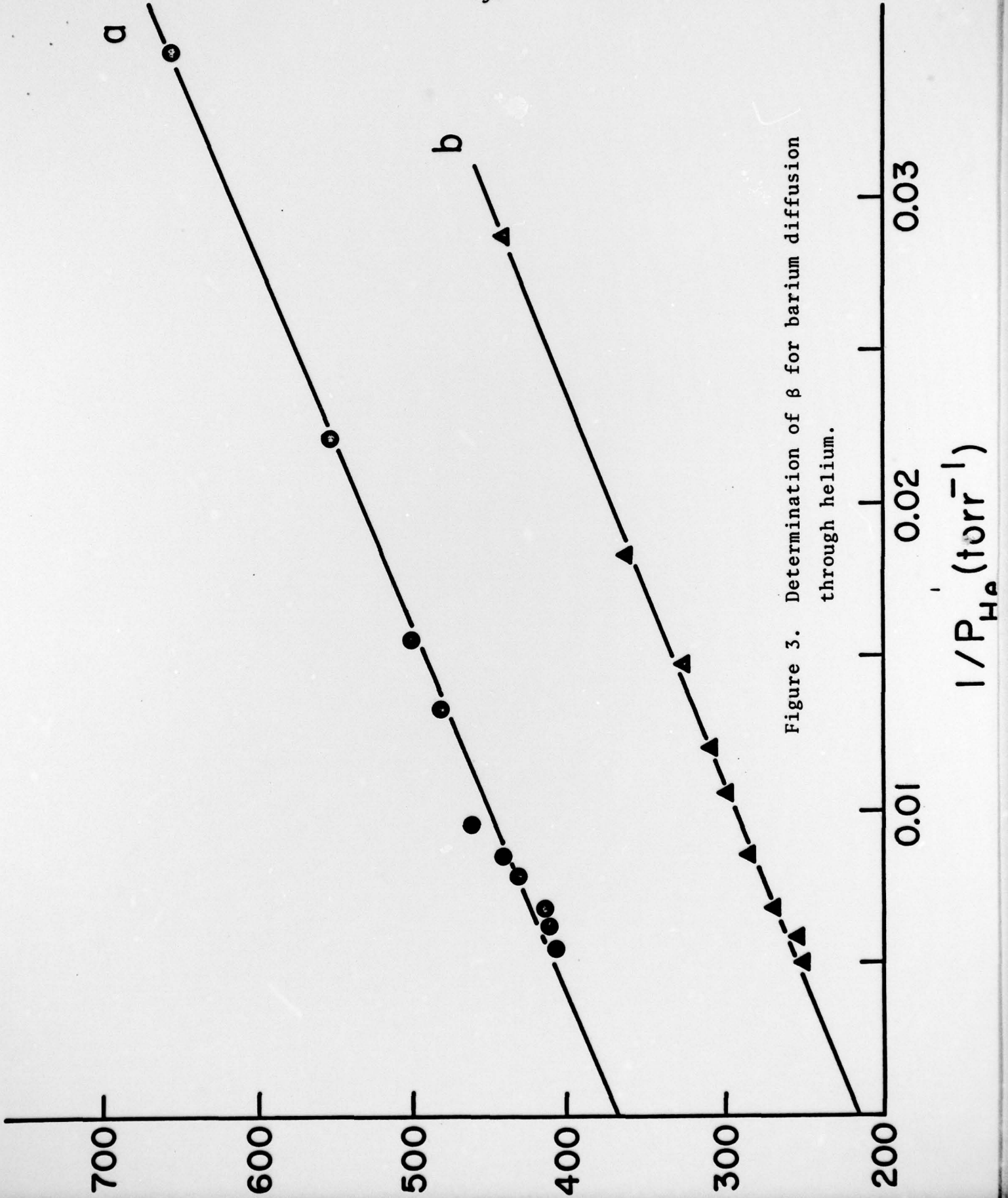
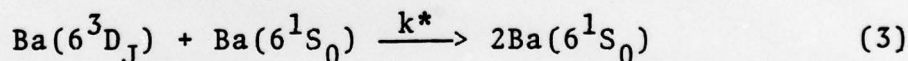


Figure 3. Determination of β for barium diffusion through helium.

