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STUDY OF MOLECULAR LASERS

George J. Wolga, et al

Cornell University

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This report describes Research on Molecular Lasers performed at Cornell University during the period 1 October 1973 - 30 April 1974. The work performed was oriented in five areas. These are:

1. Measurement of the vibrational deactivation of HF(v=1), $CO_2(00^01)$ and CO(v=1) by collisions with atoms. The atoms employed were H, F, O, N, D, Cl.
2. Measurement of the rate of vibrational deactivation at low temperature of the bending mode of $CO_2(010)$ by Argon.
3. Completion of a complete computer model for the CS_2-O, CO chemical laser system.
4. Study of new H atom sources for HF lasers.
5. Laser double resonance studies of vibration to rotation energy transfer in HF.

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Technical Report Summary

This report describes research performed at Cornell University aimed at furthering the understanding of energy transfer and deactivation mechanisms in chemical and molecular lasers as well as the study of new laser systems and new chemical sources for laser systems. This research is motivated by the interest of the sponsor in chemical lasers as efficient sources of coherent optical emission. Emphasis is placed upon the development of new and efficient lasers operating at wavelengths not previously available, and upon the basic processes that underlie all molecular lasers.

The methodology employed consists of laboratory experiments, data analysis including computer modeling, and literature review.

The work reported consists of results in several areas. These are:

1. Measurement of the vibrational deactivation of $HF(v=1)$, $CO_2(00^01)$ and $CO(v=1)$ by collisions with atoms. The atoms employed were H, F, O, N, D, $C\ell$.
2. Measurement of the rate of vibrational deactivation at low temperature of the bending mode of $CO_2(010)$ by Argon.
3. Completion of a complete computer model for the CS_2-O, CO chemical laser system.
4. Study of new H atom sources for HF lasers.
5. Laser double resonance studies of vibration to rotation energy transfer in HF.

The deactivation rates upon HF and CO_2 by atoms has shown that not all atoms are efficient deactivators but that some are very efficient. To further our understanding of these phenomena we shall carry out similar studies on related systems such as $HC\ell$, HBr and CO so that systematic correlations will become more apparent. In particular, the role of orbital degeneracy of the atomic colliding partner proposed by Nikitin as a determining factor for rapid deactivation, will continue to be studied as it appears to be operative in our studies to date.

Atom Deactivation of Molecular Vibration -- Professor G. J. Wolga

A. HF

We have completed our study of the deactivation of $HF(v = 1)$ by O, F, and H atoms. This work was written up and accepted for publication in Chem. Phys. Letters. Our rate determinations for deactivation by D, $C\ell$ and Br and related studies on $DF(v = 1)$ are in progress. A preprint of the above-mentioned publication is appended to this section.

CO_2

We have completed our experimental work on the deactivation of $CO_2(00^{0}1)$ by O, H, D, F, and $C\ell$ atoms. This work will be written up for publication in the very near future.

$HC\ell$ and HBr

Our complementary studies on atom deactivation of $HC\ell(v = 1)$ and $HBr(v = 1)$ by H, D, and halogen atoms will commence upon the final completion of the HF and CO_2 studies.

To be published in Chem. Phys. Letters

DEACTIVATION OF HF(v=1) BY F, O, AND H ATOMS

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Abstract

The laser induced fluorescence method has been used to measure the rate of deactivation of HF(v=1) by F, O, and H atoms at 300°K. The rate for F-atoms was found to be $k_{F-HF} = 0.9 \pm .2 \times 10^4$ sec^{-1} torr^{-1}, for O-atoms $k_{O-HF} = 1.0 \pm .2 \times 10^5$ sec^{-1} torr^{-1}, and for H-atoms, an upper limit to the rate was found to be $k_{H-HF} < 0.5 \times 10^3$ sec^{-1} torr^{-1}. The results are explained qualitatively in terms of a vibronic to translational energy transfer mechanism.

I. Introduction

A large body of literature exists on experimental studies of vibrational energy transfer processes involving HF[1-3,6-9,16,17]. The initial motivation for this work was its relevance to the HF chemical laser. Subsequent discovery of anomalous effects such as the unusual temperature dependence for the V→R,T self-relaxation rate and the magnitude of this rate (the absolute magnitude as well as the relative magnitude compared to the V-V rate) have also added to the great interest.

