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TECHNICAL PROGRESS REPORT NO. 10

Pittsburgh Atomic Sciences Institute
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I. Summary of Research

The following research projects are identified by title, senior investigator(s) in charge of the work, and the general program to which they belong. This summary only covers advances during the period since our last progress report (dated October 30, 1975).

A. Laser Studies

1. Laser Ion Molecule Reaction Rates (M. A. Biondi)

The spectroscopic measurements on the formation of the $N_2^{+*}(B^2\Sigma_u^+)$ states at thermal energies through the fast, non-resonant charge transfer (NRCT) process

$$He_2^+ + N_2 \rightarrow 2\ He + N_2^{+*}$$

are presently being repeated using the same drift tube - mass spectrometer-optical spectrometer apparatus employed in the earlier studies. The repetition of the earlier experiments became necessary in order to find the origin of the apparent inconsistency between our measurements of the 3914Å and 4278Å intensity ratio and that found in electron excitation experiments. Results obtained so far confirm our earlier results, but the measurements have been temporarily interrupted because of failure of the RCA 31034A photomultiplier used as detector in the experiment. (Beam studies of the NRCT reaction at ~ 10 eV [J. J. Lowenthel and coworkers, University of Missouri-St. Louis] yield a 3914Å/4278Å consistent with our results and at odds with the electron excitation data.) This reaction is central to the Helium-Nitrogen laser

operation. After completion of the studies in N_2 we intend to investigate the analogous process in carbon monoxide.

2. Metal Atom Chemi-Excitation (F. Kaufman, M. A. Biondi)

The line shape experiments on chemi-excited Na using Fabry Perot interferometry were continued only during the first month of this reporting period and then temporarily suspended. It was attempted to study electronic energy transfer from Ar metastables, $^3P_{0,2}$ to Na, but the available pumping speeds were insufficient to permit the Ar^* to reach the heated mixing chamber. Major modification of the apparatus are under consideration, but the success of the energy transfer project (A.3., immediately following) led us to concentrate our efforts in directions which are of immediate interest to a wide variety of laser systems.

3. Energy Transfer Processes of Laser Interest (F. Kaufman)

Vibrational energy transfer from highly excited states produced by chemical reaction are studied in our infrared chemiluminescence apparatus. Cooled, background-limited InSb detectors view an emission region in a rapidly pumped two-inch flow tube at linear velocities near 10^4 cm sec^{-1}. Molecular reactants are added to small flows through movable injectors upstream of the observation region. The flow of atomic reactants such as H-atoms, which are formed far upstream in electrodeless discharges, is square-wave modulated so that the emission is similarly modulated and detected by lock-in amplification. This eliminates interference due to drifting thermal emission signals at wavelengths beyond 3 μm. Moderate spectral resolution is attained with cooled, circularly variable filters of 1 to 2% spectral bandpass. The detection sensitivity of the system is such that excited reaction products of a chemiluminescent reaction such as $H + ClNO \rightarrow HCl^{\ddagger} + NO$ are accurately measured at reactant densities of about 10^{12} cm^{-3} and at total pressures of 1 torr. At those product densities ($\leq 10^{11}$ cm^{-3}) secondary quenching reactions due to reactant or product

molecules become negligibly slow and virtually unrelaxed initial distributions of, say, $HCl^{\ddagger}$ are observed even though the total pressure is 4 to 5 orders of magnitude higher than in the so-called arrested relaxation experiments of Polanyi et al.

To facilitate the interpretation of measured spectra, Dr. Piper has written a computer program which does a least squares fit of computer generated, synthetic band spectra in the fundamental and first overtone region to the experimentally measured emission and extracts the fractional populations of the vibrational levels. This calculation takes account of the best available spectral data such as rotational line frequencies, line strengths, Einstein coefficients, vibration-rotation intereaction constants, as well as the known slit function of the circularly variable filter. As an example of the agreement of our results for the H + ClNO chemiluminescence, the relative populations of HCl^{v} for v = 1 to 7, normalized at v = 5 are given where the first number gives our results at 1 torr and the second the low pressure data by Polanyi et al. v = 1:0.11, -; v = 2: 0.17 -; v = 3: 0.42, 0.82; v = 4: 0.84, 0.96; v = 5: 1.00, 1.00; v = 6: 0.51, 0.48; v = 7: 0.13, 0.10.

