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MASTER

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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) . The product states from the sensitized reaction of $\text{Xe}(^3\text{P}_1)$ with Cl_2 and COCl_2 also were studied in this apparatus. The new XeF(B) quenching rate constants obtained by Mr. Brashears will be described in this report. Dr. Chang has continued to utilize the pulsed laser induced fluorescence technique to measure radiative lifetimes and two-body quenching rate constant (with Ar) for the low energy $\text{Xe}(6\text{p})^*$ states. We have encountered serious signal/noise problems for the lowest two states in the $\text{Xe}(6\text{p})$ manifold. We are awaiting the delivery of a transient digitizer, which should improve the signal/noise by a factor of 10, and we then hope to complete the $\text{Xe}(6\text{p})^*$ work. Bob also has measured the radiative branching ratios of all the $\text{Ar}(4\text{p})$, $\text{Kr}(5\text{p})$ and $\text{Xe}(6\text{p})$ states. Combining these branching ratios with the measured radiative lifetimes permits the assignment of the oscillator strengths for the $\text{Ar}(4\text{s}-4\text{p})$, $\text{Kr}(5\text{s}-5\text{p})$ and $\text{Xe}(6\text{s}-6\text{p})$ optical transitions. The manuscript describing the $\text{Ar}(4\text{p})$ work is complete (except for editing) and the abstract and important tables are attached to this report. The complete manuscript is available if anyone wishes to read it. The manuscript describing the $\text{Kr}(5\text{p})^*$ work has been started.

The principal investigator has continued the writing of drafts of manuscripts based mainly upon the Ph.D. dissertation work of Dr. Velazco. The manuscript summarizing the quenching rate constants for $\text{Ar}(^3\text{P}_2)$, $\text{Ar}(^3\text{P}_0)$, $\text{Kr}(^3\text{P}_2)$ and $\text{Xe}(^3\text{P}_2)$ is complete and is being circulated to various colleagues for criticism. We also are writing manuscripts that will describe the vibrational and electronic energy distributions of the XeCl^* states produced from reactive quenching of $\text{Xe}(^3\text{P}_2)$ by chlorine donor molecules. Dr. Tellinghuisen (Vanderbilt University) has

completed the papers describing the analysis of the XeF(B-X) and XeF(D-X) spectroscopy. The analysis was based, in part, upon spectra obtained by Dr. Velazco. That paper has been added to the cumulative listing of papers.

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. 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., Submitted (1978).

XeF(B) QUENCHING STUDIES

The apparatus constructed and tested last quarter has been used to obtain a number of quenching rate constants (see Table 1). Initially the collection of data was delayed by a design error in the pressure measurement (the volume of the lines leading to the pressure transducer was too large relative to the photolysis cell, and this resulted in changing XeF_2 pressure in the cell as high pressures of gases were added to the cell). This problem has been corrected and we believe the present data are reliable. They are, at least, quite reproducible.

For analysis of the data the following set of reactions has been considered.

Where Q is any reagent gas and M is any diluent gas, including the reagent. The quenching by XeF_2 need not be included in the scheme providing the XeF_2 pressure is maintained below ~ 0.5 torr. This formulation does not include any explicit dependence upon vibrational level of XeF(B) . Application of the steady state to this set of reactions for $[\text{M}] = 0$ gives

$$\frac{I_o^B}{I^B} = 1 + \frac{k_Q' [Q]}{\tau_B^{-1}}$$

where τ_B is the radiative lifetime of XeF(B) ,^{1,2,3} and the total emission intensity

of XeF(B) in the presence and absence of Q is I^B and I_0^B , respectively. The term k_Q' is $k_Q^f + k_Q^B$, that is, it includes both quenching and crossover to the C state (if such occurs). In order to obtain the simple linear plot that is observed, it is necessary that $k_Q^f[\text{XeF(C)}][Q]$ be unimportant relative to the photolysis rate for formation of XeF(B) .