The present study is concerned with the deactivation of HF by reactive atomic species. These rates are of importance because it is thought that atoms of this kind have a substantial effect on the rate of decay of vibrationally excited species. The F and H atom rates are also needed to characterize the HF laser system for the purpose of optimizing efficiency.

II. Experimental

The vibrational relaxation data reported here were obtained in a fast flow system with the laser induced fluorescence technique[4]. The laser source was a pulsed HF chemical laser ($SF_6 : H_2 = 16:1$) of the transverse electrode type. The laser was operated multiline and the gas flow, SF_6 and H_2 mixture, and discharge pulse rate were adjusted to give optimum HF v = 1 → v = 0 output. The pulse energy was 1 mJ 55% of which was on the 1→0 transitions (P_6, P_7, P_8). The total pulse duration (including 3→2, 2→1, and 1→0 transitions) was less than 1 μsec.

A schematic diagram of the experimental apparatus is shown in figure 1. There are two distinct parts to this experiment. First, the effect of the atoms on the population of $HF(v=1)$ is determined by measuring the change in the decay time of the HF laser induced fluorescence with and without a discharge in the diluent plus parent molecule flow. Second, the atom concentration in the fluorescence cell was measured with an EPR spectrometer by recreating all flow and wall conditions in another section of the flow system (upstream) with an EPR cavity in the same location relative to the discharge as was the fluorescence cell.

The procedure was to set up a flow of diluent (usually argon) plus parent molecule ($X_2 = F_2, O_2, H_2$). This flow is uniquely determined by the pressures P_2 and P_1 (likewise P_4 and P_3) which were measured with a corrosive gas resistant capacitance manometer. A small amount of HF was added downstream (less than 1% of the total flow) through small holes distributed around the circumference of the Teflon tube. The HF is well mixed with the $Ar + X_2$ flow at the fluorescence cell.

The microwave discharge took place in a quartz tube. All other tubes were either Teflon or quartz with a Teflon insert to reduce wall recombination.

The HF fluorescence was monitored with an In Sb PV detector. A narrow band interference filter passed only the HF 1→0 R-branch emission. The overall response of the system was less than 0.5 μsec. The laser power was reduced to avoid overpumping the HF and thus eliminating the problems of V-V transfer and heating of the gas due to V-R,T energy transfer processes. The resultant loss in signal to noise was made up by the Biomation 8100 - Northern Scientific 575 signal averaging system.

A complete block diagram for the EPR spectrometer is not shown in the figure. A detailed description of this system will be given elsewhere. This technique for measuring absolute concentrations of gas phase radicals is well known and described by Westenberg[5].

The gas flow is along the axis of the high Q cylindrical cavity in a 10 mm i.d. quartz tube. The thin-walled Teflon tube insert substantially reduces or eliminates wall recombination and hence nonuniformities in the atom concentration without significantly affecting the sensitivity of the spectrometer. Taking the sine-squared dependence of the microwave magnetic field into account, the 3.5 cm long EPR cavity gives a resolution of about 2 cm over which the average atom concentration is determined. The usual problems of saturation of the spin system by high power microwave fields and broadening due to large amplitude magnetic field modulation were scrupulously avoided.

The following gas samples were used: F_2: Air Products technical grade (purity > 98%); O_2: Linde UHP (purity > 99.99%); H_2: Matheson UHP (purity > 99.999%); Ar: Matheson Purity (purity > 99.9995%); He: Matheson Purity (purity > 99.9999%); HF: Matheson (purity > 99.9%).

Further purification involved passing each gas (except HF) through a liquid nitrogen cold trap. The HF was purified by trap to trap distillation between 77°K and 195°K.

III. Results

For F_2 and O_2 in an argon diluent, the pertinent energy transfer processes in the deactivation of HF (v = 1) are:

$$HF\ (v = 1) + HF\ (v = 0) \xrightarrow{k_{11}} 2HF\ (v = 0) \quad (1)$$

$$HF\ (v = 1) + X_2\ (v = 0) \xrightarrow{k_{12}} HF\ (v = 0) + X_2\ (v = 0) \quad (2)$$

$$HF\ (v = 1) + Ar \xrightarrow{k_{13}} HF\ (v = 0) + Ar. \quad (3)$$

These apply while the microwave discharge is off, and the decay time of the fluorescence is given by:

$$\frac{1}{\tau_0} = k_{11}\,[HF] + k_{12}\,[X_2] + k_{13}\,[Ar]. \quad (4)$$

This assumes that [HF (v = 1)] is small.

