EXPERIMENTAL INVESTIGATION OF THE CHEMISTRY
OF EXCITED STATES OF RARE GASES

MASTER

Final Report

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SUMMARY

Mr. Harold Brashears (student) and Dr. Hiroyuki Horiguchi (postdoctoral fellow) worked on this contract full time. A new student, Mr. Y. C. Yu, also worked during the summer. Mr. Yu learned techniques and his efforts will not be described. Mr. Brashears' photo-sensitized studies of $\text{Xe}(^3\text{P}_1)$ and $\text{Kr}(^3\text{P}_1)$ reactions with halogen donors have been very productive and will constitute one-half of his Ph.D. thesis. Dr. Horiguchi worked on the laser excitation methods for generating selected states of the rare gas atoms lying above the $np^5, n+1s$ set of levels. Both of these projects are summarized in the report. Also a final tabulation of XeF(B) and XeF(C) transfer and relaxation rate constants are given. These are the result of Mr. Brashears' earlier work.

The principal investigator completed three manuscripts, see attached listing of publications, and also had extensive correspondence with Drs. Tamagke and Kolts (former associates) regarding writing of additional manuscripts describing state-to-state reaction dynamics of $\text{Xe}(^3\text{P}_2)$ atoms with bromine and iodine donors. The principal investigator visited France for two weeks giving invited lectures at the Congress of the French Physical Society and several French universities. This trip has resulted in the beginning of collaborative work with Dr. Sadgehi at Grenoble University. Dr. Sadgehi will spend 6 months at Kansas State University during 1980.

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. 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. Ramagake 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. Lett., 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 $\text{Xe}(6s^3P_2)$ Metastable Atoms by Chlorine Containing Molecules," J. Chem. Phys. 71, 1247² (1979).
15. D. W. Setser, T. D. Dreiling, H. C. Brashears and J. H. Kolts, "The Analogy Between Electronically Excited States and Alkali Metal Atoms," Faraday Disc. Chem. Soc., 67, In Press (1979).
16. R. S. F. Chang and D. W. Setser, "Radiative Lifetimes and Collisional Deactivation Rate Constants of Excited $\text{Ne}(2p^53p)$ Atoms," J. Chem. Phys., In Press (1979).
17. D. W. Setser, H. C. Brashears, Jr., and T. D. Dreiling, "Formation, Relaxation and Quenching of Rare Gas Halide Molecules," Presented to Congress of French Physical Society Toulouse, France, July (1979) and to be published in J. de Phys. (Paris) (1980).
18. H. C. Brashears, Jr., and D. W. Setser, "Reaction of $\text{Xe}(^3P_1)$ and $\text{Kr}(^3P_1)$ Resonance Atoms with Halogen Donor Molecules," J. Phys. Chem. 84, 224 (1980).
19. R. S. F. Chang, H. Horiguchi and D. W. Setser, "Radiative Lifetimes and Collisional Deactivation Rate Constants in Argon for $\text{Kr}(4p^55p)$ and $\text{Kr}(4p^55p')$ States," J. Chem. Phys., In Press (1979).
20. H. Horiguchi, R. S. F. Chang and D. W. Setser, "Radiative Lifetimes, Radiative Branching Ratios and Collisional Deactivation Rate Constants in Ar for $\text{Xe}(5p^5,6p)$ States" to be submitted, J. Chem. Phys. (1980).
21. H. C. Brashears, Jr. "Reactions of $\text{Xe}(^3P_1)$ and $\text{Kr}(^3P_1)$ Atoms with Halogen Donors" Ph.D. Dissertation (1980).

Photosensitized Studies of Reactions of Xe(³P₁) and Kr(³P₁) with Fluorine,
Chlorine, Bromine and Iodine Donors

Mr. Brashears' photosensitization studies, illustrated by the chemical equations below for Xe, have been highly successful.

The Xe(³P₁) state is produced by absorption of a resonance photon from a microwave powered resonance lamp. In addition to being a technique to study the reactions of the ³P₁ state atoms, the method provides a way of studying the relaxation of the XeX(B,C) molecules in the presence of He, Ne, and Ar bath gases from 0.1 - 3000 torr. Thus we can study B - C transfer and vibrational relaxation over a wide range (v' = 0 - 100) of vibrational levels. A communication mainly describing XeCl has been published and is included in this report. Therefore, only results for KrCl and KrF will be summarized. Similar results are in hand for XeBr and XeI but these will not be discussed in this report.

In general there is very little difference in the appearance of the XeX* or KrX* spectra from reactive quenching of the ³P₂ and ³P₁ states for a given halogen donor (see reprint for XeCl and KrCl spectra). Thus, the B vs C distribution and the vibrational energy disposal are very similar for a given halogen donor. From qualitative inspection of emission intensities it also appears that the branching fractions for XeX* formation from a given donor with Xe(³P₁) and Xe(³P₂) also are similar. Although this has not been proven, we are fairly certain of this result. Once these general conclusions have been recognized, the most interesting aspect of the work is B - C electronic state transfer and vibrational relaxation of XeX* molecules in He, Ne and Ar bath gases for a wide range of vibrational levels.

