EXPERIMENTAL INVESTIGATION OF THE CHEMISTRY
OF EXCITED STATES OF RARE GASES

Second Quarterly Progress Report
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MASTER

D. W. Setser

Chemistry Department
Kansas State University
Manhattan, Kansas 66506

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SUMMARY

During this second quarter, Mr. Harold Brashears and Dr. Hiroyuki Horiguchi worked on this contract, Dr. Horiguchi is continuing the laser induced fluorescence work of the former postdoctoral fellow, Dr. Bob Chang. Dr. Horiguchi has completed the study of the kinetics of the $\text{Kr}(4p^5 5p)$ states in argon buffer gas and a manuscript describing this work is 90% completed. Dr. Horiguchi also has been engaged in development of new techniques. He has interfaced a Biomation transient digitizer to a mini-computer, built a rare gas resonance cell (see following section) which will soon be tested for compatability with the tunable dye laser induced fluorescence technique.

Mr. Brashears has worked full time on the reactions of $\text{Kr}(^3P_1)$ and $\text{Xe}(^3P_1)$ resonance state atoms with halogen containing compounds, i.e.,

We have obtained good spectra for all of the Xenon halides and for KrF and KrCl . The results appear to be similar to reactions of the metastable Xe and Kr atoms. One great advantage of this method of obtaining XeX^* or KrX^* spectra is that non reactive diluent gases can be added to the resonance cell. Thus, one can add He , Ne and Ar to the $\text{Kr}(^3P_1)$ system, or He , Ne , Ar and Kr to the $\text{Xe}(^3P_1)$ system. The pressures can be increased to 3 atmosphere; at higher pressure difficulties are encountered due to rupture of the LiF window interfacing the resonance lamp and fluorescence cell. Since spectra also can be obtained down to pressure of 0.1 torr, the complete range from high to low pressure can be covered. This permits study of the electronic and vibrational relaxation in He , Ne and Ar bath gases. The details of our findings will be fully described in our next report. We note here some results for the B and C states distribution of XeF in Ar . The low pressure data are in Figure 1-A

(shown as I_B/I_C vs pressure) in making Figure 1 we have ignored any contribution from the XeF(B-A) transition. The most important result is that the high pressure ratio of I_C/I_B (~ 3) is the same as reported by Brashears using the photodissociation of XeF₂ as the XeF source. This confirms* that XeF(C) is lower in energy than XeF(B). The second important point is that the I_C/I_B ratio goes through a minimum on the P^{-1} plot.

In order to convert I_C/I_B to a ratio of steady-state concentrations, the I_C/I_B intensity ratio must be multiplied to τ_C/τ_B , which is 10. At zero pressure the steady-state intensity ratio reduces to the ratio of formation processes; however, the low pressure, steady-state concentration ratio is ~ 7 in favor of the C state. As the pressure is increased, molecules in the C state are transferred to the B state and in the flat part of the P^{-1} plot the steady-state ratio is close to 1.5, which is expected for a high temperature distribution. Further increase in pressure results in vibrational relaxation in both B and C. Apparently the magnitude of the electronic state transfer rate constants decline with decreasing v and the high electronic state distribution is frozen during the relaxation to a 300K vibrational Boltzmann distribution. It is only at very high pressure that a true 300K Boltzmann electronic state distribution can be established, and hence, the increase in I_C/I_B at high pressure in the P^{-1} plot.

The third point to note is a correction to our former report on the XeF(B)/XeF(C) ratio vs pressure from the metastable atom reaction (Kolts and Setser, J. Phys. Chem. 82, 1976 (1978)). In that work the C state emission extending to long wavelength was underestimated at low pressure and the background was underestimated at high pressure. The corrected results are shown in Figure 1-A. The corrected results now closely resemble the ArF and KrF curves. It is not possible to reach sufficiently high pressure in the flowing after glow experiments

*Klinger et al, App. Phys. Lett., 33, 39 (1978) also reported this ratio for XeF(C)/XeF(B).

to observe the rise in the I_C/I_B ratio at high pressure. Thus, the after-glow experiments always give a lower limit to the true 300K Boltzmann I_C/I_B ratio.