When the microwave discharge is turned on, some of the X_2 is dissociated giving an additional channel for deactivation:

$$HF\ (v = 1) + X \xrightarrow{k_{14}} HF\ (v = 0) + X. \quad (5)$$

In this case, the decay time of the fluorescence is given by:

$$\frac{1}{\tau_D} = k_{11}\,[HF] + k_{12}\,\left([X_2] - \frac{[X]}{2}\right) + k_{13}\,[Ar] + k_{14}\,[X]. \quad (6)$$

The difference between (6) and (4) gives:

$$k_{14} = \frac{1}{[X]}\left[\frac{1}{\tau_D} - \frac{1}{\tau_0}\right] \frac{k_{12}}{2}. \quad (7)$$

The rates used for k_{12} were: for O_2 [6,7] $k_{12} = 400\ sec^{-1}\ torr^{-1}$ and for F_2 [8] $k_{12} = 100\ sec^{-1}\ torr^{-1}$. These turn out to be negligible corrections.

The importance of using the EPR spectrometer for measuring [X] is that it allows one to determine the absolute concentration of the atomic species in a fast flow system without the need to alter the flow (as in titration or catalytic probe methods) or even to know what the flow rates are. For F and O atoms, the absolute accuracy of the EPR measurement of concentration is better than 10%.

Another source of error is in measuring the change in the total fluoresecence decay rate. For 0 and F atoms, the change is significant and hence the error is small (10%). A typical run showing the change in decay rate of HF (v = 1) in a mixture of 0, 0_2, Ar and HF as a function of 0 atom partial pressure (P_0) is shown in figure 2. Similar results were obtained with fluorine.

Using equation (7), one can plot ($\tau_D^{-1} - \tau_0^{-1}$) as a function of atom partial pressure. The result should be a straight line of slope equal to the atom deactivation rate k_{14} and intersecting the origin. The results of such a plot for the F and 0 atom data are shown in figure 3. The rates determined from these data are:

$$k_{F\text{-}HF} = 0.9 \pm 0.2 \text{ X } 10^4 \text{ sec}^{-1} \text{ torr}^{-1}$$

$$k_{0\text{-}HF} = 1.0 + 0.2 \text{ X } 10^5 \text{ sec}^{-1} \text{ torr}^{-1}.$$

For the case of H atoms, the energy transfer is complicated by the near resonance of the first vibrational levels of H_2 and HF. This gives rise to a double exponential decay[9]. The fast decay is due to V-V transfer from HF to H_2 and HF self-relaxation, and the slow process is related to the decay of the H_2 - HF vibrational energy pool through V-R,T transfer from HF(v=1). The atoms would be expected to effect this slow rate by deactivating both H_2(v=1) and HF(v=1). The former rate is known to be[10]:

$$k_{H\text{-}H_2} = 1.0 \pm 0.5 \text{ X } 10^4 \text{ sec}^{-1} \text{ torr}^{-1}.$$

However, under no circumstances was there any change observed due to the presence of H atoms.

The only safe thing that one can say in this case is that the hydrogen atoms are not as effective as H_2 in relaxing HF(v=1). This puts an upper limit on the atom deactivation rate of[9]:

$$k_{H\text{-}HF} < \frac{k_{H_2\text{-}HF}}{2} < 0.5 \times 10^{3}\ \mathrm{sec}^{-1}\ \mathrm{torr}^{-1}.$$

IV. Conclusion

These and other preliminary results of this laboratory (D, N on HF(v=1)[11]; O, Cl, H on $CO_2(001)$[12]) lend support to the non-adiabatic theory of Nikitin[13] which is based on a vibronic to translational energy transfer mechanism. Briefly, as it applies to our experiments, atoms with electronic orbital angular momentum degeneracy would be expected to be more efficient in transferring vibrational energy from HF(v=1). During a collisional encounter, the degeneracy which exists at infinite separation is split and electronic transitions are possible between these states. When the frequencies of the electronic transition in the atom and the vibrational transition in HF become equal, there is a large increase in the cross-section for energy transfer.

