EXPERIMENTAL INVESTIGATION OF THE CHEMISTRY
OF EXCITED STATES OF RARE GASES

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D. W. Setser

Chemistry Department
Kansas State University
Manhattan, KS 66506

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Summary

During this quarterly period, Mr. Harold Brashears (graduate student) and Dr. Bob Chang (postdoctoral fellow) have worked full time. Mr. Brashears has used his new apparatus for studying the quenching of XeF(B) using the steady-state photolysis of XeF_2 as the source of XeF(B) . Harold has been successful in observing the XeF(C) state, as well as the XeF(B) state, by using a very clean CO(A-X) resonance lamp to photolyze the XeF_2 . Some of the preliminary data are discussed in this report. We have found that XeF(C) must be included in the kinetic scheme in order to understand the quenching of XeF^* . Dr. Chang has continued using the pulsed laser induced fluorescence technique to measure radiative lifetimes and two-body quenching rate constants for the Xe(6p) , Kr(5p) and Ne(3p) states. The transient digitizer, has been delivered and is being interfaced to the computer for signal averaging. The manuscript describing the Ar(4p) work has been submitted to J. Chemical Physics. Manuscripts describing the Kr and Xe work are being written. Some of the work with Ne(3p) is mentioned in this report, as well as attempts to use a resonance lamp to give $\text{Kr}(^3\text{P}_1)$ which would be subsequently pumped with the pulsed laser.

The principal investigator has completed the manuscript summarizing the quenching rate constants for $\text{Ar}(^3\text{P}_2)$, $\text{Ar}(^3\text{P}_0)$, $\text{Kr}(^3\text{P}_2)$ and $\text{Xe}(^3\text{P}_2)$. This paper has been added to the cumulative listing of papers; the abstract and the table of rate constants are included in this report. The principal investigator participated in a rare gas excimer symposium organized by M. Golde for the Southeastern Regional ACS Meeting and visited Avco Everett Research Labs during this report period.

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).
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. Letts., 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).
9. P. C. Tellinghuisen, J. Tellinghuisen, J. E. Velazco, D. W. Setser and J. A. Coxon, "Spectroscopic Studies of Noble Gas Halides: Vibrational and Rotational Constants for XeF(B,D,X). J. Chem. Phys., In Press (1978).
10. J. E. Velazco, J. H. Kolts and D. W. Setser, "Rate Constants and Quenching Mechanisms for the Metastable States of Ar, Kr and Xe," J. Chem. Phys., Submitted (1978).
11. R. S. F. Chang and D. W. Setser, "Lifetime and Two-body Deactivation Rate Constants for Ar(4p) States", J. Chem. Phys. submitted (1978).

XeF* QUENCHING STUDIES

In our previous work we have been unable to observe the XeF(C-A) emission because of scattered light from the microwave-discharge powered resonance-lamp used to produce the vacuum U.V. light for photolysis of the XeF₂. This problem finally was solved by using ultra pure He in the discharge lamp. Such a discharge is a good source for the CO(A-X) emission, but has very little scattered light from 250 - 500 nm. The XeF* spectrum obtained from ~0.5 torr of XeF₂ with this lamp is shown in Figure 1. The spectrum from 180 torr of added Kr is shown in Figure 2. In the latter the XeF(C-A) emission is quite strong. One can immediately conclude that less than 10% of XeF(C) is produced directly from the photolysis. However, the addition of Kr results in the formation of XeF(C) from collisional transfer.

We have observed similar results using Ne and Ar as the bath gases. It is quite clear that for these gases the predominant removal process for XeF(B) is formation of XeF(C). Inspection of the high pressure limit of the XeF(C)/XeF(B) ratios from addition of Ne, Ar and Kr suggests that the limiting ratio is ~3 at 300°K. Using Hay and Dunning values for the radiative lifetime of the B and C states and this high pressure ratio of the relative emission intensities leads to the conclusion that the XeF(C) state is ~0.08 eV below the XeF(B) state. Thus, XeF(C) must be included in modeling the kinetics of the XeF laser.

Detailed work is in progress to assign rate constants to the collisional transfer process shown in (1) for a series of gases and to compare these values to our previously measured rate constants for the total collisional removal processes for XeF(B).

Figure 1

Figure 2

STUDIES OF THE RARE GAS(n+1,p) STATES

In previous work we have used the tunable pulsed dye laser technique to generate the Ar(4p), Kr(5p) and Xe(6p) states by pumping the atoms from the metastable (3P_2) levels with a tunable dye laser. The metastable states were produced in an argon flowing afterglow. In an attempt to develop a method that could be used with bath gases other than argon, we have used a microwave powered discharge lamp with a static sensitization cell to produce the lower state, e.g.

The dye laser generates the Kr(5p)^{**} states as with the flowing afterglow. The method should work because the Kr(3P_1) concentration in the sensitization cell is comparable to the Kr(3P_2) concentration in the afterglow apparatus, as judged from the krypton halide emission intensities from the reaction with F₂ or Cl₂. In our first experiments we encountered a severe problem from the scattered light from the discharge lamp. This scattered radiation, which is of the same wavelength as the laser pump and the laser fluorescence, is so strong that we were unable to do the experiments. We have ordered an interference filter that will pass the vacuum U.V. resonance lines but not the red emission from Kr(5p-5s) transitions. We anticipate that this will solve the problem. The great advantage of the static resonance cell is that Xe and Kr can be studied in rare gas buffers and also possibly with added reagents. In particular, Kr(5p) in Kr and Xe(6p) in Ne are of technological interest.

While waiting for delivery of the transient digitizer (now on hand and being interfaced to the computer) and the interference filter mentioned above, Bob Chang started a study of the Ne(3p) in Ne using the flowing afterglow technique. Neon metastable atoms are easily produced in Ne carrier gas,

although the costs of Ne gas are high. By carefully conserving Ne, we believe that a good overview of the lifetimes and two body rate constants for the Ne(3p) states can be obtained for a reasonable cost. Preliminary work shows that the two-body rate constants for Ne(4p) are substantially smaller than those found for Ar(4p) in Ar.