Our objective is to utilize the B - X and C - A emission spectra at various pressures to (i) assign populations to the vibrational levels of B and C and (ii) to model the variation of these populations with pressure in order to deduce rate constants for vibrational relaxation and B - C transfer for several rare gas halides in He, Ne and Ar. The first step is computer simulation of the bound-free spectra. Since our experience with simulation is for the KrF and XeCl spectra, we began by simulating the XeCl emission because the potential curves were more satisfactory for XeCl than for KrF. The simulation for the XeCl(B - X) spectra have been completed from 0.1 to 10 torr of Ar; and these distributions are shown in Figure 1. We also have simulated the C - A spectra over the same pressure region. Although the relaxation mechanism is different, the vibrational distribution for the C state is rather similar to that of the B state from 0.1 to 10 torr. Based upon the work done so far, we expect no difficulty in meeting our goal of assigning state-to-state rate constants for B - C transfer and vibrational relaxation of XeCl and KrF in He, Ne and Ar. A qualitative description of the relaxation mechanisms for XeCl is given in the reprint and this will not be repeated. By noting the vibrational distributions in Figure 1, the C/B ratio plot in the reprint and the discussion in the reprint, a qualitative picture for XeCl relaxation should be evident to the reader.

A description of the variation of the KrF and KrCl B/C ratios vs pressure will end this section. As with XeCl, extensive vibrational relaxation occurs as the pressure is increased from 0.1 to 10 torr of Ar. At about 10 torr the distributions are Boltzmann-like (several thousand degrees). With further increase in pressure, the Boltzmann temperature is reduced. The variation of the B to C steady-state ratios are displayed in Figures 2 and 3. The KrCl results below 2000 torr appear to be straightforward, except for the need to subtract out the Cl_2^* emission, and

VIBRATIONAL RELAXATION OF XeCl(B)

FIGURE 1. XeCl(B) vibrational distributions at various Ar pressure from formation by reactive quenching (solid curves). The dashed curve is the XeCl(B) distribution arising from B-C transfer in the 0.1-4.0 torr pressure range.

the Ar data give a high pressure extrapolated limit of $C/B = 1.7$ (using the calculated τ_C and τ_B and ignoring any $KrCl(B-A)$ in this preliminary analysis. The He and Ne data are not at the high pressure limit even for 3000 torr. At Ar higher pressures than 2000 torr, a new band slightly to longer wavelength of the $KrCl(C-A)$ maximum becomes evident. We suspect that this is emission from $ArKrCl^*$. The plot shown on page 8 has not utilized any of the data for which this longer wavelength band obviously is present. Nevertheless, after full allowance for this band and subtraction of $KrCl(B-A)$ emission the C/B ratios may be somewhat less than 1.7. Thus, the ordering of the $KrCl(B)$ and $KrCl(C)$ states is still not certain.

Complications have been encountered which, so far, have prevented us from assigning a definitive high pressure limit for KrF . The data, as well as the comparison between XeF and $XeCl$, suggest that the KrF C/B ratio will be ~ 4.0 . The complications are as follows. With He and Ne the high pressure limit is not reached at 3000 torr. With $Kr/Ar/F_2$ mixtures, there is an emission band that overlaps the $KrF(C-A)$ band for pressures ≥ 1000 torr. It seems likely that the main source of the new band is $ArKrF^*$ rather than (or in addition to) Ar_2F^* . Work is in progress to attempt to resolve this problem; however, based upon the shape of the curve and the absolute B/C ratio at 1000 torr of Ar or 3000 torr of He and Ne, we expect the $KrF(C)$ state to be below the $KrF(B)$ state.

-8-
KrCL RATIOS

KRF RATIOS

Irradiation of the Ar/Kr/F₂ mixtures at low pressure also gives ArF* emission. The source of the ArF* emission is a puzzle. The interface between the lamp and the cell is a MgF₂ window. Therefore, the Ar(³P₁) resonance line can not enter the cell, even if some Ar resonance emission is generated by the microwave discharge lamp in Kr. Further support that Ar(³P₁) + F₂ is not the source of the ArF* emission is that ArF* is not formed from irradiation of Ar/F₂ mixtures with the Kr resonance lamp. The ArF* emission is relatively weak and conversion of ArF* to Ar₂F* at high pressure will not explain the intensity of the trimer band that overlaps the KrF(C-A) emission. One explanation for ArF and Ar₂F formation is the following set of reactions.

The reaction of excited state halogens to yield rare gas halide molecules has been observed in two other laboratories,^{a,b} so there is some precedent for the above mechanism. Another reasonable possibility is the reaction between ArKr* and F₂ to give ArF*, KrF* and (ArKrF*). The ArKr* molecule should be formed by 2Ar + Kr(³P₁) + ArKr* + Ar. Actually the most likely source of ArKrF* is three-body collisions of Ar and KrF*

a) J. LeCalve, SACLAY Laboratories, Private Communication.

b) D. J. Ehrlich and M. Osgood, Jr., Lincoln Laboratory, presented at the Excimer Lasers Meeting, September 12-14, 1979.

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