This says nothing of the possibility for fast relaxation caused by atom exchange or abstraction reactions which could predominate under favorable conditions. This certainly appears to be true in the case of O and H atoms "deactivating" vibrationally excited HCl[14]. However, it does not appear to be important for the F and H atom encounters with HF(T=300°K). This is supported in part by the recent calculations of O'Neil, et al[15] which suggest a minimum barrier height for the exchange reaction:

$$F + HF(v=0) \rightarrow FH(v=0) + F \text{ of } 18\ \mathrm{kcal/mole}.$$

Previous high temperature results for the deactivation of HF(v=1) by F-atoms have been reported[2,16,17]. We choose to compare our results with those of Blair, et al[2]. This is shown in the Landau-Teller plot of figure 4. The rather substantial temperature range of 1000°K over which there is no rate measurement precludes the drawing of any but the most speculative conclusions. This figure does show however that the trend established at high temperatures, for the decreasing effect of F atoms on HF(v=1) with decreasing temperature, persists at least to room temperature (300°K). The temperature dependence of the pure HF relaxation rate[2] is shown for comparison.

Clearly, more rate measurements are needed above and below room temperature before anything definitive can be said about the effects of long range forces or chemical bonding on the efficiency of reactive atoms in deactivating HF(v=1).

Acknowledgements

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Helpful discussions with Professor S. H. Bauer, Professor T. A. Cool, Dr. M. I. Buchwald and Dr. W. D. Breshears are gratefully appreciated.

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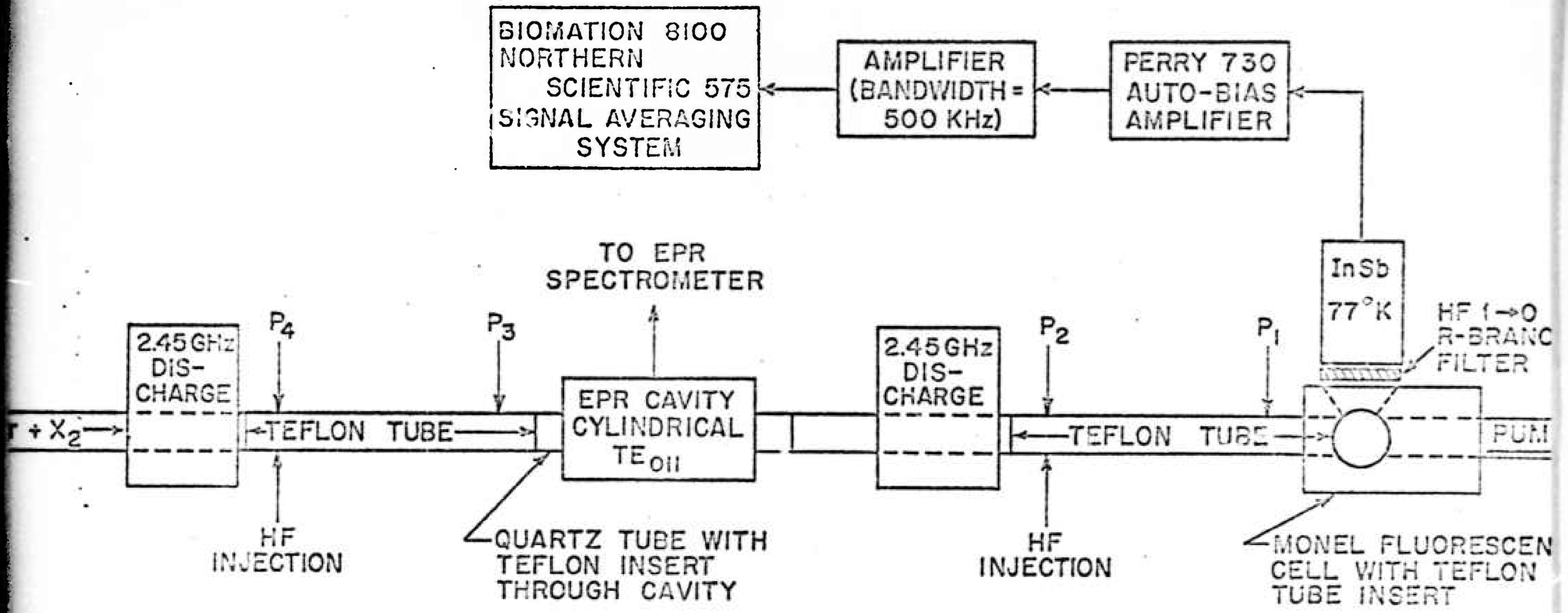
Figure Captions

Figure 1. A schematic diagram of the experimental apparatus.

