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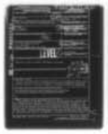
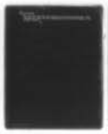
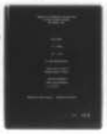
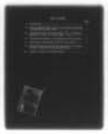
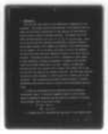
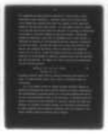
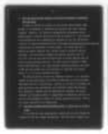
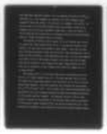
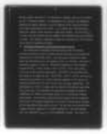
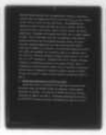
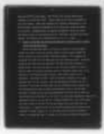
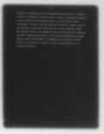
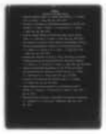
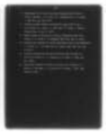

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The chemistry of the metastable states of the rare gases was studied using the flowing afterglow technique. Quantitative measurements were made for the total quenching rate constants and rate constants for product formation. This work led to the discovery of the reactive quenching processes between the metastable atoms and halogen molecules; the products are the rare gas halide excimers in high yield. These systems subsequently have been developed into useful lasers in the ultraviolet region of the spectrum. Collisions of the excited states of

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the rare gas atoms with other atoms also have been characterized. Rate constants are large and exit channels may be far below the energy of the entrance channel.

CHEMISTRY OF ELECTRONICALLY EXCITED STATES OF ATOMS, DIATOMIC MOLECULES, AND DIATOMIC IONS

FINAL REPORT

D. W. SETSER

OCT. 1, 1978

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I. Introduction

The work done under support of this AROD grant is summarized in five categories. The studies involve characterization of the quenching rate constants and the product distributions for the reactions of electronically excited states of atoms and diatomic molecules. The emphasis was on the lowest excited metastable state ($np^5\ n + 1s$, $^3P_2$) of the rare gases. Since all of the work has been completed and published in scientific journals, each category contains only a summary and reference to the published papers in that category. All of the papers are listed by title in the Appendix. The productivity has been quite substantial relative to the dollar value of the grant. This happy situation is partly a consequence of other support by NATO, Department of Energy and Department of Defense, which provided funds which allowed related work to be done. However, the AROD grant provided the long term, reliable base of support from October 1974 to June 30, 1978 that has permitted our program to function. The NATO funds supported collaborative efforts between Dr. Clyne's group (U. of London) and our own laboratory. This collaborative work mainly involved vacuum U.V. emission measurements from products formed by collision with the metastable rare gas atoms.

At least one development from our laboratory has had significant technological impact. We initially suggested (paper #1) that two-body reactive quenching of metastable rare gas atoms with formation of rare gas halide excimers could be good laser systems.

$$M^* + RX \rightarrow MX^* + R \qquad (1)$$

$$MX^* \rightarrow h\nu + M + X$$

X = halogen atom, M* = metastable rare gas atom, R = any chemical group

This suggestion has been verified by observation of laser action on these transitions in many laboratories. Laboratory model rare gas halide lasers now are commercially available and efforts are underway to build large scale commercial rare gas halide laser devices. In a more general sense our studies of the rare gas atom excited states were important for providing an understanding of processes in electrically pumped rare gas laser systems. Although much progress has been made, a great deal of fundamental work is still required to understand the chemistry of rare gas/additive mixtures subjected to deposition of electrical energy. The work done under this contract also provides a data base for rate constants and product states for reactions of the metastable states of Ar, Kr and Xe. A much less topical application, but perhaps just as important, is the development of analytical techniques based upon the metastable rare gas atom reactions. For example, Dr. Clyne's laboratory has demonstrated that the following reaction,

$$\mathrm{Ar}(^3P_{0,2}) + \mathrm{Cl}_2 \rightarrow \mathrm{Ar} + \mathrm{Cl} + \mathrm{Cl}^*(4s) \qquad (2)$$

$$\mathrm{Cl}^*(4s) \rightarrow h\nu + \mathrm{Cl},$$

provides an excellent source lamp for resonance absorption spectroscopy of Cl atoms. By using different atomic lines a wide Cl concentration range can be monitored.