The principal purpose of our work is the study of subsequent collisional relaxation processes. This is accomplished by the addition of known quencher concentrations upstream of the molecular reactant and by the measurement of the partially relaxed chemiluminescent emission. At constant quencher concentration the movable injector is retracted along the flow tube and for each position the vibrational population is determined. A simplified master equation is set up for the step-wise relaxation process and in another least squares computer program the experimental vibrational populations are fitted to the solution of the master equation. From this fit we extract the quenching rate constants on the assumption that the $\Delta v = 1$ relaxation steps dominate the relaxation. Results for HCl^{v} relaxation by CO_2 and by ClNO have provided

the following initial results, all at rotational-translational temperatures of about 300°K: For v = 2 to 7, k_{CO_2} = 2.4 x 10^{-12}, 1.9 x 10^{-11}, 3.6 x 10^{-11} 4.7 x 10^{-11}, 4.8 x 10^{-11}, and 2.9 x 10^{-11} cm^3 sec^{-1}. For quenching by ClNO for v = 3 to 7, very large k_{ClNO} are obtained, viz. 8.6 x 10^{-11}, 1.3 x 10^{-10}, 2.6 x 10^{-10}, 3.6 x 10^{-10}, and 4.6 x 10^{-10} cm^3 sec^{-1}. No satisfactory explanation for these extremely large k_0's has yet been found. The results are being repeated and checked now. Experiments have also been performed with added N_2 and H_2 both of which are far less efficient than CO_2 or ClNO. The method is capable of providing a large number of important rate parameters in a short time, once the analysis has been worked out to its present state.

Future experiments will first involve several other quencher molecules and will then proceed to other excited product species such as HF, DF, OH and others.

4. Production of Excited States by Dissociative Electron-Ion Recombination and Dissociative Excitation (M. A. Biondi and E. C. Zipf)

The studies of the capture of electrons by Xe_2^+ ions to form excited Xe^* atoms is being carried out as a function of electron temperature to duplicate conditions encountered in laser plasmas. As the electron temperature T_e is raised from 300K the total recombination coefficient $\alpha(Xe_2^+)$ falls off roughly as $T_e^{-\frac{1}{2}}$ (i.e. close to the theoretical prediction for diatomic ions); however new excited states are observed as new repulsive potential curves are reached with increasing electron energy. This is the first information on control of excited state production by recombination via electron temperature changes. These studies will be extended to Ar_2^+ and Kr_2^+ recombination - processes of importance in Kr^* state formation in the KrF laser.

In recent months we have studied the radiative recombination of NO^+ ions with particular interest in the possibility that this process might give rise to the preferential excitation of the NO γ-bands. Recently this process was

postulated to have a very large recombination coefficient (~ 4×10^{-10} cm^3/sec) but these experiments have shown that this is not the case and have established an upper limit two orders of magnitude smaller. Stimulated by our work on the excitation of the CO fourth positive band and the Cameron System by CO_2^+ dissociative recombination we have begun to study NO_2^+ and N_2O^+ as efficient sources of middle ultraviolet radiation (2000Å - 3000Å).

In a separate apparatus we continue to study the direct and dissociative excitation of metastable, pseudo-metastable and Rydberg species by electron impact. These cross section measurements are prompted in part by an interest in the excited species produced by these processes as well as by a desire to determine the magnitude of the electron energy loss via dissociative channels - an energy sink that cannot be evaluated from conventional inelastic electron energy loss data. Our preliminary results show quite clearly that the dissociative loss rate is comparable to and often larger than the total ionization loss rate.

5. Theoretical Studies - Laser Physics (J. N. Bardsley)

A. Analysis of Reaction Rate Measurements in Drift Tubes

Our Monte Carlo simulations of the motion of atomic ions through a drift tube filled with an atomic buffer gas are almost complete. In our work we have improved the efficiency of the simulation approach so that it can be applied to all ion-atom systems and not just to idealized model problems. The accuracy of our computed mobilities appears to be comparable with that of the best experiments and enables one to test the validity of assumed interaction potentials. The availability of our data has already led to significant improvements in the transport theory of ion motion. The Monte Carlo method is currently the only technique available for the computation of ionic velocity distributions in non-thermal plasmas. Our distributions for O^+ ions have led to a consistent interpretation of the measurements of the reaction rates of O^+ ions with O_2, N_2 and NO from which we have calculated the thermal rates for these processes.

Studies of the effects of inelastic collisions are now in progress.

