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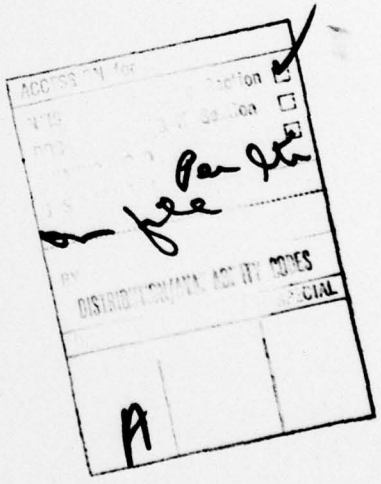

TECHNICAL PROGRESS REPORT NO. 24

Pittsburgh Atomic Sciences Institute

University of Pittsburgh

Pittsburgh, PA 15260

I. Summary of Research

This semi-annual progress report contains descriptions of the researches carried out under contract N000-14-76-C-0098 during the period September 1977 to April 1978, identifying the topics by title, senior investigator(s) in charge of the work, and the general program to which they belong.

A. Laser Physics

1. Energy Transfer Processes of Laser Interest (F. Kaufman and E. C. Zipf)

a. F. Kaufman's Group

Much progress was achieved in various aspects of our studies of V-V relaxation of highly excited $HCl^{\neq}$ by a large variety of quencher molecules in which we use a fast-flow infrared chemiluminescence apparatus for the quantitative measurement of HCl with up to 7 quanta of vibrational excitation ($\sim$ 2.2 eV).

(1) For inefficient collision partners such as SF_6 large concentrations must be added in order to produce easily measureable effects. When the flow speed must also be reduced, the experimental procedure of adding ballast gas (N_2) immediately upstream of the large Roots blower produces less of a pressure increase than the partial throttling of the flow which had been used earlier. Remeasurement of the quenching rate constants resulted in an increase of the k_M^v rate constants for M = SF_6 which we now estimate to be 3.4, 1.3, 0.8, 0.7, 0.7, 0.7, and 0.7 x 10^{-13} cm^3 sec^{-1} for v = 1 to 7.

(2) Careful re-examination of the quenching by CCl_4 has shown that there is a slow reaction of CCl_4 with H-atoms which removes H and thereby decreases the infrared emission intensity and which produces some HCl in v = 1. Generating reactions for HCl^v other than the widely used H + ICl reaction must be used to measure the quenching efficiency of CCl_4.

(3) A series of additional quenching species was examined, viz. CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$; and CH_4, C_2H_6, C_4H_{10}. Results are presented in Table 1.

TABLE 1

Quenching of HCl^v by M

Rate Constants, k_M (10^{-13} cm^3 sec^{-1})

v	M = CF_4	CF_3Cl	CF_2Cl_2	$CFCl_3$	CH_4	C_2H_6	C_4H_{10}
1			3		17	30	
2	1.7		2		25	40	120
3	1.7	2	2	1.5	21	40	130
4	2.2	2	4	4	28	45	160
5	1.6	3.3	10	11	57	75	170
6	2.2	5.4	22	32	103	130	230
7	2.2	7.9	36	82	156	180	270

Where values are not given for low v, inaccuracies due to cummulative errors in the multistep cascading process made the rate constants unreliable. The general behavior of increasing k_M with greater Cl substitution and with increasing v is seen in the chlorofluoromethane series as is the increase of k_M with molecular size of the hydrocarbon.

(4) Two very important quenching molecules, NO and NO_2 presented special problems. NO had to be freed from all impurities of higher N-oxides because these react very rapidly with H. This was accomplished by careful

purification and the following k_{NO}^{v} (10^{-13} cm^3 sec^{-1}) were measured: 2.4, 3.7, 8.5, 45, 150, 220, 190 in the order v = 1 to 7. NO_2 cannot, of course, be investigated using the H + ICl generating reaction. By using the reaction Cl + HI → HCl^v + I, it was possible to produce HCl with v up to 4 and to obtain values of $k_{NO_2}^{v}$ of 15, 18, 19, and 38 for v = 1 to 4 in 10^{-13} cm^3 sec^{-1} units. The only interference to guard against here is the fairly rapid three-body recombination reaction Cl + NO_2 + M → $CLNO_2$ + M, k = 7.1 x 10^{-31} cm^6 sec^{-1}, but by keeping the pressure fairly low (~ 0.5 torr) and adding the NO_2 close to the chemiluminescence detector, this interference was kept sufficiently small.

