MASTER

**EXPERIMENTAL INVESTIGATION OF THE CHEMISTRY
OF EXCITED STATES OF RARE GASES**

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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(2P_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., 68, 5187 (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. In Press (1978).
11. R. S. F. Chang and D. W. Setser, "Lifetime and Two-body Deactivation Rate Constants for Ar(4p) States", J. Chem. Phys. In Press (1978).
12. H. C. Brashears, Jr. and D. W. Setser, "Transfer and Quenching Rate Constants for XeF(III,1/2) and XeF(II,3/2)." App. Phys. Lett. Submitted (1978).

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 . We have found that XeF(C) must be included in the kinetic scheme in order to understand the quenching of XeF^* . A preprint of the results of Harold's work is attached to this report. The preliminary work that has been done with the $\text{Xe}(^3\text{P}_1)$ and $\text{Kr}(^3\text{P}_1)$ resonance atom reactions also is summarized. Dr. Chang has continued using the pulsed laser induced fluorescence technique to measure radiative lifetimes and two-body quenching rate constants. The study of $\text{Ne}(3\text{p})^{**}$ in Ne Buffer has been completed and tables of these results are included in the report. Some exploratory work searching for new emission spectra and with an emphasis on rare gas oxide spectra has been done by some first year students during June and July. This exploratory work is described in the report.

The principal investigator participated in the Group VI Laser Workshop held at Chicago during this report period. Also work is being done on a review chapter concerned with generation and detection of excited states in flow systems.

EXPLORATORY STUDIES SEARCHING FOR RARE GAS OXIDE EMISSION

It is known that the reactions of metastable rare gas atoms with oxygen atom donors give some rare gas oxide emission spectra (the upper states are the ionic states rather than the better known excimers from the $O(^1S) + Rg$ potential).

However, the branching fractions from common oxygen atom donors (O_3 and N_2O) are very small. We have investigated some transition metal oxides as possible oxygen atom donors. However, OsO_4 , CrO_2Cl_2 and $VOCl_3$ gave no XeO^* or ArO^* excimer emission. In fact these compounds gave no interesting emission spectra of any sort from quenching of Ar^* , Kr^* or Xe^* metastable atoms.

A longer term effort involves the synthesis of XeO_4 and the subsequent study of its photolysis and reactions with the metastable rare gas atoms.

The synthesis involves the following steps.

- (i) Preparation of XeF_6 .
- (ii) The XeF_6 is reacted with excess $HOPOF_2$ to liberate XeO_3 , which is trapped and treated as described in (iii).
- (iii) The XeO_3 is dried in vacuum and $NaOH$ (or $Ba(OH)_2$) is added to give Na_4XeO_6 (or Ba_2XeO_6) crystals and Xe gas. The crystals are filtered and stored.
- (iv) The Na_4XeO_6 (or Ba_2XeO_6) salt will be reacted with H_2SO_4 at 0° to generate XeO_4 gas.

We have produced some Na_4XeO_6 ; however, the solubility appears to be too high and the recovery of the sodium salt is low and we now are investigating the use of the barium salt. If step (iii) is successful, this will permit safe and convenient handling of the XeO_4 precursor. By simply adding acid, we can generate the XeO_4 in a flow system. We are hopeful that the XeO_4 will provide interesting excimer emission either by photochemical dissociation or by reaction with metastable atoms.

RARE GAS EXCIMER FORMATION FROM REACTIONS
OF KRYPTON AND XENON RESONANCE EXCITED ATOMS

Because of their usefulness in high-power, efficient lasers, much recent attention has been given to the formation steps for the excited states of the rare gas halide excimers. Quantitative measurements for the rate constants and branching fractions of the metastable states of the rare gases ($^3P_{2,0}$) with halogen containing molecules have been made. The resonance states, (3P_1) and (1P_1), also are present in the rare gas halide laser medium and their presence may affect the reaction kinetics. However, very little information is currently available regarding the chemistry of the resonance states with halogens. In this work we report the formation of $KrCl^*$, $XeCl^*$, KrF^* and XeF^* from the reactions of the resonance states of Kr and Xe; the emission spectra from these reactions is compared to that from the metastable states.

The experimental apparatus is basically the same as that used for the photolysis of XeF_2 . The rectangular stainless reaction cell was fitted with a LiF window on one side and a quartz observation window on the other side. The resonance lamp was interfaced to the cell through the LiF window, while the rare gas-halide emission was observed through the quartz window at right angles to the path of the resonance lamp. The lamps were standard electrodeless, microwave driven discharge lamps, which had a 6-7 cm extension arm for cooling. The Xe lamp was cooled with liquid O_2 and the Kr lamp with liquid N_2 . The lamp output has been examined for both lamps, and was found in each case to consist almost entirely of the (3P_1) and (1P_1) resonance lines (for Xe, 1470 and 1295 Å, and for Kr 1236 and 1165 Å).

The reaction cell was first filled with the halide donor to be studied and photolyzed with no rare gas present, in order to check for photodissociation processes that might give fluorescence. The cell was then evacuated and filled

with mixtures of the rare gas and donor. Normally the rare gas/halogen donor mixture was flowed through the cell to avoid possible reactions of secondary products. The following chemical equations describe the system for Xe.

