FINAL TECHNICAL REPORT
THERMOCHEMISTRY, KINETICS AND SPECTROSCOPY OF KrF* AND Kr₂F*

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SUMMARY

The subcontract from Los Alamos National Laboratory to Kansas State University has been completed and this is the final report. The progress under this contract is described in three sections (i) electronic quenching kinetics of KrF(B,C) and Kr₂F(4²T) molecules, (ii) photochemical excitation of van der Waals molecules containing Xe and Kr, and (iii) cumulative listing of papers published with support of this contract. The subcontract provided funds to pay the annual salary of one postdoctoral fellow.

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I. Quenching Kinetics of KrF(B,C) and Kr₂F(4²T)

The experiments to measure the quenching rates of KrF(B,C) and Kr₂F(4²T) by rare gases and a variety of molecules at 300K were successfully completed. Two papers have been published and a poster paper was presented at the Fall (1992) ACS Meeting. All of the goals identified in the proposal with regard to measuring quenching rate constants of KrF(B,C) and Kr₂F(4²T) have been achieved. Considerable interest still exists in the interpretation of the molecular mechanisms of the formal two-body and three-body quenching processes for KrF(B,C), and several Russian groups are currently studying the KrF(B,C) and XeCl(B,C) systems. The measurements completed at Kansas State University are the most comprehensive set of quenching rate constants for KrF(B,C) now in the literature.

II. Photochemical Excitation of van der Waals Molecules containing Xe and Kr

We assembled and used the equipment required to do pump-probe LIF experiments with van der Waals molecules containing Xe and Kr. The free-jet apparatus with a F₂ compatible pulsed nozzle and associated vacuum pumps is operative. We installed a new Lambda Physik (model 3002) dye laser (purchased with NSF funds) to use with an old excimer laser to provide the probe laser beam to induce the fluorescence. We have used the free-jet apparatus and the probe dye laser to excite Xe₂ van der Waals molecules by a two-photon process from an expansion of a Xe/He mixture; atomic fluorescence from Xe(6p) was observed following the two-photon induced predissociation of the Xe₂^{*} molecules.

This experiment provides a useful way to refine the alignment of the jet, the laser beam and the fluorescence detection optics. A paper describing the two-photon photochemistry of the $\text{Xe}\bullet\text{Xe}$, $\text{Xe}\bullet\text{CO}$ and $\text{Xe}\bullet\text{Ar}$ van der Waals molecules has been published. New work is in progress to characterize the two-photon photochemistry of the $\text{Xe}\bullet\text{F}_2$ van der Waals molecule. The latter can be called a two-photon, laser-assisted reaction of $\text{Xe}\bullet\text{F}_2$ van der Waals molecules giving XeF(B,C) . The XeF(B,C) emission is quite strong and this system will be studied in some detail in the future.

Observation of the laser-induced fluorescence from the $\text{Kr}\bullet\text{F}$ van der Waals molecule was the ultimate goal of this contract. Therefore, a second XeCl excimer laser was added to the experiment to serve as the photolysis laser for the purpose of generating F atoms from a $\text{He/F}_2/\text{Kr}$ mixture as it emerged from the free-jet. The trigger pulse sequences to open the nozzle, to fire the two lasers, and to activate the recording equipment have been successfully tested. The pulse energies from the photolysis and probe lasers systems appear to meet specifications. The sequence of desired molecular events is summarized below.

The photolysis beam (308 nm) is passed through the gas plume very close to the nozzle and the dye laser beam (~ 225 nm) is located 1-2 cm lower, near the bottom of the gas plume. The first attempt at this experiment failed because of poor design of the photolysis laser beam optics with a resulting high intensity of 308 nm scattered light. A second design with longer baffle arms

for the 308 nm laser photolysis beam gave significant improvement, but the signal from the scattered 308 nm laser pulse was still strong. We have purchased another filter to reduce the 308 nm light that reaches the photomultiplier tube, and we soon will be ready for a third try to observe the KrF(B,v') fluorescence. Our design employs the photolysis of F_2 at 308 nm to generate F atoms in the free jet.. An alternative method for generating F atoms could be a pulsed electrical discharge at the nozzle. Such a discharge was used by a French laboratory in a similar experiment to generate XeCl(X) from a Xe/Cl_2 mixture for study of the XeCl(B,C) states by LIF. Both pulsed photolysis and pulsed discharge excitation of Xe and Kr with various other molecules in a free-jet environment has considerable promise for studies of various van der Waals molecules containing Xe and Kr.

We have made a good estimate for the KrF(X) potential using existing spectroscopic data of the KrF(B-X) transition. But bound $\leftarrow$ bound absorption data from $\text{Kr}\bullet\text{F}$ molecules are needed to refine the description of the KrF(X) potential. A paper summarizing the current status of the KrF(X) and KrF(B) potentials has been accepted by J. Chem. Phys. in October, 1993. This work, which is based largely on analysis of chemiluminescence spectra, has been done in collaboration with Dr. Glenn Lo of Southeastern Louisiana University. We have a computer code for simulating the KrF(B,X) absorption and emission spectra, including both the bound-bound and the bound-free transitions as a consequence of this collaboration. The 300K gas phase photoassociation spectrum of Kr/F pairs suggests that high v' levels of KrF(B) can be excited from KrF(X,v''=0) . The subsequent KrF(B-X) bound-free fluorescence will be red shifted from the laser pump wavelength, and the KrF(B-X) fluorescence can be monitored with a photomultiplier tube through a properly selected set of filters. The calculated fluorescence

spectrum from a range of $\text{KrF}(\text{B}, \nu')$ levels is shown in Figure 1. A filter that passes 240-250 nm light, but discriminates against the photolysis beam (308 nm) and the probe beam (~ 225 nm) will be used to observe the LIF signal. We hope to complete this work in 1994 using support from a NSF budget.

III. Listing of Published Papers

1. W. Gadomski, J. Xu, D.W. Setser and T.O. Nelson "Quenching Constants of $\text{KrF}(\text{B}, \text{C})$ by Kr and Xe and the $\text{KrF}(\text{B}, \text{C})$ Equilibrium Constant", Chem. Phys. Lett. 189, 153 (1992).
2. J. Xu, W. Gadomski and D.W. Setser, "Electronic Quenching Rate Constants of $\text{KrF}(\text{B}, \text{C})$ and Kr_2F^+ " J. Chem. Phys. 99, 2591 (1993).
3. M. Richmann, D.W. Setser and T.O. Nelson, "Two-photon Studies of the $\text{Xe}\bullet\text{Xe}$, $\text{Xe}\bullet\text{Ar}$, $\text{Xe}\bullet\text{CO}$ and $\text{Xe}\bullet\text{BrCCl}_3$ van der Waals Molecules", Chem. Phys. Lett. 20, 71 (1993).
4. G. Lo and D.W. Setser "Improved Potentials for $\text{KrF}(\text{B})$ and $\text{KrF}(\text{X})$ " J. Chem. Phys. In Press (1993).
5. T.O. Nelson, D.W. Setser and M. Richmann "Quenching Rate Constants of the $\text{Xe}(6\text{p})$ and $\text{Xe}(6\text{p}')$ States and the Energy-Pooling Ionization Reactions of $\text{Xe}(6\text{s})$ Atoms" J. Phys. Chem. to be submitted (1993).

Figure 1 - Calculated KrF(B, $v' \rightarrow X$) Emission Spectra