For the studies with 100 torr Ar , the Stern Volmer relation must be modified to,

$$\frac{I_0^B}{I^B} = 1 + \frac{k_Q''[Q]}{k_{\text{Ar}}'[\text{Ar}] + \tau_B^{-1}}$$

where the quenching by Ar is included in the term k_{Ar}' ($= k_{\text{Ar}}^B + k_{\text{Ar}}^f$). In addition to giving some quenching, ~100 torr of Ar results in substantial relaxation of the XeF(B) vibrational distribution. Thus k_Q'' pertains to a nearly room temperature Boltzmann distribution of XeF(B) vibrational states. In order for the plot to be linear, it is again necessary that the collisional rate of formation of XeF(B) , $k_Q^f[\text{XeF(C)}][Q] + k_{\text{Ar}}^f[\text{XeF(C)}][\text{Ar}]$ be much less important than the rate of formation via photolysis of XeF_2 .

The data were collected by scanning the XeF(B) emission with a 1/2 meter monochromator. The total XeF(B-X) fluorescence intensity was integrated by planimeter to obtain I and I_0 . Linear Stern-Volmer plots were obtained for all the bath gases. The maximum extent of quenching is indicated in Table 1, no curvature was observed over this range of I_0/I . The slopes of the plots were converted to rate constants using $\tau_B^{-1} = 15 \text{ nsec}^{-1}$ and $k_{\text{Ar}}' = 4.9 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$. For the quenchers with relatively small rate constants, vibrational relaxation and electronic quenching are competitive processes.

It can be seen that, as was stated in the last quarterly report, the quenching rate constants are consistently larger when measured with 100 torr of Ar bath gas. We attribute this to a difference in quenching behavior for the lower vibrational levels of XeF(B) . It also is possible that the measurements

with 100 torr of Ar may involve the XeF(C) state or that there is a three body (Ar + Q + XeF(B)) component to the quenching. We have ordered an interference filter (~ 6 weeks ago) that will eliminate the scattered light from the discharge being observed in the cell. This should permit us to observe the XeF(C-A) emission and to determine whether or not XeF(C) is present in sufficient extent to affect the interpretation of the XeF(B) quenching results in Table 1.

The results in the table agree qualitatively with our former published data and with the Xe and Ar quenching data in references 1 and 3. With the exception of F₂, our new rate constants are somewhat larger than the previous results. In the earlier work the F₂ source was a pre-prepared mixture of F₂ in Ar. Thus, that k_{F_2} should be compared with the new data using 100 torr of Ar. Also the earlier k_Q values were measured with ~ 5 torr of XeF₂ which, as noted in the last report, has the consequence of increasing the previously reported k_Q values. In summary, the rate constants of the table appear to be a big step along the way toward obtaining reliable quenching rate constants for XeF(B). An interesting and surprising point was the CF₄ and SF₆ have small rate constants. Thus, for discharge pumped lasers that employ ionic processes for generating XeF(B), there still may be chemical sources other than F₂ of NF₃^{*} that will perform well as donors of F⁻ but not give rapid quenching.

1. R. Burnham and N. N. Harris, J. Chem. Phys. 66, 2742 (1977).
2. J. J. Ewing, "7th Winter Colloquium on Quantum Electronics", Park City, UT (1977).
3. J. G. Eden and R. W. Wayant, Optics Lett., 2, (1978).

* These are normally used because of the good branching fractions for XeF*, KrF* or ArF* formation via reactions with the metastable atoms.

Quenching of XeF(B) formed by 184.9 nm photolysis of XeF₂.

Quencher	Maximum I ₀ /I	k_Q (100 torr Ar bath) cm ³ /sec	k_Q (no bath gas) cm ³ /sec
F ₂	3.2	2.6×10^{-10}	2.1×10^{-10}
CO ₂	3.5	5.3×10^{-10}	3.7×10^{-10}
Xe	6.0	1.2×10^{-10}	6.1×10^{-11}
NF ₃ (a)	3.1	----	4.3×10^{-11} (a)
CF ₄	4.0	2.8×10^{-11}	1.6×10^{-11}
Kr	5.4	1.9×10^{-11}	1.5×10^{-11}
N ₂	4.4	1.7×10^{-11}	1.4×10^{-11}
SF ₆	4.0	----	1.0×10^{-11}
Ar	2.6	----	4.9×10^{-12}
He	2.8	1.8×10^{-12}	1.1×10^{-12}
Ne	2.0	9.9×10^{-13}	5.8×10^{-13}

a. corrected for absorption by NF₃ at 184.9 Å.

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