All of our studies utilize the flowing afterglow technique; emission or absorption spectroscopy was used to monitor reactant and product concentrations. The flowing-afterglow technique permits us to selectively generate and monitor the first excited metastable states of the rare gases. An important point with regard to technique was the development of reference reactions with known rate constants for formation of specific products in electronically excited states. By simply comparing relative emission intensities, the rate constants for new product channels (that give emission) can be assigned.

II. Rare Gas Halide Excimer Formation from Reactive Quenching of Metastable Rare Gas Atoms.

In order to realize the potential of the rare gas halide excimer laser systems, it was necessary to understand the processes that lead to excimer formation. Therefore, our laboratory systematically investigated various halogen donors to find the best source for MX* in reaction (1). This involved first measuring the total quenching rate constants for Ar*, Kr* and Xe* with a variety of halogen-containing molecules. All halogen containing molecules have large rate constants near the gas-kinetic collision number. The second step was to measure the product formation rate constants using the reference reaction technique. Only the diatomic halogens and triatomic molecules with O-F, O-Cl, N-F, N-Cl and S-Cl bonds are good sources of excimer emission from the direct two-body quenching reaction. For these cases the excimer is formed with 50-100% efficiency. For larger halogen-containing molecules, the yields of MX* drop very rapidly due to the existence of competing exit channels. Papers 1, 4, 5, 10 and 13 describe this work.

The emission spectra from reactive quenching (reaction 1) is a beautiful example of bound-free spectra and provide an opportunity to study and better understand this type of spectroscopy. Analysis of the spectra is possible and gives electronic state distributions and vibrational energy distributions. This information, together with the quenching rate constants, and product formation rate constants provide a large amount of information which can be used for the development of models for reactive quenching reactions. This is the current objective of our ongoing work.

III. Excitation Transfer Reactions Between Ar($^3P_{0,2}$) and Kr, Xe, O, Cl and H Atoms.

In this work the total quenching rate constant and the rate constant for formation of each exit channel are measured. The work with Kr (paper 3) has been especially important because it is the reference reaction for Ar($^3P_{0,2}$) reactions, e.g., rate constants for emission from other reagents can be assigned by using the Ar($^3P_2$) + Kr reaction as a standard. The Ar($^3P_2$) + Kr reaction also is of intrinsic interest since the potential curves can be estimated and the reaction discussed in some depth. Since all details of the Kr study and its utilization as a reference reaction have been published, (paper 3) further discussion here is not needed.

The reaction of Ar($^3P_2$) with Xe (paper 11) is of the same type as with Kr, except that there are many more (∿25 vs 2) excited Xe* states as exit channels, and the total rate constant is much larger. Since less is known about the Xe*-Ar potential curves than for Kr*-Ar, less interpretation can be given for the Xe reaction. Some interesting point are: (i) all exit channels are within 0.25 eV of the entrance channel, (ii) within the 0.25 eV range there was no favoring of exit channels with small energy defects and (iii) there was no indication of exit channels with particular changes of ΔJ or ΔL being favored.

The studies with Cl, O, and H have been done in collaboration with Dr. Clyne, U. of London (papers 11 and 12). The most important result is that Cl* states with large energy defects, even as much as 2.5 eV for Cl, are the favored exit channels. The total quenching rate constants are quite large, $\sim 50 \times 10^{-11}$ cm^3 molec^{-1} sec^{-1}. The Cl* and O* exit channel distributions were explained by the curve crossing possibilities based upon estimated potentials in the entrance and exit channels. The important feature of the Cl and O potential diagrams is the presence of the strongly bound covalent potentials in the entrance channel between Ar($^3P_2$) and the non-closed shell atom. This facilitates crossings to exit channels well below the entrance channel energy.

The only product from the Ar* + H interaction is H*(n=2), which is 1.5 eV below the Ar* + H entrance channel. The experimental rate constant was assigned by comparing the Lyman-α emission to the Kr* emission in the vacuum ultraviolet for a known concentration of Kr and H. It is unusual that a reaction with a single exit channel should have such a large rate constant. For the Ar($^3P_{0,2}$) + H case, both the entrance and exit channels have potentials that are attractive in nature. This system is sufficiently simple that calculation of the potential curves should be possible and useful.