B. Potential Curves for Excimers

Some of our calculations on alkali dimers have been published, and others are still being analysed. It appears that in Na_2 laser operation between the $X^1\Sigma_g$ and $A^1\Sigma_u$ states will not be hampered by predissociation of the upper state, but that this may be a problem with Rb_2 and Cs_2. Calculations on Mg_2 and Hg_2 have been initiated in collaboration with Dr. Stevens of the National Bureau of Standards in Boulder.

C. Charge Transfer at Low Energies

Our calculations of resonant charge transfer have been accepted for publication and this project has been terminated. Our results on Xe^+ ions in Xe have been confirmed in experiments by Helm at the Australian National University at Canberra.

B. Atmospheric Radiation Backgrounds

6. Particulate Technology (W. L. Fite)

The past six months have seen two balloon-parachute flights carrying a surface ionization monitor for particulates in the stratosphere, following the first flight on October 19, 1975.

In the October flight, the count rate channel was inoperative and problems with the entire flight, such as telemetry loss at times and the balloon's drifting too far downwind, made it less than a fully successful flight. Nonetheless, the detector did seem to work in its dc current channel and signals of the type expected from particulates were seen, suggesting a layer of small particulates at an altitude of about 22 km.

In a second flight, on January 12, 1976, the flight was fully successful and the particle detector seemed to work well. Data were taken in both the count output and current output channels. The package yielded data down to

altitudes of about 9 km, so that the Junge layer of particles at about 12 km could be detected. Analysis of the data suggests the presence of particulates above the Junge layer, with a layer in the neighborhood of 29 km. Postflight calibrations of the instrument were in progress until the opportunity arose to go on a third piggy-back flight in late March.

The March flight was not successful. After a scrub due to the launch site people not putting enough helium in the balloon, the flight finally occurred on April 4. However, telemetry problems prevented turning anything on after ascent. It was a "dead bird", and the flight yielded no data from any of the experiments on board.

The flight package has now been returned to us and calibrations of the apparatus needed to make final interpretation of the second flight are being resumed.

It is anticipated that this original flight package, whose function was simply to see whether particulates could be detected by surface ionization, will not be flown again. A number of improvements are evident, and we want to construct an improved package for future experiments.

Laboratory work on basic processes operative in surface ionization monitoring of particulates continues.

C. Infrared Chemiluminescence and Early Warning

6. Infrared Emission from Atom-Molecule and Fuel-Oxidizer Reactions: Vibrational Relaxation (F. Kaufman)

The experimental apparatus used in these studies is the same as that described in section A. 3 above. The primary difference between the two studies is in the choice of initial reactants which produce the infrared or visible chemiluminescence and in the emphasis on either the initial emission or its subsequent modification by relaxation processes. In the study of fuel-oxidizer reactions the spectral distribution and intensity of the primary emission is of major interest, especially

for exotic fuel-oxidizer combinations. Such emissions for some O-atom plus substituted hydrazine reactions were briefly examined in the last reporting period. Future work in this area must await input from ARPA or other agencies as to the particular fuel-oxidizer pairs which are of present interest.

II. Publications and Technical Presentations

A. Publications

Computation of Speed Distributions for Ions in Drift Tubes, S. L. Lin and J. N. Bardsley, J. Phys. B 8, L461, 1975.

Psuedopotential Calculations for Na_2^+, Na_2 and Na_2^-, J. N. Bardsley, B. R. Junker and D. W. Norcross, Chem. Phys. Lett. 37, 502, 1976.

Theory of Low-Energy Electron-Atom Collisions, IXth International Conference on the Physics of Electronic and Atomic Collisions, Invited Lectures, University of Washington Press, Seattle, 1976, p. 151.

Spectroscopic Studies of the Charge Transfer Reaction $He^+ + Hg \rightarrow He + (Hg^+)^*$ at Thermal Energy", Edward Graham IV, Manfred A. Biondi, and Rainer Johnsen, Phys. Rev. A 13, 965, 1976.

Spatial Separation of Fringe Fields in Quadrupole Mass Filters, W. L. Fite, Rev. Sci. Instr. 47, 326, 1976.

Submicron and Centimicron Particulate Detection Using Surface Ionization, American Laboratory, December 1975, R. L. Myers and W. L. Fite.

The Reaction of CO_2 with Active Nitrogen, W. T. Rawlins and F. Kaufman, J. Chem. Phys. 64, 1128, 1976.

Kinetics of the Reaction $Cl + O_3 \rightarrow ClO + O_2$, M. S. Zahniser, F. Kaufman, J. G. Anderson, Chem. Phys. Lett. 37, 226, 1976.

