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# Excited State Chemistry Of PF, NF AND NCI

#### Air Force Office Of Scientific Research (F49620-92-J-0275)

Annual Report (May, 92 - May, 93)

### A. INTRODUCTION

The objective of our research program is to develop gas phase, chemically driven, energy storage systems that can serve as the media for short wavelength, electronic-transition lasers. We have selected the PF, AsF, and NF molecules for study, because of the success in the chemical generation and utilization of the excited singlet states of  $O_2$  in the oxygen-iodine laser. Our goals are to develop laboratory sources of the singlet states of PF and AsF and to characterize these states. We also wish to develop chemical sources of these molecules and then to utilize this stored energy, perhaps by energy-pooling reactions, to form a suitable upper laser state. Our laboratory already has considerable experience with the chemistry of the NF system. Unfortunately, NF(a) has not been successfully coupled to an acceptor state (other than perhaps I atoms) to build a laser. All of the Group V diatomic halides molecules have the  $\sigma^2 \pi^4 \pi^{*2}$ molecular orbital description for the lowest three electronic states, which are the  $X^{3}\Sigma^{2}$ ,  $a^{1}\Delta$  and  $b^{1}\Sigma^{+}$  states in order of increasing energy. We currently are exploring the PF chemical system and we hope to begin work with the AsF molecule during the next 12 month period. The attractive feature of these two molecules and most other Group V diatomic halide molecules (except for NF and NCl) is the existence of a  $A^{3}\Pi_{0,1,2}$  state that, in principle, can serve as an upper laser state. The energies of these states and sketches of the PF(X,a,b,A) molecular potentials are given in Figure 1. If the energy storage properties of the PF singlet states are satisfactory then coupling to a second chemical system to achieve energy extraction (which usually introduces numerous complications) possibly can be avoided. Even if the PF(a) and AsF(a) molecules can not be directly generated by chemical reactions, high concentrations can



be formed by energy transfer from  $O_2(a)$  to the ground states. Thus, elucidation of the basic reaction chemistry of the AsF and PF systems seems to be very worthwhile. All experiments are done in discharge-flow reactors to isolate individual states, measure rate constants and identify products.

A long term goal of our research is to characterize energy-pooling reactions among the singlet metastable states of  $O_2$ , NF, PF, AsF, etc. The energy of these singlet states is generally too low to be directly useful, and the energy from several molecules must be pooled in some way. For example, three or more molecules of  $O_2(a)$  are required to produce the  $I({}^2P_{1r_2})$  laser state in COIL. If we can develop chemical sources of PF(a) and AsF(a), or even better PF( $b^1\Sigma^+$ ) and AsF( $b^1\Sigma^+$ ), then the energy-pooling processes between the different a and b states offer interesting possibilities. Since these are second-order reactions, absolute concentrations are needed to obtain rate constants.

#### **B.** PROGRESS IN THE STUDY OF THE PF(a,b,A) STATES

Figure 1 gives a summary of the energies of the PF, AsF, NF and O<sub>2</sub> singlet states, plus the location of the A<sup>3</sup>II<sub>0,1,2</sub> states for PF and AsF. The PCl system has energy levels similar to those for PF. The <sup>1</sup>II and <sup>3</sup>II states arise by promoting an electron to the  $\pi^{*}$  antibonding orbital giving the  $\sigma^{1}\pi^{4}\pi^{*3}$  configuration. The presence of these <sup>3</sup>II and <sup>1</sup>II excited states is what makes LIF such a powerful analytical tool for monitoring the concentration of the lower states of AsF and PF. The radiative lifetimes of the <sup>1</sup>II and <sup>3</sup>II states are ~1 and 4  $\mu$ s, respectively, and they have long v" progressions in their transitions to the lower states. We began our work with the PF system in May of 1992. Progress has been rapid because electrical discharges through dilute flows of He/PF<sub>3</sub> and Ar/PF<sub>3</sub> are rich sources of the PF(X,a,b) states, as well as PF<sub>2</sub>( $\tilde{a}^{4}A_{1}$ ). Preliminary experiments suggest that electrical discharges through flows of He/PCl<sub>3</sub> also provide entry into PCl chemistry. We also have started an investigation into ways of <u>chemically</u> generating PF( $a^{1}\Delta$ ). A low power dc discharge ( $\sim 300$  volts) in a dilute mixture of PF<sub>3</sub> in either He or Ar provides an adequate concentration ( $\sim 10^9$  cm<sup>-3</sup>) of PF(b) to systematically study the quenching rate constants for PF(b<sup>1</sup> $\Sigma^+$ ). The relative concentration was monitored by the PF(b-X) transition, which has a radiative lifetime of 9.5 ms. The PF(b) molecules are readily quenched upon contact with the Pyrex glass wall of the reactor, but coating the walls with halocarbon wax provides an inert surface. Quenching constants have been measured for more than 20 reagents. The magnitudes of the rate constants are similar to those for the quenching of NF(b). The rate constants generally are small and the pattern for the magnitudes of the rate constants implies that the mechanism is E-V transfer with concomitant formation of PF(a). This tentative conclusion about the mechanism needs to be directly confirmed by measuring the growth of the PF(a) concentration, as the PF(b) concentration is quenched by added reagent, and this can be done by the LIF technique.

