EXPERIMENTAL INVESTIGATION OF THE CHEMISTRY
OF EXCITED STATES OF RARE GASES

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MASTER

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Summary

Because of the delay of arrival of funds to the university only the student, Mr. Harold Brashears, worked on the contract this quarter. Mr. Brashears continued the analysis of XeF(B) and XeF(C) state quenching from photodissociation of XeF₂. Harold also made important progress on reactive quenching of the resonance states, Xe(³P₁) and Kr(³P₁). The attached summary of Brashears' work constitutes this report.

The principal investigator completed the review chapter on generation and detection of excited states in discharge flow systems. Also, a paper, number 14 on the attached list, was accepted for publication.

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. 69 4357 (1978).
11. R. S. F. Chang and D. W. Setser, "Lifetime and Two-body Deactivation Rate Constants for Ar(4p) States", J. Chem. Phys. 69, 3885 (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. Letts. 33, 821 (1978).
13. D. W. Setser, T. D. Dreiling and J. H. Kolts, "Product Distributions from Quenching of Metastable Rare Gas Atoms," J. Photochem. 9, 91 (1978). Presented at IX International Conference on Photochemistry, Cambridge, England.
14. J. H. Kolts, J. E. Velazco and D. W. Setser, "Reactive Quenching of Xe(6s, 3P_2) Metastable Atoms by Chlorine containing Molecules", J. Chem. Phys. In Press. (1979).

INVESTIGATION OF XeF(III,1/2) and XeF(II,3/2): TRANSFER AND QUENCHING

H. C. Brashears

The investigation of the collisional quenching of the XeF(III,1/2) and XeF(II,3/2) states has been essentially completed. We have utilized the following reaction mechanism in the analysis of the steady-state photodissociative excitation of XeF₂.

For photolysis with both the Xe resonance line and the CO 4th positive emission $\phi_2 < 0.1 \phi_1$, i.e., with no added buffer gas the XeF(C-A) emission is negligibly weak. In all of the steady-state expressions it was assumed that $\phi_2 = 0$. Steady-state expressions for the variation of the emission intensities of XeF(III,1/2) and XeF(II,3/2) with [Q] were derived from this mechanism. In all of the work we used τ_{III} as 15 nsec and τ_{II} as 150 nsec.

If better values become available, appropriate changes should be made for the rate constants. The k^1 and some k^3 values were reported in Applied Physics Letters, 33, 821 (1978). That work has been extended by observation of the emission from both XeF(III,1/2) and XeF(II,3/2) for a greater pressure range and by a more thorough analysis of all the data.

The XeF(III,1/2)/XeF(II,3/2) intensity ratio at various pressures of [Q] is described by;

$$\frac{I_{III}^Q}{I_{II}^Q} = \frac{\tau_{III}^{-1}}{k^1 [Q]} + \frac{(k^2 + k^4) \tau_{III}^{-1}}{k^1 \tau_{II}^{-1}}$$

Thus, the value of k^1 can be obtained directly from the slope of a plot of the intensity ratio versus [Q]. For those quenchers with $k^4 \ll k^2$, the intercept plus the ratio of lifetimes will yield the room temperature value of the equilibrium constant, $K_{eq} = k^1/k^2$. The average value obtained for K_{eq} is 32(±4). From the k^1 and K_{eq} values, k^2 is calculated for each reagent by detailed balance. For those reagents with $k^4 \approx k^2$, the intercept of the XeF(III,1/2)/XeF(II,1/2) plot is used to obtain k^4 . After these 3 rate constants are known, then computer fitting of the plots of I_{III}^O/I_{III}^Q versus [Q] gives k^3 ; I_{III}^O and I_{III}^Q are the emission intensities of XeF(III,1/2) in the absence and presence of quencher, respectively. The combined data provide a complete set of rate constants for the reagents with $k^2 \approx k^4$. For reagents with $k^4 \lesssim 0.2 k^2$, the data from plots of I_{III}^O/I_{III}^Q only can be used to get the sum, $k^3 + k^4 K_{eq}$. If the assumption is made that $k^3 \approx k^4$ then the quenching rate constant is given by dividing the sum by $1 + K_{eq} \approx 33$. Stated another way, unless k^3 is quite large, the experimental determination mainly reflects the magnitude of k^4 .

A summary of results are listed in Table 1. Transfer from XeF(III,1/2) to XeF(II,3/2) is dominant for N_2 , CF_4 , SF_6 and the rare gases (except Xe) k_3 and k_4 can not be separated, except by assumption. Transfer is competitive with quenching for Xe, NF_3 , CHF_3 and CClF_3 , and quenching appears dominant for F_2 . Since NF_3 and F_2 are used in the rare gas halide lasers, they are of special interest. These happen to be the only cases for which k^3 and k^4 appear to greatly differ. The plots of $I_{\text{III}}^0/I_{\text{III}}^Q$ were made using 1849 Å photolysis and correction (small) was made for absorption by NF_3 . As far as we know, the NF_3 results should be reliable. With F_2 the C-A emission is quite weak and this introduces large error limits into the intercept value upon which k^4 is based. Measurement of quenching by HF and CO_2 were also attempted, but the reduction of the XeF(III,1/2) and XeF(II,3/2) emission intensity with added reagent was too rapid for reliable measurement, though we can be certain of the limiting low values of $k^3 + k^4 > 2 \times 10^{-10}$.

