EXPERIMENTAL INVESTIGATION OF THE CHEMISTRY
OF EXCITED STATES OF RARE GASES

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ABSTRACT

Tunable dye laser fluorescence has been combined with the flowing afterglow technique as a method for studying reactive intermediates present in the flowing afterglow. The radiative lifetimes and two-body quenching rate constants (with Ar carrier gas) for the $\text{Ar}^*(3p^5, 4p)$ and $\text{Ar}^*(3p^5, 5p)$ excited states were reported in the preceding year. During this year, we have measured the Ar^* product states from the two-body quenching. More than 50% of the quenching leads directly to intermultiplet transfer to $\text{Ar}(4s)$ states, rather than to intramultiplet cascade down the $\text{Ar}(4p)$ manifold. Using this technique we also have studied the $\text{Xe}(5p^5, 6p')$ and $\text{Xe}(5p^5, 7p)$ excited states and radiative lifetimes, two-body quenching and the product states from quenching have been ascertained. These data should be of value for modeling energy flow pathways of rare gases excited by high energy electrons.

A method has been developed for studying the quenching of the $\text{XeF}(B)$ and $\text{KrF}(B)$ by a variety of reagent molecules. A preliminary account of this work was published (number 5 in the publication list). Much additional experimental work has been done and a definitive study of the electronic quenching of $\text{XeF}(B)$ and $\text{KrF}(B)$ is in progress.

Efforts to interpret (and publish) our comprehensive studies of the reactive quenching of the $\text{Kr}(^3P_2)$ and $\text{Xe}(^3P_2)$ by fluorine and chlorine-containing molecules has continued (see numbers 4, 6 and 8 in the publication listing). Two more manuscripts are in final stages of preparation. Of particular importance has been the development of methods for simulating and interpreting the bound-free emission spectra from the very high vibrational levels of the xenon and krypton fluorides and chlorides. Experiments have been done to measure the branching ratios for (i) ArF^* formation from reactive quenching of $\text{Ar}(^3P_2)$ with fluorine-containing reagents and (ii) KrBr^* and Br^* formation for $\text{Kr}(^3P_2)$ reacting with some bromine-containing molecules.

Scope of Investigation:

The principal objectives of the experimental work for the 1976-77 contract year were the following:

- (i) Characterize the rate constants and products from quenching of argon metastable atoms by fluorine-containing molecules and krypton metastable atoms by bromine and iodine-containing molecules.
- (ii) Develop the resonance sensitization technique for the purpose of examining products from the interaction of $\text{Xe}(^3\text{P}_1)$ and $\text{Kr}(^3\text{P}_1)$ resonance state atoms with halogen-containing molecules.
- (iii) Measure the radiative lifetimes and two-body quenching rate constants (by argon) of the $\text{Xe}(7p)$ states.
- (iv) Develop methods to study the electronic quenching of XeF(B) .
- (v) Attempt to find an efficient donor for formation of ArO^* , KrO^* or XeO^* from reactive quenching of the metastable states of Ar, Kr and Xe.

As can be noted from the abstract, significant progress was made on items (i) - (iv). The photochemistry of XeF_2 and KrF_2 developed for (iv) proved to be so interesting (and productive) that no effort was made to study (v). Summaries of items (i) - (iv) are presented as part of this report. In addition to the experimental work, efforts were made to interpret the rate constants and product distributions from reactive quenching of the metastable ranges atoms in terms of models for electronic quenching reactions.