where β is the diffusion coefficient characterizing the apparatus. The linearity of Figure 3 illustrates the importance of diffusion as well as the lack of $\text{Ba}(6^3\text{D}_J)$ quenching by He. The interaction of barium atoms with helium can be described within the context of ideal gas behavior as is illustrated by the temperature dependence of the diffusion constant $\beta \propto T^{3/2}$. This kinetic parameter was determined at 773 and 743^oK, respectively, to be $8.12 \pm 0.17 \times 10^3$ and $7.77 \pm 0.23 \times 10^3$. The ratio $\beta(773)/\beta(743) = 1.05$ compares to the theoretical value 1.06.

Inspection of Figure 3 also suggests, from the relatively large intercepts, that another process must be removing $\text{Ba}(6^3\text{D}_J)$, even at (extrapolated) infinite pressure of helium. The dependence of the removal rate was measured in the range $750 < T < 983$. If one hypothesizes that the deactivation of $\text{Ba}(6^3\text{D}_J)$ proceeds via collisions with $\text{Ba}(6^1\text{S}_0)$



then the overall rate coefficient for $\text{Ba}(6^3\text{D}_J)$ removal can be expressed by

$$k_{\text{obs}} = \frac{1}{\tau} + \frac{\beta}{P_{\text{He}}} + k^*[\text{Ba}]$$

where τ is the optical lifetime (presumably very long) of $\text{Ba}(6^3\text{D}_J)$. The vapor pressure of barium (in torr) is, in turn, given by

$$P_{\text{Ba}} = \exp(-22408/T + 18.0) \quad .$$

So long as the activation energy of (3) is small, the observed rate constant may be corrected for diffusion and expressed by

$$k_{\text{obs}}(T) - \beta(T)/P_{\text{He}} = k^*[\text{Ba}] + 1/\tau \quad .$$

Such a plot is presented in Figure 4. The resulting measured rate constant, $7.1 \pm 0.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ is very large, especially for a process such as (3) in which an excited state is being deactivated by a closed-shell atom. The calculated thermal cross-section, $127 \pm 12 \text{ \AA}^2$, is comparable to the corresponding parameter for deactivation of $\text{Na}(^2\text{P}_{3/2})$ by $\text{Na}(^2\text{S}_{1/2})$.¹⁰

Currently, experiments designed to probe the TOP excitation of $\text{Ba}(6^1\text{D}_2)$ are underway. Specific deactivation processes resulting in the production of ground state Ba atoms will be examined with regard to their relative efficiency for production of $\text{Ba}(6^3\text{D}_J)$ following relaxation.

The following publications have resulted from this contract:

"Kinetic Study of the Reaction $\text{Sn} + \text{N}_2\text{O} \rightarrow \text{SnO} + \text{N}_2$ ", J.R. Wiesenfeld and M.J. Yuen, Chem. Phys. Lett., 42, 293 (1976).

"Effect of Diabatic Correlations on the Oxidation of N_2O and CO_2 by O Atoms", J.R. Wiesenfeld, Chem. Phys. Lett., 45, 384 (1977).

"Kinetic Studies of Tin and Germanium Atom Oxidation in the Gas Phase", J.R. Wiesenfeld and M.J. Yuen, J. Phys. Chem., 82, 1225 (1978).