The total loss of XeF(III,1/2) plus XeF(II,1/2) was measured for those reagents which do not absorb the CO excitation (160-180 nm). This ratio of total emission intensity in absence and presence of reagents was measured at various pressures. The results in Table 2 show the reduction observed at a reagent pressure of 3 atmospheres.

The final work on XeF_2 will consist of measuring the quenching of XeF(IV,1/2) . This presents the experimental difficulty that the XeF(III,1/2) emission extends into the region of the XeF(IV,1/2) emission. However, the (IV,1/2) band can be isolated by adding buffer gas, Ar, to force vibrational relaxation. The (IV,1/2) state is 0.5 eV above the other states and transfer from the (III,1/2) and (II,3/2) back to (IV,1/2) need not be considered.

The products from quenching can not be ascertained by our experiments.

To date only Ar has been studied, with the result: $k^5 = 9.3 (+1.5) \times 10^{-12}$ molec/cm³ sec.

A further project which has been some progress during this report period has been study of the reactions of the resonance states of the rare gases. Work was concentrated on the $\text{Kr}^* + \text{Cl}_2$ reaction. Though final results have not yet been obtained, we can report several items of interest.

- 1) The $\text{Kr}(^3\text{P}_2) + \text{Cl}_2$ results of J. H. Kolts and D. W. Setser's for flowing afterglow studies are similar to $\text{Kr}(^3\text{P}_1)$ are similar though not identical.
- 2) The KrCl^* emission intensity from the $\text{Kr}(^3\text{P}_1) + \text{Cl}_2$ reaction is linear in Cl_2 pressure for $\text{Kr} \lesssim 10$ millitorr and $\text{Cl}_2 < 50$ millitorr. This set of conditions will permit relative rate constant measurements for chlorine donors.
- 3) The $\text{Kr}(^3\text{P}_1) + \text{HCl}$ reaction gives KrCl^* emission, which is quite vibrationally relaxed, the KrCl emission from $\text{Kr}(^3\text{P}_1)$ appears to be stronger than for $\text{Kr}(^3\text{P}_2)$ reactions. The rate of formation of KrCl^* from $\text{Kr} + \text{HCl}$ is ~ 0.01 of the $\text{Kr} + \text{Cl}_2$ reaction.
- 4) The sensitization technique should be easily extended to $\text{Xe}(^3\text{P}_1)$ and other halogen donors.

Table 1. Rate Constants for XeF(III,1/2) and XeF(II,3/2)

[Q]	k^1 ^a (molecules cm ⁻³ sec ⁻¹)	k^3 ^a (molecules cm ⁻³ sec ⁻¹)	k^4 ^a (molecules cm ⁻³ sec ⁻¹)
CClF ₃	2.1(+0.4) × 10 ⁻¹⁰	9.0(+2.0) × 10 ⁻¹¹	1.2(+0.5) × 10 ⁻¹⁰
CHF ₃	2.0(+0.3) × 10 ⁻¹⁰	9.6(+1.0) × 10 ⁻¹¹	1.2(+0.4) × 10 ⁻¹⁰
NF ₃	5.1(+0.3) × 10 ⁻¹¹	3.5(+2.0) × 10 ⁻¹¹	4.2(+0.8) × 10 ⁻¹²
CF ₄	2.7(+0.2) × 10 ⁻¹¹	9.2(+3.0) × 10 ⁻¹³	3.3(+0.6) × 10 ⁻¹³
F ₂	2.4(+1.0) × 10 ⁻¹¹	1.9(+1.5) × 10 ⁻¹⁰	3.0(+2.0) × 10 ⁻¹²
Xe	4.7(+0.3) × 10 ⁻¹¹	2.5(+0.6) × 10 ⁻¹¹	1.2(+0.3) × 10 ⁻¹¹
N ₂	2.6(+0.1) × 10 ⁻¹²		3.0(+0.5) × 10 ⁻¹² ^b
Kr	2.3(+0.1) × 10 ⁻¹¹		3.5(+0.6) × 10 ⁻¹² ^b
SF ₆	2.8(+1.0) × 10 ⁻¹¹		7.0(+2.0) × 10 ⁻¹² ^b
Ar	5.7(+0.2) × 10 ⁻¹²		2.2(+2.0) × 10 ⁻¹² ^b
He	2.0(+0.1) × 10 ⁻¹²		2.5(+1.0) × 10 ⁻¹² ^b
Ne	7.6(+0.4) × 10 ⁻¹³		6.5(+1.0) × 10 ⁻¹³ ^b

a) Uncertainties are the standard deviations.

b) If one value is given for k^3 and k^4 , it is the sum $k^3 + k^4 K_{eq}$, where $K_{eq} = k^1/k^2 = 32(+4)$.

Table 2. Loss of Total Emission Intensity $\text{XeF(III,1/2)} + \text{XeF(II,3/2)}$

Reagent	Intensity reduction at 3 atmospheres (except for Xe)
Ne	7(+2)%
He	29(+7)%
Ar	31(+7)%
N_2	42(+7)%
Kr	48(+8)%
SF_6	53(+6)%
CF_4	73(+7)%
Xe	85(+5)% - at 250 torr