Cumulative Listing of Published Papers

1. J. E. Velazco, J. H. Kolts and D. W. Setser, "Quenching rate constants for metastable argon, krypton, and xenon atoms by fluorine containing molecules and branching ratios for XeF and KrF formation," J. Chem. Phys., 65, 3468 (1976).
2. D. L. King, J. Rodriguez and D. W. Setser, "Lifetime and two-body rate constants of Ar(4p)** states," Third Summer Colloquium on Electronic Transition Lasers, Aspen, Colorado (Sept. 1976). Published in Electronic Transition Lasers II. Ed. by Wilson, Sachard and Steinfeld.
3. J. E. Velazco, J. H. Kolts and D. W. Setser, "Quenching rate constants for Ar($^3P_{0,2}$), Kr(3P_2) and Xe(3P_2) by halogen containing molecules and branching ratios for XeF and KrF formation," Twelfth International Photochemistry Conference, Washington, D.C. (July, 1976).
4. J. E. Velazco, J. H. Kolts, D. W. Setser and J. A. Coxon, "Excitation of XeF by the reactions of XeF₂ with Ar($^3P_{0,2}$), Xe(3P_2) and Kr(3P_2)," Chem. Phys. Letts., 46, 99 (1977).
5. H. C. Brashears, Jr., D.W. Setser and D. DesMarteau, "Vacuum-ultraviolet Photolysis of XeF₂: XeF(B) Fluorescence and Quenching," Chem. Phys. Lett., 48, 84 (1977).
6. J. E. Velazco, "Quenching Reactions of Xe(3P_2) Reactions," Ph.D. Dissertation, Kansas State University (1977).
7. J. H. Kolts, H. C. Brashears and D. W. Setser, "Redetermination of the N₂(C):N₂(B) Branching Ratio from the Ar($^3P_{0,2}$) Reaction," J. Chem. Phys. 67, 2931 (1977).
8. K. Tamagake and D. W. Setser, "Simulation of the Bound-free KrF Emission Spectra from Reactive Quenching of Kr(5s[3/2]₂ and Kr(5s[3/2]₁) Atoms," J. Chem. Phys. 67, 4370 (1977).

Summary of Personnel:

The personnel supported by this contract were Mr. Enrique Velazco (for ~ 2 months), Mr. Harold Brashears (for 12 months) and Dr. Robert Chang (for ~ 11 months). Mr. Brashears (graduate student) and Dr. Chang (postdoctoral fellow) spent 100% of their time on this contract. Mr. Velazco completed his Ph.D. Dissertation in January 1977 and now is doing postdoctoral work at Colorado State University. The principal investigator spent approximately 25% of this research time working on the ERDA contract. In addition, Mr. Ajit Manocha, a graduate student, was hired for three summer months to investigate the possibility of using a cw dye laser as a means of exciting species in the flowing afterglow.

Research Results:

Detailed quarterly progress reports were prepared during the contract year. Therefore, only brief summaries of the research projects are given here. We also wish to note that the vacuum monochromator purchased with funds provided by this grant was delivered (August) and has been installed. Since we are building our own vacuum system, final operation has been delayed somewhat by construction of components in our shops. This monochromator will provide valuable capability for observation of emission spectra in the vacuum ultraviolet.

- (1) Rare gas halide excimer formation from reactions of $\text{Ar}(^3\text{P}_2)$ and $\text{Kr}(^3\text{P}_2)$ atoms with halogen-containing molecules.

Total quenching rate constants and the branching fractions for formation of ArF^* and KrBr^* were measured for reactions of $\text{Ar}(^3\text{P}_2)$ and $\text{Kr}(^3\text{P}_2)$ with fluorine and bromine-containing molecules. The trends for the efficiency of ArF^* formation with various fluorine donors are very similar to the findings with $\text{Kr}(^3\text{P}_2)$ and $\text{Xe}(^3\text{P}_2)$, with one major addition. Namely, the ArF^* branching ratios for all donors are lower than for the $\text{Kr}(^3\text{P}_2)$ and $\text{Xe}(^3\text{P}_2)$ reactions.

Molecular F_2 is still the best donor, but the branching ratio is ~ 0.5 rather than unity. The $Kr(^3P_2)$ results with the bromide donors are interesting because the $KrBr^*$ has the opportunity to predissociate to Br^* if the $KrBr^*$ has sufficient vibrational energy. The results for ArF^* and $KrBr^*$ formation will be integrated with the results from prior studies of XeF^* , $XeCl^*$, $XeBr^*$ and XeI^* and published. We are hopeful that this work will provide a comprehensive understanding for this type of reaction.