The principal investigator gave invited talks to a symposium sponsored by the American Chemical Society and to the Discussion of the Faraday Society (paper #8 is the attached list). The manuscript describing the lifetime and two-body deactivation study of the $Ne(2p^5 3p)$ states was completed and submitted during this quarter. Abstracts of both papers are attached.

Cumulative Listing of Published Papers

1. Eight papers were published in 1976-1977; see earlier reports for a listing.
2. 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).
3. 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).
4. 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).
5. 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).
6. 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.
7. 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).
8. 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).
9. R. S. F. Chang and D. W. Setser, "Radiative Lifetimes and Collisional Deactivation Rate Constants of Excited Ne(2p⁵3p) Atom," J. Chem. Phys. Submitted (1979).

THE CHEMICAL SOCIETY FARADAY DIVISION

General Discussion No. 67

"KINETICS OF STATE SELECTED SPECIES"

THE ANALOGY BETWEEN ELECTRONICALLY EXCITED STATE ATOMS AND ALKALI METAL ATOMS

D. W. Setser, T. D. Dreiling, H. C. Brashears, Jr. and J. H. Kolts

Chemistry Department
Kansas State University
Manhattan, Kansas 66506

ABSTRACT:

A comparison is made between the reactions of alkali metal atoms and highly electronically excited atoms. The $np^5n+1s(^3P_2)$, and $(^3P_1)$ states of Ar, Kr and Xe are used as examples of excited states. The reactive quenching data of the rare gases with halogens and polyatomic halides are summarized and compared to similar data for the alkali metal atoms. The entrance channel properties are very similar for both classes of reagents. Also, the vibrational energy disposal to the products is similar in both cases. The main difference is that a relatively small fraction of the total quenching for most polyatomic reagents results in rare gas halide formation. A second difference is that the rare gas atom reactions yield two electronic state products rather than one as for alkali metal atom reactions. The low branching fraction for rare gas halide formation illustrates the extensive coupling between electronically excited state potentials at energies above 8 eV. Simulation of the XeX^* bound-free spectra from the $Xe(^3P_2) + Cl_2$, Br_2 and I_2 reactions strongly suggests that $\langle f_v \rangle$ declines in this series.

RADIATIVE LIFETIMES AND COLLISIONAL DEACTIVATION

RATE CONSTANTS OF EXCITED $\text{Ne}(2p^5 3p)$ STATES

R. S. F. Chang* and D. W. Setser
Department of Chemistry
Kansas State University
Manhattan, Kansas 66506

Abstract:

The radiative decay and collisional deactivation of eight of the ten neutral atomic neon ($2p^5 3p$) levels have been studied. Neon metastable atoms were generated by a hollow-cathode discharge in a flowing afterglow apparatus and were optically pumped by a pulsed tunable dye laser to selected p states; the decay rates then were determined as a function of neon pressure from 1-8 torr by analyzing the decay of spontaneous emission from the excited level. The radiative lifetimes of these eight p states have been measured with an uncertainty of $\pm 3\%$. These lifetimes were combined with the radiative branching ratios from a given p level to assign absolute transition probabilities for the $\text{Ne}(3p-3s)$ transitions. Two-body deactivation of the $\text{Ne}(3p)$ states by collisions with ground state neon atoms have rate constants in the range of $0.5 \times 10^{-11} \text{ cm}^3 \text{ atom}^{-1} \text{ sec}^{-1}$. Intramultiplet relaxation is the dominant quenching mechanism for the p_3, p_4, p_5, p_6, p_7 and p_8 levels. However, for p_9 intermultiplet and intramultiplet relaxation are competitive and for p_2 and p_{10} intermultiplet relaxation is dominant. The relaxation mechanism of these excited $\text{Ne}(3p)$ states is discussed.