Figure 2. Semilog plot of relative intensity as a function of time for different discharge conditions in Ar + 0_2.

Figure 3. Distribution of data points as calculated from Eq. (7) about the measured atom deactivation rates for (a) F on HF(v=1) and (b) 0 on HF(v=1).

Figure 4. Landau-Teller plot of the temperature dependence of the F atom deactivation of HF(v=1).

BIOMATION 8100
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SCIENTIFIC 575
SIGNAL AVERAGING
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AMPLIFIER
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PERRY 730
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InSb
77°K
HF 1→0
R-BRANC
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+ X₂
2.45 GHz
DIS-
CHARGE
P₄
TEFLON TUBE
P₃
HF
INJECTION
EPR CAVITY
CYLINDRICAL
TE₀₁₁
QUARTZ TUBE WITH
TEFLON INSERT
THROUGH CAVITY
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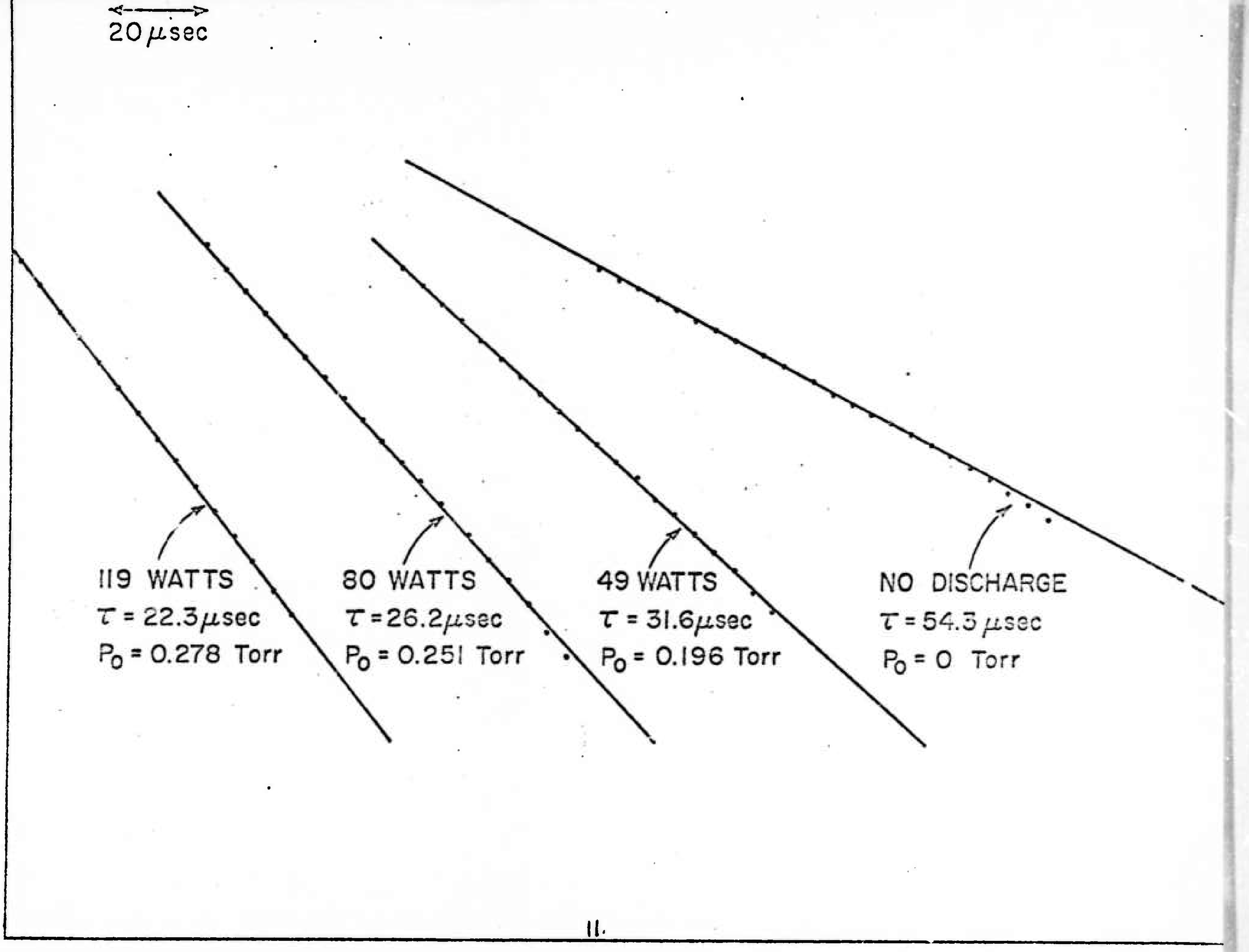
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80 WATTS
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49 WATTS
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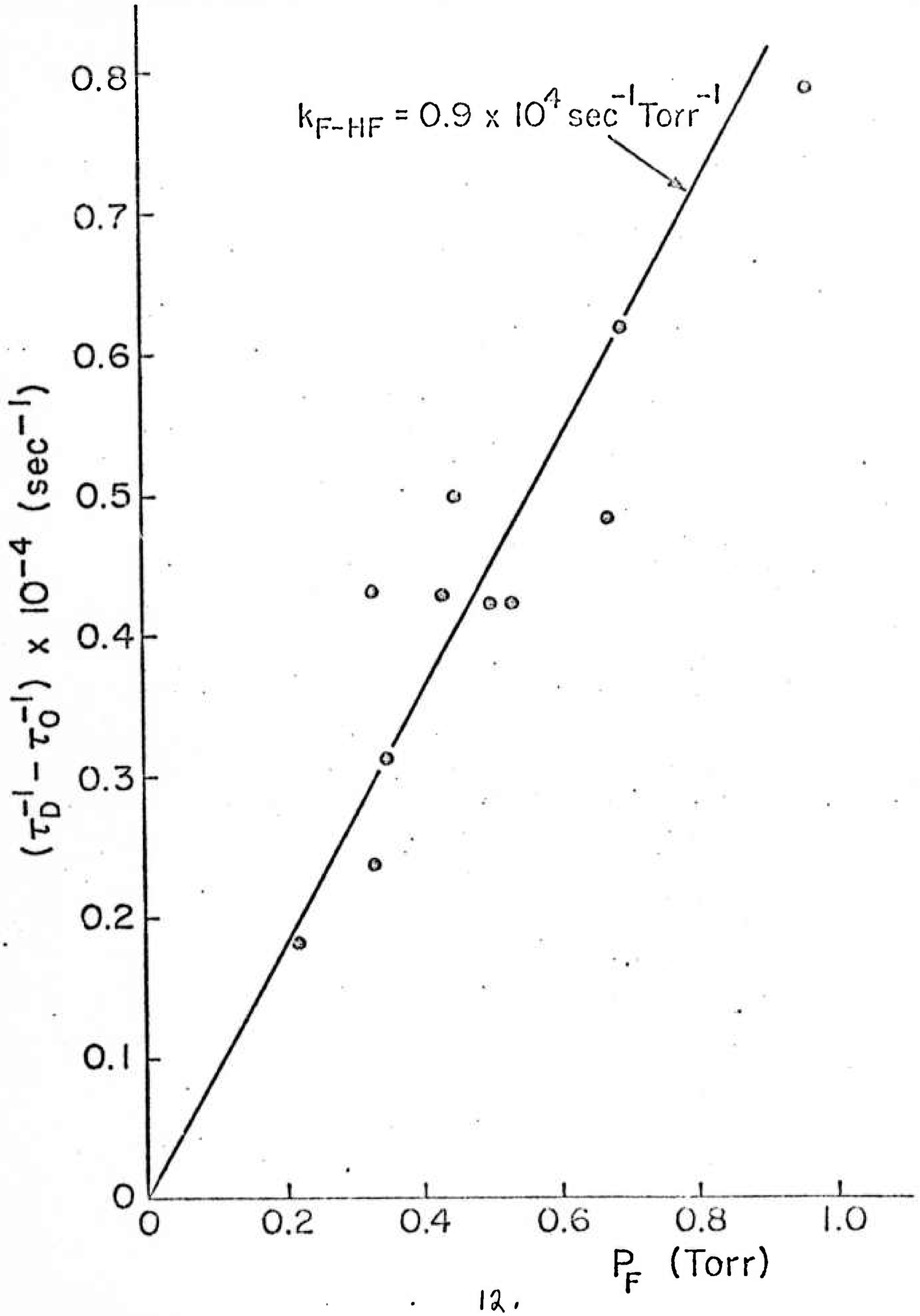
$P_0 = 0.196$ Torr
NO DISCHARGE
$\tau = 54.3\,\mu$sec
$P_0 = 0$ Torr