IV. Vibrational Relaxation of Electronically Excited States.

The interaction of metastable argon and helium atoms with various precursor molecules was used to prepare diatomic molecules in non-equilibrium distributions of vibrational levels. The collisional relaxation of these levels was then monitored vs. the pressure of He or Ar bath gas. This work is described in papers 6, 8 and 15. Vibrational relaxation of electronically excited $CO^+(A^2\Pi_i$, v'=0-6), $CS(A^1\Pi$, v'=0-5), $CO(a^3\Pi$, v'=0-4), and $C_2(A^3\Pi_g$, v'=0-5) by helium atoms was investigated. The $CS(A^1\Pi$, v=0-5) molecule also was studied in an argon bath gas. The $CO^+(A^2\Pi)$, $CS(A^1\Pi)$, $CO(a^3\Pi)$, and $C_2(A^3\Pi_g)$ molecules were produced in a flowing afterglow apparatus by the reaction of metastable helium atom (2^3S) with CO, CS_2, CO_2, and C_2H_2, respectively. The investigation of $CS(A^1\Pi)$ in argon used the reaction of metastable argon atoms ($^3P_{2,0}$) with CS_2. The relaxation was monitored by observing the emission intensities as a function of pressure using a 0.75 m Jarrell-Ash scanning monochromator. The fractional populations were deduced from the integrated band areas of the emission intensities, corrected for monochromator response, and the appropriate Franck-Condon factors. The data have been analyzed using a master equation formulation of cascade deactivation. The model assumed that Δv=1 transitions ($P_{v\rightarrow v-1}$) are the predominant process. The results of these calculations indicate that the probabilities (relative to gas kinetic collision rate) for relaxation of $CO^+(A)$ (in the form $v'(P_{v \rightarrow v-1})$) are: 1(0.005), 2(0.02), 3(0.03), 4(0.03), 5(0.03), and 6(0.03). The probabilities for relaxation of CS(A) by helium and argon are 1(0.01), 2(0.015), 3(0.045), 4(0.04), and 5(0.03), and 1(0.015), 2(0.04), 3(0.05), 4(0.05), and 5(0.05), respectively. Preliminary data indicate that $CS(A^1\Pi)$ also is readily quenched by argon. This is unfortunate since CS(A) is generated in high yields by metastable excitation with CS-containing molecules; however, the facile electronic quenching suggests that any laser system band upon CS(A-X) transition is unlikely to be efficient. The vibrational relaxation of $CO(a^3\Pi)$ and $C_2(A^2\Pi_g)$ was negligible for the pressure range of our apparatus, which sets limits for vibrational relaxation collision probabilities of $<1.6 \times 10^{-6}$ and $<1.1 \times 10^{-3}$, respectively. Although $CO(a^3\Pi)$ did not undergo collisional relaxation, the vibrational populations did change with time. This is a consequence of infrared radiative cascade, since the lifetime for vibrational radiative decay is comparable to electronic radiative lifetime for $CO(a^3\Pi)$. The data were analyzed to obtain infrared radiative lifetimes for $CO(a^3\Pi)$ in paper 8.

V. Spectroscopic Observations of $CS^+(A^2\Pi)$ and $CS(A^1\Pi)$

During the course of our studies on the quenching of metastable argon and helium atoms, new emission systems and extensions of known systems frequently are observed. The reactions of $He(2^3S)$ and $Ar(^3P_{0,2})$ with CS_2 constitutes an example, see paper 6. Wavelength measurements were made for the $CS^+(A^2\Pi-X^2\Sigma^+)$ system and intensity measurements were made for the well known $CS(A^1\Pi-X^1\Sigma^+)$ band system. The $CS^+(A-X)$ data yielded spectroscopic constants for $CS^+(A)$ and $CS^+(X)$. Franck Condon factors were calculated for both band systems. These were combined with intensity measurements for the CS(A-X) bands to deduce the dependence of the electronic transition moment on r-centroid. Recommendations for $\Delta H_f^\circ(CS)$ and $\Delta H_f^\circ(CS^+)$ values were made. This work was done in collaboration with Dr. John Coxon (Dalhousie University, Canada), who formerly was a co-worker with Dr. M. A. A. Clyne.