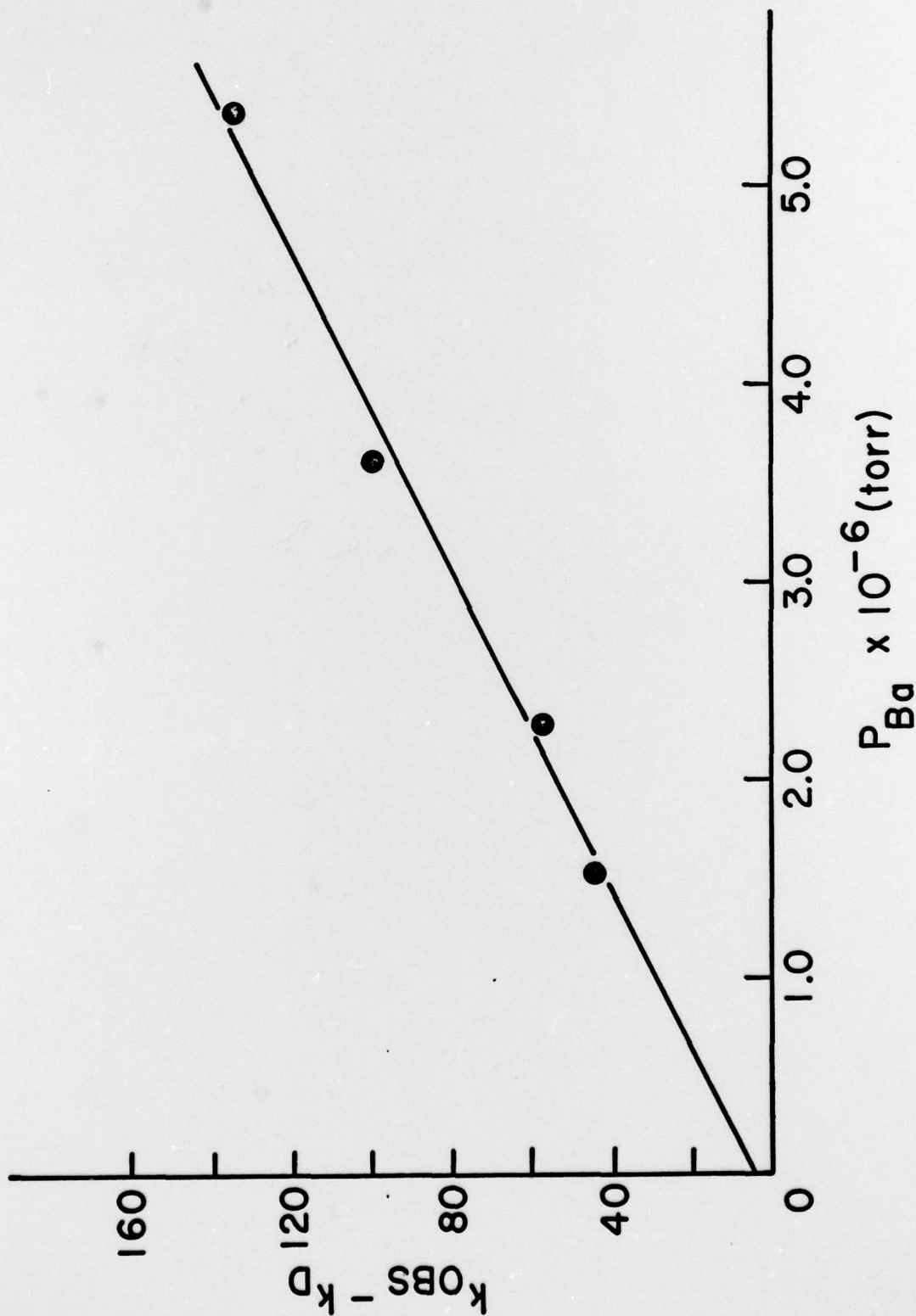


Figure 4. Determination of rate constant for $Ba(^3D_J)$ quenching by $Ba(^1S_0)$.

The following individuals have been supported during their graduate or postdoctoral studies:

Postdoctoral Associates

Sherwin Amimoto

Peter Whitkop

Graduate Research Associate

Maria Josephine Yuen

Table I

Bimolecular Rate Constants for the Reaction of Tin and Germanium
Atoms with Oxidants (295 K)

<u>Oxidant</u>	<u>Ge</u>	<u>Sn</u>
Cl ₂	6.1 ± 0.3 x 10 ⁻¹¹	5.3 ± 0.2 x 10 ⁻¹¹
O ₂	2.5 ± 0.1 x 10 ⁻¹⁰	1.05 ± 0.08 x 10 ⁻¹¹
	1.2 ± 0.1 x 10 ⁻¹⁰	
COS	3.4 ± 0.2 x 10 ⁻¹⁰	1.29 ± 0.01 x 10 ⁻¹¹
N ₂ O	9.9 ± 0.9 x 10 ⁻¹²	6.2 x 10 ⁻¹⁶
NO ₂	4.6 ± 0.4 x 10 ⁻¹⁰	4.0 ± 0.2 x 10 ⁻¹⁰

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