(5) The initial, unrelaxed vibrational energy distribution of HCl^v as produced by both the Cl + HI and Cl + HBr reactions was measured under our conditions of very small [Cl] and with variable amounts of HI and HBr. The relative rate constants were found to be 0.285, 0.465, 1.00, and 0.506 for v = 1 to 4 in Cℓ + HI, and 1.00, 0.218 for v = 1 and 2 for Cl + HBr. These values differ fro those obtained by Polanyi's group which were reported as 0.22, 0.35, 1.00, and 0.74 for Cl + HI, and 1.0, 0.4 for Cl + HBr. Those values seem to be based on a single experiment for each reaction and may be somewhat unreliable, particularly since their paper reports rather different values for other experiments with only slightly different experimental conditions.

2. <u>Electron-Ion Recombination under Laser Plasma Conditions (M. A. Biondi)</u>

The studies of the variation of the total rate coefficient, $\alpha(Ar_2^+)$, and excited state production with electron temperature have been completed and the results will be published momentarily (Phys. Rev. <u>A17</u>, 868, 1978). Studies are underway in neon to complete the noble gas dimer series (Xe_2^+, Kr_2^+, Ar_2^+ and Ne_2^+) of interest to laser modelling. These are preliminary to our planned

studies of whether or not fast dissociative recombination can occur between electrons and diatomic molecular ions which do not exhibit the usual chemical bonding. Included in this are rare gas-metal atom systems such as ($R Hg^+$), where R represents a rare gas atom such as Kr or Ar.

3. Ion-Molecule Charge Transfer Processes (M. A. Biondi)

The work on nonresonant charge transfer reactions between rare gas atoms and ions has continued. While many nonresonant charge transfer processes for singly charged species are found to occur with very small two-body rate coefficients, on the order of 10^{-15} to 10^{-14} cm^4/sec, it has also been found that such processes can occur in the form of three-body reactions. For example, the reaction:

$$Ne^+ + Ar \rightarrow Ne + Ar^+$$

is observed to proceed with the very small two-body rate coefficient of 6×10^{-15} cm^3/sec, probably due to radiative charge transfer. At higher gas densities, however, a three-body process of the form:

$$Ne^+ + Ar + Ar \rightarrow Ne + Ar^+ + Ar$$

is observed to occur with a rate coefficient of 5×10^{-32} cm^6/sec. This finding implies that at gas densities of several atmospheres, such as used in gas lasers, the effective two-body charge transfer rate would approach 10^{-11} cm^3/sec, about three orders of magnitude higher than the low density limit. From this it seems evident that charge transfer rate coefficients obtained in typical low density experiments may seriously underestimate the importance of such processes in actual laser applications.

As part of a related program, a series of measurements on charge transfer of doubly charged ions has been undertaken which show that the three-body effects tend to be considerably more important in the heavier

rare gases such as krypton and xenon. As those gases are frequently employed in laser applications, we plan to study some reactions of singly charged ions with the heavier rare gases in the near future.

4. Dissociative Excitation of Molecules by Electron Impact (E. C. Zipf)

Work continues on the construction of a second generation Time-of-Flight [TOF] apparatus in which ion and neutral dissociation fragments can be detected simultaneously. The apparatus is designed so that associative ionization processes involving the kinetically and electronically energetic products can also be studied.