The quenching rate for PF(b) by added  $O_2$  is relatively fast ( $k_{O_2} = 2.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ) and from the weak  $O_2(b-X)$  emission we have identified  $O_2(b)$ as a product from the excitation-transfer reaction.

$$PF(b^{1}\Sigma^{+}) + O_{2}(X^{3}\Sigma^{-}) \longrightarrow O_{2}(b^{1}\Sigma^{+}) + PF(X^{3}\Sigma^{-}); \quad \Delta H^{*} = -240 \text{ cm}^{-1}$$

The reaction seems to be quantitative, but direct observation of PF(X) is desirable. This reaction can provide  $O_2(b)$  in a flow reactor in the absence of  $O_2(a)$ , a rather rare situation.

The general lack of chemical reactivity of PF(b) (and also PCl(b)) is encouraging with respect to energy storage by the PF system. One of our next planned experiments is to study the interaction of PF(b) with NF(b). The question to be answered is the ratio of the physical energy-pooling rate to the chemical reaction rate.

$$NF(b) + PF(b) \longrightarrow PF(A^{3}\Pi) + NF(X^{3}\Sigma^{-})$$
  $\Delta H_{o}^{-} = -2800 \text{ cm}^{-1}$   
 $\longrightarrow \text{chemical reaction}$ 

We have previously developed a source of NF(b) molecules, and we believe that the [NF(b)] will

be high enough to study this important reaction under pseudo first-order conditions, i.e. [NF(a)] > [PF(b)]. This experiment has been delayed because of the lack of  $N_2F_4$  in our laboratory. The valve on our old  $N_2F_4$  tank failed, and the tank and contents could no longer be used. We currently are scheduled to receive another tank of  $N_2F_4$  from the Aerospace Laboratory, when the tank arrives we will do the experiment.

During the course of our study of PF(b), we also have discovered and assigned the spectrum of the metastable  $PF_2(\tilde{a}^4A_2)$  state. The dc discharge in a  $PF_3$ /He flow also generated this metastable radical.

A microwave discharge through a dilute  $PF_3/He$  flow provides an excellent source of  $PF(X^3\Sigma^-)$  molecules that subsequently can be excited by a pulsed laser to selected vibrational levels of the  $PF(A^3\Pi_{0,1,2})$  states. Very detailed, state specific relaxation processes in PF(A) can be studied. We have completed a comprehensive examination of the electronic state quenching of PF(A) by a series of molecular reagents and the vibrational and spin-orbit state relaxation in He and Ar. These data were acquired by observing the change in the pseudo first-order fluorescence decay constants of PF(A) with added reagent. These data (which were reported at the SPIE conference) provide the following points of view about the properties of PF(A) as a candidate for an upper laser state.

- (1) The radiative lifetime (4  $\mu$ s) and the long progression in v" is a positive factor.
- (2) The bond energy  $(\geq 1eV)$  is adequate to prevent dissociation (or predissociation).
- (3) The stability toward electronic quenching by He and Ar is excellent.
- (4) The vibrational and spin-orbit relaxation rates are fast enough to enable the PF(A,v') populations to reach Boltzmann conditions.
- (5) The quenching rate constants for most molecular reagents, other than perfluorinated molecules, tend to be larger than desirable.

Identification of the mechanism responsible for the electronic quenching of PF(A) remains as

a future goal. Since collision-induced predissociation is not possible, collisional transfer to a nearby PF<sup>\*</sup> metastable state or to PF(b) is about the only viable alternative mechanism. Although there are no known states close in energy to PF(A), molecular orbital considerations suggest that a <sup>3</sup> $\Delta$  state could be in this energy region. An in-depth study of the rotational perturbations in the  $\Omega = 0,1,2$  states of PF(A<sup>3</sup>II) for a range of v' levels might provide some evidence about the location of a PF(<sup>3</sup> $\Delta$ ) or some other PF<sup>\*</sup> state.

