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RESEARCH ON MOLECULAR LASERS

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Cornell University  
Ithaca, N.Y. 14853

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13. ABSTRACT Research concerning molecular and chemical lasers was conducted in the following areas: 1. Deactivation of molecular vibrational energy by atoms. 2. Metal atom laser systems. 3. V-R energy transfer in HF. 4. Low temperature vibrational energy transfer in H <sub>2</sub> -HCl and H <sub>2</sub> -D <sub>2</sub> systems. 5. Vibrational deactivation of CO by O and H and Br <sub>2</sub> and of CO <sub>2</sub> by Br <sub>2</sub> . 6. Laser ignited chemical laser systems containing boron.			

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Technical Report Summary

↙ This report describes research conducted at Cornell University on molecular and chemical laser systems. The objective of this work has been to provide precise, quantitative information concerning: the rates with which vibrational and rotational molecular energy in important laser molecules is transferred to other molecules, redistributed among the degrees of freedom of the same molecule or relaxed by collisions with molecules or atoms; the temperature dependence of these rates; conditions for rapidly generating high densities of electronically and/or vibrationally excited boron containing diatomics and triatomics; the rates of reaction between various boron hydrides and oxidizers to provide kinetic information relevant to new laser systems; homogeneous chemical reaction initiation by means of laser induced gas heating.

The methodology employed consisted of laboratory experiments utilizing: laser induced fluorescence measurements; quantitative EPR determination of atom concentrations; optical double resonance experiments; laser heating with high energy ~~CO<sub>2</sub>~~ laser pulses coupled with chemiluminescence spectroscopy. *carbon dioxide*

Specific technical results obtained were: *as follows: --*

1. *(a)* A new method for obtaining temperature dependent rates for atom deactivation of molecular vibration was devised, and
2. *(b)* Preliminary experimental results for laser ignited homogeneous chemical reactions of interest to high frequency lasers are described.

Professor G. J. Wolga

Deactivation of Molecular Vibrational Energy by Atoms

The primary emphasis of our work during the present reporting period was in the development of an experimental method for studying the deactivation of molecular vibrational energy by atoms at low temperatures. The method we used previously would not work well at low temperatures because the EPR cavity cannot be cooled and thus a temperature gradient would exist between the laser fluorescence cell (at low temperature) and the EPR cavity (at room temperature). Although corrections resulting from the temperature gradient could be estimated we felt that a more accurate method should be devised.

We now feel that such measurements can be made successfully by combining gas phase titration (with an appropriate fast chemical reaction) to determine the atom concentration with resonance fluorescence to obtain an accurate end point determination. EPR can be used to calibrate the method at room temperature.

We shall try this method on the  $H + HCl^+(v)$  system during the next reporting period.

Professor T. A. Cool

Metal Atom Laser Systems

During the past 6 months work has been completed on our investigations of new metal atom laser systems. Forty new laser transitions were observed at wavelengths from 1.152 to 14.542  $\mu$  in As, Bi, Cd, Fe, Ga, Ge, Hg, In, Ni, Pb, Sb, Se, Si, Sn, Te, Tl, V, and Zn. The results for half of these new lasers were published in J. Appl. Phys 47, 1055 (1976); the remaining data will be presented in a second paper to be submitted to the Journal of Applied Physics.

V $\rightarrow$ R Energy Transfer

Computer calculations of R $\rightarrow$ R and V $\rightarrow$ R energy transfer in HF have been performed with use of the Polanyi-Woodall relaxation model. These calculations have been useful in the interpretation of our experimental difficulties in the measurement of V $\rightarrow$ R energy transfer in HF.

Low Temperature Vibrational Energy Transfer

Vibrational energy transfer studies have been carried out for the H<sub>2</sub>-HCl and H<sub>2</sub>-D<sub>2</sub> systems at low temperatures (220-450°K). The results of this work will appear in an early issue of Chemical Physics Letters.

Professor R. A. McFarlane

Quenching of Vibrationally Excited Carbon Monoxide  
by Atomic Oxygen and Atomic Hydrogen

Measurements have been continued on the temperature dependence of the second order quenching rate constant for the deactivation of vibrationally excited CO molecules by oxygen atoms. Data in addition to the measurements reported in the last annual report have been obtained and provide confirmation of the temperature dependence already indicated.

Studies have begun on quenching by atomic hydrogen and an initial set of measurements is being analysed. Some difficulty with asymmetric EPR atom line shapes is giving rise to an uncertainty in the determination of atom densities. It is expected that this will limit the accuracy of the measurement to within a factor of two until the source of the asymmetry can be established and corrected.

Quenching of Vibrationally Excited Carbon Monoxide  
and Vibrationally Excited Carbon Dioxide by Molecular Bromine

The present interest in the pumping of CO and CO<sub>2</sub> lasers by E→V energy transfer from excited halogen atoms prompted a set of measurements on the vibrational deactivation of these molecules by molecular Bromine. This experiment used a static fluorescence cell and excited CO at 4.8μ and CO<sub>2</sub> at 10.6μ. Fluorescence traces at varying Br<sub>2</sub> pressures are being analysed and the second order quenching rate data will be available shortly for observations at room temperature.

Professor S. H. Bauer

Laser Ignited Chemical Laser Systems

As noted in our annual report (1 November 1975) emission spectra from laser ignited mixtures of  $B_2H_6/SF_6/N_2O$  (or other oxidizers) were recorded. Their intensity levels, referred to a black body at  $4050^\circ K$ , indicated that approximately 1 photon per 7 boron atoms were generated during the rapid combustion, following initiation by a  $20J/CO_2$  laser pulse. During the past half year we obtained extensive time-intensity data with the 14 channel spectrophotometer (resolution per channel approximately  $70 \text{ \AA}$ ) to determine optimum concentrations of reagents. The following general trends were observed:

(i)  $BO^*$ ,  $S_2^*$  emissions increase with  $p(N_2O)$ , up to 100 torr.

(ii)  $CuF^*(A,B,C \rightarrow X)$  and  $Cu(I)$  rise with  $p(N_2O)$  up to approximately 60 torr, and then level off.

(The Cu impurity comes from the cell walls, or is deliberately inserted.)

(iii)  $BO_2^*(\lambda 5200)$  levels off at  $\approx 40$  torr of  $N_2O$ .

(iv) All emissions peak at  $p(SF_6) \approx 30-40$  torr.

A substantial enhancement of the  $CuF^*$  emissions was achieved by adding several torr  $NF_3$  to the  $B_2H_6/SF_6/N_2O$  mixtures. With  $NF_3$  the high intensities appeared later in time, rising from about  $40 \mu s$  following initiation and continue up through  $200 \mu s$ . Further studies with  $NF_3$  are indicated.

Our shop has completed construction of a small laser for tests in the visible. The contents of the 10" cell will be ignited by sidewise incidence of four appropriately directed  $CO_2$  laser beams. The alignment has been completed and the tests will be made shortly. In our first search we will concentrate on emissions from  $S_2^*$ .