Our work on the dissociation of N_2, O_2, methane and related hydrocarbons is progressing. In nitrogen we have assembled an essentially complete set of absolute cross sections for the principal channels involved in the dissociation of the molecule either by electron impact or by EUV photoabsorption, and it has been possible to model in detail Winter's original total dissociation cross section work. We have also been able to determine the product species created by the impact of 100 eV electrons. The abundances of N_2, $N(^2P)$, $N(^2D)$ and $N(^4S)$ atoms are given approximately by the proportion 0.25:0.16:0.17:0.42. Our work in oxygen has also been fruitful. The excitation cross sections for approximately 50 OI transitions at EUV to far infrared wavelengths have been measured and their energy dependence determined. The relative transition probabilities for atomic oxygen inferred from these measurements are in excellent agreement with the recent theoretical calculations of Pradhan and Saraph (1977) and also show that there are major errors in the NBS compilation. This set of cross sections is sufficiently large that the dependence of the cross section on the principal quantum number n could be determined and the quantum defect parameter evaluated for the triplet and quintet manifolds. Using these expressions, we calculated the

total cross section for the dissociative excitation of OI Rydberg atoms produced by e-impact on O_2 and compared these results with our TOF measurements. Encouragingly good agreement was obtained. Curiously, these experiments show that when the quintet manifold is excited ^5P, ^5S, ^5D Rydberg atoms are formed with equal probability, but when the triplet system is excited, only ^3S and ^3D Rydberg atoms appear in equal measure but no ^3P states are observed.

5. Theoretical Calculations (J. N. Bardsley)

a. Three-body recombination of ions

Our Monte-Carlo model for this process has been developed and is being tested for plasmas at relatively low pressures. The model is based on a simulation of mutual neutralization events using the Landau-Zener theory. The presence of the background gas leads to changes in the speed and trajectory of the recombining ions which changes the probability of neutralization.

Our classical technique is being applied further, in particular for the neon-buffered systems recently studied by the AVCO-Everett group.

b. Electron transport in ionized gases

The modelling of laser plasmas is usually based on solutions of the Boltzmann equation using a two-term spherical harmonic expansion, as for example in the computer code developed by Rockwood and Canavan. Also many important cross sections are determined through similar analyses of experiments performed in drift tubes. Doubts have arisen recently concerning the validity of this analysis. In conjunction with members of the Australian National University we have begun an investigation to check this technique by comparison with Monte-Carlo simulations.

c. Related research on electronic and ionic collisions*

In continuation of our efforts to assist the analysis of experimental studies of ion-molecule reaction rates we have completed studies of the mobilities of simple ions, for which accurate information is available concerning the relevant interactions. This work has provided direct checks on the experimental data and should give insight into the interpretation of experiments on more complex ions carried out in Biondi's laboratory and elsewhere.

Studies of vibrational excitation and dissociative attachment in electron-molecule collisions have been resumed. Wadehra has been involved in an analysis of recent experiments on H_2. Bardsley is writing a review article which will include a discussion of these processes in molecules of laser interest, such as F_2.

B. Optics

1. Particulate Technology (W. L. Fite)

Progress during this period has been in two directions. First, in a low pressure "wind tunnel" simulating passage through stratospheric pressures at parachute drop speeds, measurements have been made to determine signal height pulse distributions associated with detection of particulates of a given size. This is proceeding satisfactorily for alkali compound particulates. Measurements will also be made on alkaline earth compounds which more nearly simulate meteoritic materials.

The second activity has been the laboratory experimentation on detection of microscopic ice crystals using surface ionization. This experiment is not working completely but data are being obtained. In general the

*Most of the support for this work is provided by the National Science Foundation and the University of Pittsburgh.

finding is that the pulses produced by the release of ions from doped hot surfaces upon impact by ice crystals are about two orders of magnitude slower than for release of ions when particles containing surface-ionizable constituents impact upon un-doped surfaces.

This work is being done with a view toward having a two-surface particulate detector that is flyable on either a parachute or a rocket which can discriminate between ice particulates and meteoritic dusts. If the particulates in the stratosphere and upper atmosphere that are detected by light scattering means are primarily meteoritic dust the consequences for high power laser transmission would be expected to be quite different.