The relaxation mechanism between the spin-orbit states seems to be complicated with transfer from  $\Omega = 2$  to  $\Omega = 0$  being faster than transfer  $\Omega = 2$  to  $\Omega = 1$ . The relaxation scheme with preliminary assignments to the rate constants in He buffer are summarized below. The separation between the spin-orbit levels of PF( $^{3}\Pi$ ) is ~ 140 cm<sup>-1</sup>



The magnitudes of the rate constants for the up-transition are set by detailed balance. The more facile collisional coupling between  $\Omega = 2$  and 0 rather than 2 and 1 is in accord with a theoretical prediction. However, the magnitudes and pattern for the spin-orbit relaxation rate constants are rather different from the isoelectronic SO(A<sup>3</sup> $\Pi_{0,1,2}$ ) case. The vibrational relaxation from PF(A,v'=1)) is slower than spin-orbit state relaxation, so equilibration within the v'=1 spin-orbit states occurs before the population passes to v'=0. Very little quantitative data are available in the literature for spin-orbit relaxation processes. Comparison of the results for the SO, PF, PC1 and AsF series of isoelectronic molecules should help elucidate the spin-orbit relaxation and electronic quenching mechanisms for these  ${}^{3}\Pi_{0,1,2}$  states.

We began experiments to develop the LIF technique from  $PF(a^{1}\Delta)$  using  $PF(d^{1}\Pi)$  as the upper state in April. We found that the microwave discharge source for PF(X), i.e., a

discharge through a dilute flow of PF<sub>3</sub>/He, also provides an adequate concentration of PF(a<sup>1</sup> $\Delta$ ) for LIF detection. This welcome finding has several experimental implications. We can very easily measure the quenching constants of PF(d<sup>1</sup>II) for comparison with the quenching constants of PF(A<sup>3</sup>II). Furthermore, we can use the intensity of the LIF to monitor the relative concentration of PF(a<sup>1</sup> $\Delta$ ) for a fixed reaction time as a reagent is added to the reactor. The time integrated PF(d→a) fluorescence intensity is proportional to the total [PF(a)] concentration and pseudo first-order decay constants can be measured. Thus, the chemistry of PF(a) will be characterized during the summer months using LIF detection in our flow reactor. The reactions of PF(X) with the same reagent can be examined in the same experiment by using the A ← X transition to monitor the concentration of PF(X). Such a comparison will help understand the differences between the reactivity of the singlet and triplet states of the  $\sigma^2 \pi^4 \pi^{-2}$  configuration. Comparison of the PF(a) rate constants with the published results for NF(a) should be helpful. For energy storage applications, a chemically inert PF(a) molecule is required.

We also have investigated a method for chemically producing the  $PF(a^{1}\Delta)$  states. This effort was aided by Mr. C. Liu, a visitor from China. The plan was to use the H +  $PF_{2}$ reaction, which by analogy to th<sup>r</sup> H +  $NF_{2}$  reaction, could generate PF(a) with high efficiency. Mr. Liu synthesized  $PF_{2}Cl$  and  $PF_{2}Br$  because  $PF_{3}$  does not react with H atoms at temperatures below 250 C. The anticipated reaction scheme is given below for excess H atoms.

$$PF_{2}Br + H \longrightarrow HBr + PF_{2}$$

$$PF_{2} + H \longrightarrow H - PF_{2}^{*} \longrightarrow HF + PF(a^{1}\Delta); \qquad \Delta H_{0}^{'} \approx -8 \text{ kcal mole}^{-1}$$

$$\longrightarrow HF + PF(X^{3}\Sigma^{-}); \qquad \Delta H_{0}^{'} \approx -35 \text{ kcal mole}^{-1}$$

Based upon the observed HF emission intensity and the HF vibrational distribution for short reaction times, the branching fraction for formation of  $PF(a^{1}\Delta)$  must be less than 1.0 and the more excergic triplet channel must have some importantance. Using the LIF technique, both PF(X) and PF(a) have been directly observed in the reactor with PF(a) showing the stronger LIF

inter ity. These results must be combined with the infrared chemiluminescence data and interpreted. Qualitative interpretations suggest that [PF(X)] < [PF(a)]. One of the main experimental difficulties has been gas handing for the PF<sub>2</sub>Cl and PF<sub>2</sub>Br molecules. Although the synthesis is straightforward and the sample can be stored at low temperature, there are unresolved, as yet, problems with regard to metering the desired pure quantities to the flow reactors from room temperature reservoirs containing mixtures of PF<sub>2</sub>Cl or PF<sub>2</sub>Br with He or Ar. Both molecules seem to react with glass storage reservoirs (stainless steel is worse) and further effort is needed to develop quantative gas handling techniques. We seem to understand the H + PF<sub>2</sub> reaction better than the primary reactions of H atoms with PF<sub>2</sub>Cl and PF<sub>2</sub>Br.