Measurement of Ortho-Para Ratio in Gas Phase Hydrogen Atom Recombination, L. P. Walkauskas and F. Kaufman, J. Chem. Phys., in press.

On the Excitation of the NO γ-bands in Auroras, T. G. Finn, B. L. Carnahan, and E. C. Zipf, submitted to the Journal of Geophysical Research.

Laboratory Studies on the Excitation of the NO γ-bands by Electron-Ion Recombination, G. L. Unger and E. C. Zipf, submitted to Geophysical Research Letters.

On the Synthesis of N_2O and NO_x Compounds by Lightning, E. C. Zipf, submitted to Geophysical Research Letters.

B. Technical Presentations

Pseudopotential Calculations of Ion-Atom Interactions, American Physical Society, Division of Electron and Atomic Physics, Tucson, December 1975, J. N. Bardsley.

Associative Ionization and Reactions Involving Ions Produced by Associative Ionization, W. L. Fite, invited lecture at the 8th Annual British Conference on Atomic and Molecular Physics, Belfast, March 1976.

Apollo-Soyuz Ultraviolet Absorption Experiment, F. Kaufman, Joint Physical Chemistry and SRCC Seminar, University of Pittsburgh, November 13, 1975.

Stratospheric Ozone Chemistry, F. Kaufman, seminar at State University of New York at Buffalo, February 25, 1976.

Stratospheric Reaction Kinetics in situ and in the Laboratory, invited lecture at Research Conference on Gas Kinetics, F. Kaufman; University of Texas, Austin, Texas, March 15, 1976.

On the Synthesis of N_2O and NO_x Compounds and on the Destruction of Fluorocarbons by Lightning, E. C. Zipf, paper presented at the San Francisco meeting of the American Geophysical Union, December 1975 (EOS., 57, 156, 1976).

C. Other Activities Relating to ARPA

J. N. Bardsley participated in a workshop on ion-molecule reactions at the 28th Gaseous Electronics Conference in Rolla, Missouri on October 23, 1975.

M. A. Biondi took part in the ARPA Visible Laser Workshop at S.R.I. on December 10-11, 1975.

M. A. Biondi participated in the review of some aspects of the ARPA Visible Laser Program held at JILA on February 9, 1976.

M. A. Biondi presented a review of the University of Pittsburgh's ARPA Institute Program at ARPA, Washington, D. C. on March 1, 1976.

F. Kaufman attended meetings of the Atmospheric Chemistry Panel and of the parent committee on Impacts of Stratospheric Change, National Academy of Sciences, in Washington, D. C., on November 1 and 2, November 22 and 23, 1975, January 24 and 25, and February 28 and 29, 1976.

F. Kaufman attended meetings of the NASA Advisory Committee on the Upper Atmosphere Research Program on October 14 and 15 in Washington, D. C., December 16 and 17 at Goddard Space Flight Center, Beltsville, Md., and March 9 and 10 at the Jet Propulsion Lab, Pasadena, California.

F. Kaufman and M. A. Biondi hosted a one-day meeting of a reaction rate panel for the Defense Nuclear Agency at the University of Pittsburgh on March 30, 1976.

F. Kaufman and M. A. Biondi attended the ARPA visible laser review meeting at the Stanford Research Institute, Menlo Park, California on December 10 and 11, 1975.

F. Kaufman attended the annual review of Project Squid of the Office of Naval Research as a consultant at the Naval Research Laboratory, Washington, D. C. on March 1 and 2, 1976.

E. C. Zipf launched a Nike Apache rocket into an auroral substorm above Fort Churchill, Manitoba during March 1976 to study N, NO, and N_2O enhancements in the E region.

In collaboration with the University of Michigan and the National Research Council E. C. Zipf launched a Black Brant IV and an Aerobee 170 rocket into aurora above Fort Churchill to study Joule heating and related electric field Phenomena in magnetospheric storms.

III. Visiting Scientists

None

IV. Degrees Awarded

S. Sinha, Ph. D. October 1975

Senior Investigator	Est. Funds Expended and Committed (Thousands)
J. N. Bardsley	$ 8.6
M. A. Biondi	36.9
W. L. Fite	21.9
F. Kaufman	24.6
E. C. Zipf	6.9
Total Expended and Committed	98.9
Available Funds	140.0
Estimated Funds Remaining as of 3/31/76	41.1

University Accounting of Funds

Expended as of 3/31/76	91.0
Available Funds	140.0
Remaining Funds as of 3/31/76	49.0