VI. Radiative Lifetimes and Two-body Deactivation of Excited Ar*(4p), Ar*(5p), Kr*(6p) and Xe*(7p) States.

During the AROD grant period, we have put together a N_2-laser pumped, tunable dye laser; a Princeton Applied Research boxcar signal averager was used to monitor the laser induced fluorescence signals. The equipment was purchased with funds from the AROD grant and from University funds. Personnel operating the laser have been supported from AROD funds and Department of Energy grants. The long term goal is to use the pulsed tunable dye laser to monitor atomic and diatomic molecular states of transient species that can be produced in the flowing afterglow system. From initial results in our laboratory, and others as well, laser fluorescence promises to be a very important tool for this purpose. The main experimental problems have the reduction of the laser scattered light and the background light produced from the discharge source used to produce the metastable atoms in the flowing-afterglow. During the last two years, experiments have been done in which the laser frequency has been tuned to the (n+1s → n+1p and n+2p) absorption lines of the metastable states of Ar, Kr, and Xe. Following absorption of the laser energy, the rate of decay of the Ar*, Kr* and Xe* states can be monitored from the fluorescence. A complete report of the $Ar(4p)^*$ lifetimes and collisional decay constants is given in paper 14. We also have data for Kr*(6p) and Xe*(7p) states in an argon bath gas. We expect to use the laser induced fluorescence technique in combination with the flowing afterglow apparatus for continued studies of the chemistry of excited states of atoms. As mentioned previously, products produced in non-radiating levels can be monitored via laser fluorescence. We hope to use this analytical technique to identify products from reactions of electronic states that do not lead to emission. Based upon existing studies of the metastable rare gas atom states, most quenching reactions do not give high yields of products which subsequently give light emission; thus, the development of techniques for monitoring the "dark" states is very important to provide a complete characterization of the product distribution.

APPENDIX

(Listing of Published Papers)

1. Bound-Free Emission Spectra of Diatomic Xenon Halides, J. E. Velazco and D. W. Setser, J. Chem. Phys. 62, 1990 (1975).
2. Excitation of Nitrogen and Carbon Monoxide Emissions by $He(2^3S)$, He^+ and He_2^+, L. G. Piper, L. Gundel, J. E. Velazco and D. W. Setser, J. Chem. Phys. 62, 3883 (1975).
3. Electronic Energy Transfer from Metastable Argon Atoms to Krypton Atoms, L. G. Piper and D. W. Setser, J. Chem. Phys. 63, 5018 (1975).
4. Rate Constants for Specific Product Channels from Metastable $Ar(^3P_{0,2})$ Reactions and Spectrometer Calibration in the Vacuum Ultraviolet, L. A. Gundel, D. W. Setser, M. A. A. Clyne, J. A. Coxon and W. Nip, J. Chem. Phys. 64, 4390 (1976).
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8. Infrared Radiative Decay Constants for the Vibrational Levels of $CO(a^3\Pi)$, P. J. Marcoux, L. G. Piper and D. W. Setser, J. Chem. Phys. 66, 351 (1977).
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12. Energy Transfer in Collisions of $Ar(^3P_{0,2})$ Metastable Atoms with H Atoms, M. A. A. Clyne, P. B. Monkhouse, Chem. Phys. <u>28</u>, 447 (1978).

13. Quenching Rate Constants for $Ne(^3P_2)$ Metastable Atoms at Room Temperature, J. M. Brom, Jr., J. H. Kolts and D. W. Setser, Chem. Phys. Lett. <u>55</u>, 44 (1978).

14. Radiative Lifetimes and Two-Body Deactivation Rate Constants for $Ar(3p^5,4p^1)$ States, R. S. F. Chang and D. W. Setser, J. Chem. Phys. Dec. (1978).

15. Vibrational Relaxation of $CO^+(A)$, $CS(A)$ and $C_2(A)$ in Helium, P. J. Marcoux, M. van Swaay, L. G. Piper and D. W. Setser, J. Phys. Chem. submitted (1978).