The H + PF<sub>2</sub> reaction differs from H + NF<sub>2</sub> reaction because the weaker H-P bond and the stronger P-F bond changes the thermochemistry. Thus, formation of PF(a) from H + PF<sub>2</sub> is only slightly excergic. Since the PF and PF<sub>2</sub> thermochemistry is not well known, predicting specific products for given reactions is difficult. Nevertheless, the H + PF<sub>2</sub> reaction does have an appreciable branching fraction for generating PF(a), and the analogy to the H + NF<sub>2</sub> reaction has some validity.

A second approach to chemically generating PF(a) is to use the reaction of excess F atoms with  $PH_3$ . The first step is known to be direct H abstraction to give  $FrI_2$ . In a preliminary experiment, we have observed strong PF(b-X) emission early in the reaction chain. A possible explanation, which remains to be confirmed, is the following two reactions.

 $F + PH_2 \longrightarrow F-PH_2^* \longrightarrow H_2 + PF(a)$ 2 PF(a)  $\longrightarrow$  PF(b) + PF(X).

Another possibility is that PF(b) was formed together with PF(a).

### C. PRELIMINARY RESULTS FOR PCI(b) AND NCI(b)

Passing PCl<sub>3</sub>/He or NFCl<sub>2</sub>/He flows through the low power dc discharge used to generate

PF(b) also gave useful concentrations for PCl(b) and NCl(b), respectively. The radiative lifetimes are sufficiently long that their kinetics can be studied in a fast flow reactor. Preliminary quenching data indicate that the pattern for the quenching constants will resemble that for PF(b). Since these (b) state molecules are not highly reactive, they are of general interest for energy storage and energy-pooling. Although our dc discharge source does not give high concentrations, it does provide a clean environment that permits lifetime and rate constant measurements. Such experiments will be done during the next year.

## D. PROPOSED WORK WITH THE ASF CHEMICAL SYSTEM

We intend to initiate experiments with the AsF chemical system during the next year. Given the extensive literature on the spectroscopy of AsF from discharge sources, we are confident that our discharge apparatus with a dilute flow of AsF<sub>3</sub> in He or Ar will provide a useful source of AsF states for spectroscopic and kinetic studies. The spectroscopy of AsF is quite highly developed. Our first experiment will be to investigate the stability of AsF(A<sup>3</sup>\Pi<sub>0,1,2</sub>) toward electronic quenching. The AsF(A<sup>3</sup>Π<sub>0,1,2</sub>) states will be produced by pulsed laser excitation from AsF(X). Since D<sub>0</sub>(AsF) > D<sub>0</sub>(PF), but T<sub>e</sub>(AsF(A)) < T<sub>e</sub>(PF(A)); the AsF(A) state may be displaced enough that collisional quenching rates to other (unknown) AsF<sup>\*</sup> states will be slower than for PF(A). If this expectation is found to be true, then we will engage in a comprehensive investigation of the chemistry of the AsF (a and b) states. An intriguing consequence of the AsF energetics shown in Figure 1 is that two AsF(b) molecules have enough energy to create AsF(A) by an energy-pooling reaction.

## **CUMULATIVE LISTING OF PUBLICATIONS**

- K. Du and D.W. Setser, "Quenching Constants of NF(a) by N<sub>2</sub>F<sub>4</sub>, NF<sub>3</sub>, NF<sub>2</sub>, NF(X), SiF<sub>4</sub>, HNCO and NCO at 300K" J. Phys. Chem. In Press (1993).
- 2. S. Wategaonkar and D.W. Setser, "The F + HNCO Reaction System: A Flow Reactor

Source for HCO(X) and NF(X). J. Phys. Chem. In Press (1993).

- J. Xu, D. Raybone and D.W. Setser "Radiative Lifetime and Quenching Constants of PF(A<sup>3</sup>II)" SPIE Conference on Optics, Electro-Optics and Laser Applications to Science and Engineering, Jan (1993).
- 4. Y. Zhao and D.W. Setser "Generation of the  $PF_2(\tilde{a}^4A_2)$  Radical and Assignment of the  $PF_2(\tilde{a}\tilde{-X})$  Emission Spectrum". Chem. Phys. Lett. In Press (1993).
- E. Arunan, C.P. Liu, D.W. Setser, J.V. Gilbert and R.D. Coombe, "Infrared Chemiluminescence Studies of the H + NICl<sub>2</sub> and H + NFCl Reactions", J. Phys. Chem. submitted (1993).
- 6. Y. Zhao and D.W. Setser, "Generation of the  $PF(b^{1}\Sigma^{+})$  Molecule and Characterization of the Lifetime and Quenching Constants" J. Phys. Chem. to be submitted (1993).