(ii) Laser-Induced Fluorescence Measurements of the Lifetimes and Two-Body Rate Constants of $Ar(4p)$ and $Ar(5p)$ States

The $(np^5, n+1p)$ and $(np^5, n+2p)$ states lying above the metastable $(np^5, -n+1s)$ states of the heavy rare gases may be important to the chemistry of rare gas systems subjected to electrical excitation. We have used pulsed dye laser excitation of the metastable states present in the flowing afterglow apparatus as a technique for studying the excited p states above the metastable levels. The decay rates of the upper states are monitored by the time resolved laser induced fluorescence using a photomultiplier tube to view the fluorescence and a boxcar for signal averaging. By measuring the decay constants over a range of pressure (the flowing afterglow operates from 1 - 15 torr), the radiative lifetimes and two-body rate constants (in Ar) have been measured for the $Xe(6p')$ and $Xe(7p)$ states. It also has been possible to observe fluorescence from the product states formed by the two-body quenching. Thus, we are able to establish branching fractions for intramultiplet or intermultiplet collisional transfer. A very important development during this year was the success of Bob Chang in getting the infrared dyes to lase under N_2 -laser excitation. This permitted the low-lying levels of $Xe(6p)$ and $Ar(4p)$ to be studied. Some of the higher $Ar(4p)$ levels were reinvestigated this year and the products from the two-body quenching were assigned. We have a fairly complete map of the relaxation

processes from two-body collisions between Ar and the Ar(4p) or Ar(4p') states. Manuscripts describing this work are in preparation.

Before achieving success with the infrared dyes using pulsed N_2 laser excitation, we had decided to investigate the use of a cw tunable dye laser in the red region. The Ar-ion pumped cw dye laser at KSU normally is used for Raman studies and the graduate student operator, Mr. Manocha, was hired (for 3 months) to investigate the utility of the cw dye lasers for excitation of species in the flowing afterglow. Unfortunately the tuning range of the cw dye laser (pumped with Ar^+ laser) was far below specifications and was too narrow to be useful for our purpose. Therefore, no data were obtained. Fortunately, the pulsed dye laser approach proved to be satisfactory and we no longer have a need to use the cw laser. At least in our laboratory, the fluorescence from the pulsed laser technique has proven to be more useful than from the cw dye laser.

The combination of pulsed laser induced fluorescence and a flowing afterglow apparatus is a powerful technique for the direct study of the excited atomic levels of the rare gases that are above the metastable states. Based upon recent results in the literature, it also is possible to utilize two photon processes to produce ions and kinetic studies involving ions, electrons and neutrals should be possible in the future. By the addition of additives, it also should be possible to generate reactive intermediates, (by interaction of the metastable atoms with the additive) that can be studied by the pulsed laser induced fluorescence technique.

(iii) Quenching Studies of $XeF(B)$

The vacuum u.v. photolysis of XeF_2 provides a good source of $XeF(B)$ for study of quenching of $XeF(B)$. We have used the steady-state Stern-Volmer technique to obtain values for k_Q .

spectra strongly resembles that from $\text{Xe}(^3\text{P}_2)$ atom reactions.

(v) Models for Reactive Quenching of Rare Gas Metastable Atoms

In general terms, the ionic-covalent curve-crossing mechanism describes the reactive quenching of the metastable states by halogen-containing molecules. There are, however, many details yet to be explained, e.g., the ratios of the two rare gas halide excimer products found for the interhalogen compounds, the initial vibrational and electronic states of the rare gas halide excimers, ~~the~~ the product channels for cases in which excimer formation is not important and the dependence of the total quenching cross section on polarizability of the reagent molecule. In order to answer some of these questions, we have developed a bound-free spectral simulation procedure that permits an assignment of the vibrational distributions of the B and C excimer states and separation of the emission of the B and C states. These techniques currently are being systematically applied to the XeCl^* spectra from quenching of $\text{Xe}(^3\text{P}_2)$ by a series of chlorine-containing molecules. Some reagents, such as Cl_2 , release a large fraction, ~ 0.80 , of the energy as vibrational excitation while others, such as COCl_2 , give little vibrational energy.

In the future we hope to do detailed quantitative modeling of XeI^* and XeBr^* for a comparison with XeCl^* and XeF^* ; qualitative comparisons also will be done with KrCl^* and ArF^* . We hope that the outcome of these basic studies will be an understanding of the dynamics of these chemical reactions. This work should form a cornerstone for understanding interactions of excited states of rare gas atoms with molecular reagents of a large EA. During the next year, 2-3 papers will be written summarizing these studies.

In order to do the spectral simulations good potential energy curves are required. We have used our low pressure data, the ab initio potentials of Dunning and Hay and spectroscopic information from Tellinghuisen is high pressure spectra to synthesize the "best" potentials. Another by-product

of these studies has been a more careful characterization of the collisional transfer (by Ar) between the B and C states of the rare gas halide excimers.