II. Publications and Technical Presentations

A. Publications

Thermal energy charge transfer rates for Ne^+, Ne_2^+, Ar^+ and Ar_2^+ ions with Kr and Xe atoms, Rainer Johnsen, Jeffrey Macdonald and Manfred A. Biondi, J. Chem. Phys. 68, 2991, 1978.

II. Publications and Technical Presentations - Continued

A. Publications

Calculations of ion-ion recombination rates at high pressures, J. M. Wadehra and J. N. Bardsley, Appl. Phys. Lett. 32, 76, 1978.

Velocity and energy relaxation of ions in drift tubes, S. L. Lin, L. A. Viehland, E. A. Mason, J. H. Whealton and J. N. Bardsley, J. Phys. B 10, 3567, 1977.

The null-event method in computer simulation, S. L. Lin and J. N. Bardsley, submitted to Computer Physics Communications.

Dissociative recombination in krypton:Dependence of the total rate coefficient and excited-state production on electron temperature, Yueh-Jaw Shiu and Manfred A. Biondi, Phys. Rev. A 16, 1817, 1977.

Dissociative recombination in argon:Dependence of the total rate coefficient and excited-state production on electron temperature, Yueh-Jaw Shiu and Manfred A. Biondi, Phys. Rev. A 17, 868, 1978.

Translational spectroscopy of metastable fragments produced by dissociative excitation of chlorine, W. C. Wells and E. C. Zipf, J. Chem. Phys. 66, 5828, 1977.

On the excitation of Lyman β and Balmer α radiation by electron impact dissociation of methane, R. W. McLaughlin and E. C. Zipf, Chem. Phys. Lett., in press, 1978.

B. Technical Presentations

Dissociative recombination of electrons with molecular ions, a seminar by J. N. Bardsley presented at Yale University, the University of Western Ontario, Westinghouse Research Laboratory and The University of Texas at Austin, February and March 1978.

Complex scaling:an introduction, invited talk by J. N. Bardsley at the Sanibel Symposium on Quantum Mechanics, March 1978.

Theory of three body ionic recombination for different ionic and neutral particle masses, contributed by J. M. Wadehra and J. N. Bardsley at the Gaseous Electronics Conference, October 1977.

F. Kaufman presented seminars on H-atom recombination and on NO_2 fluorescence at the California Institute of Technology on December 5 and at UCLA on December 7, and a colloquium on the kinetics of stratospheric reactions at the University of Southern California on December 6.

F. Kaufman presented an invited paper on stratospheric Cl-and OH-reactions at the 13th Int'l. Conference on Photochemistry at Clearwater Beach, Florida on 6 January 1978.

M. A. Biondi presented a paper at the Gaseous Electronics Conference, Palo Alto, California, October 1977; the G. J. Schulz Memorial Lecture, Yale University, New Haven, Connecticut, October 1977.

M. A. Biondi presented a colloquium at New York University, N.Y., N.Y. in February 1978, and a seminar at NOAA-Dept. of Commerce, Boulder, Colorado, March 1978.

E. C. Zipf, "$N(^2P)$ and $N(^2D)$ Atoms: Their Production by e-Impact Dissociation of N_2 and Destruction by Associative Ionization, E. O. S. 59, 336, 1978.

III. Degrees Awarded

Jeffrey Halle, November 1977, Ph.D.

Yueh-Jaw Shiu, March 1978, Ph.D.

Senior Investigator	Estimated Funds Expended and Committed (Thousands)
J. N. Bardsley	58.9
M. A. Biondi	135.1
W. L. Fite	46.0
F. Kaufman	117.0
E. C. Zipf	38.0
Total Expended and Committed	395.0
Available Funds	485.0
Estimated Funds Remaining as of 3/31/78	90.0

University Accounting of Funds	
Expended as of 3/31/78	393.9
Available Funds	485.0
Remaining Funds as of 3/31/78	91.1