Searches were made for the rare gas-halide emission with rare gas/halogen donor ratios from 0.1 to 10 at pressures of 0.05 - 1 torr and with 0.05 torr to 100 torr of added Ar. The XeF* emission was recorded with CF₃OF, NF₃ and F₂ as donor molecules; XeCl* was observed from reaction with PCl₃, Cl₂ and COCl₂. KrCl* was observed with Cl₂ and COCl₂ and KrF* was observed with F₂ and NF₃. For F₂ and Cl₂ the rare gas-halide emission intensity was very strong, comparable to that observed from reactions of metastable rare gas studies, which utilized the same detection system. The relative intensities of the RgX* emissions from the reaction Rg(^3P₁) + RX closely approximated those observed from reactions of the metastable atoms. For X=F, the best donor was F₂, followed by CF₃OF, then NF₃. For X = Cl, Cl₂ gave the strongest emission followed by COCl₂; only very weak excimer emission was obtained from PCl₃. Based upon these observations and upon the magnitude of the quenching rate constants for metastable atoms, we expect the E-V reaction, 3c, to be unimportant. Reaction 3b is important, however, judging from the observation of weak Cl₂* emission from reactions of Xe(^3P₁) and Kr(^3P₁) with Cl₂ and the reduced excimer yields from larger donor molecules. A similar trend holds for the reactions of the metastable rare gas atoms.

The (B-X) emission spectra for XeCl and XeF are shown in Figures 1 and 2. In addition to the B-X spectra shown, each reaction also gave the C-A

emission which extends to the red of the B-X emission. The strong oscillatory pattern is characteristic of XeCl* and XeF* molecules in high vibrational levels. There are two features which distinguish the emission from Xe(³P₁) reaction from that of Xe(³P₂) atom reactions.

- i) In general, the spectra from Xe(³P₁) reactions extend to shorter wavelength than for the Xe(³P₂) atom reaction.
- ii) The spectra from Xe(³P₁) reactions appear to show, as revealed by the pattern of oscillations, a generally higher vibrational excitation at a given pressure.

These differences can be attributed to the 960 cm⁻¹ greater available energy for Xe(³P₁). The Kr(³P₁) is separated from Kr(³P₂) by 945 cm⁻¹, and points i) and ii) also were noted for the excimer emission obtained from Kr(³P₁) atom reactions.

The different J values of the resonance and metastable states could affect the chemistry of the two states. One difference that could be studied is the (B → X)/(C → A) ratio from the two reactions. The pressure dependence of the emission ratio from the reaction of Xe(³P₁) + Cl₂ and Kr(³P₁) + F₂ was examined. The low pressure limits from the metastable and resonance atom reactions do differ. With XeCl I_B/I_C = 2.0 and 1.3 for the resonance and metastable atoms, respectively. The KrF* results follow the same trend.

At high pressures (> 5 torr) the RgX*(B → X) emission shifts to longer wavelength and XeF* begins to show predominantly bound-bound character above 10 torr. The RgX*(C → A) emission shifts to shorter wavelength and declines in intensity relative to (B → X) with increasing pressure. The limiting ratio observed at 200 torr for XeCl* was the same for both Xe(³P₁) and Xe(³P₂) atom reactions. This ratio, I_B/I_C = 6.2, can be used to assign the energy separation between XeCl(B) and XeCl(C). Using the calculated value of τ_C and τ_B leads to the conclusion that XeCl(C) is the lower state by 0.015 eV. It

should be possible to determine the pressure dependence of the $(B \rightarrow X)/(C \rightarrow A)$ ratio for $KrCl^*$ and KrF^* . Such studies will give the energy ordering of the (B) and (C) states. In the case of XeF^* the scattered Xe lines from the lamp makes the acquisition of $XeF(C \rightarrow A)$ spectra very difficult.

The only reagent which gave significant emission from direct photolysis was $COCl_2$. A survey spectrum first was taken of $COCl_2$ with the Xe lamp. This spectrum revealed continua at 246, 258 and 307 nm similar to that described by Okabe, Laufer and Ball. These features have been assigned to Cl_2^* . The $COCl_2$ flow was stopped so that 0.4 torr of $COCl_2$ was left in the cell and 60 torr of Ar was added to the static mixture. The scan was repeated, and the 307 nm continuum, which was very weak compared to the intense feature at 257 nm in the low pressure spectrum, had increased and was ^{now} ~~not~~ comparable in intensity to the 257 nm band. Repeated scans of the same mixture revealed that the 307 nm continuum increased in intensity with time whereas the 258 nm continuum was constant. From this preliminary work it seem unlikely that the 307 nm and 258 nm bands arise from the same process.

From these early results, it is obvious that the resonance states of Xe and Kr do react with chloride and fluoride donors to yield the rare gas halides as products. Further quantitative work is required to obtain rate constants and branching ratios.

Figure Captions

- Figure 1. The $XeCl(B-X)$ emission from $Xe(^3P_1) + Cl_2$, total pressure 0.1 torr with $Xe:Cl_2 = 2.3$; the $XeCl(C-A)$ spectra was observed at longer λ . Spectrum taken with a 0.75 m Jarrell-Ash equipped with EMI 9558Q PMT.
- Figure 2. The $XeF(B-X)$ emission from $Xe(^3P_1) + F_2$, total pressure ~ 0.1 torr with $Xe:F_2 = 3:2$. The $XeF(C-A)$ spectrum was observed at longer λ . Spectrum taken with a 0.75 m Jarrell-Ash equipped with EMI 9558Q PMT.

Figure 1

XeF(B-X)

Figure 2