11.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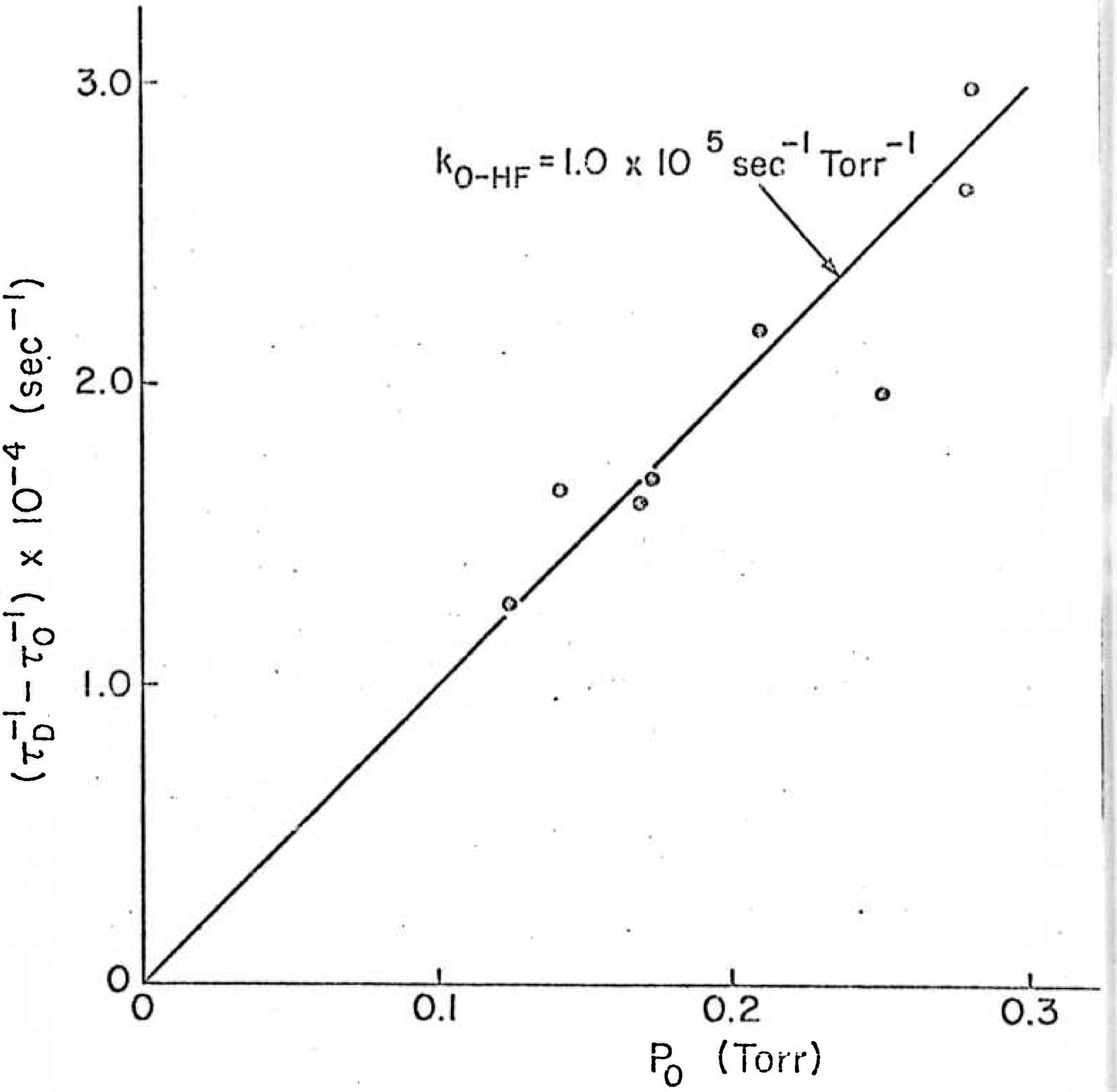
$(\tau_D^{-1} - \tau_0^{-1}) \times 10^{-4}$ (sec^{-1})
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1.0
P_F (Torr)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$(\tau_D^{-1} - \tau_O^{-1}) \times 10^{-4}$ (sec^{-1})
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2.0
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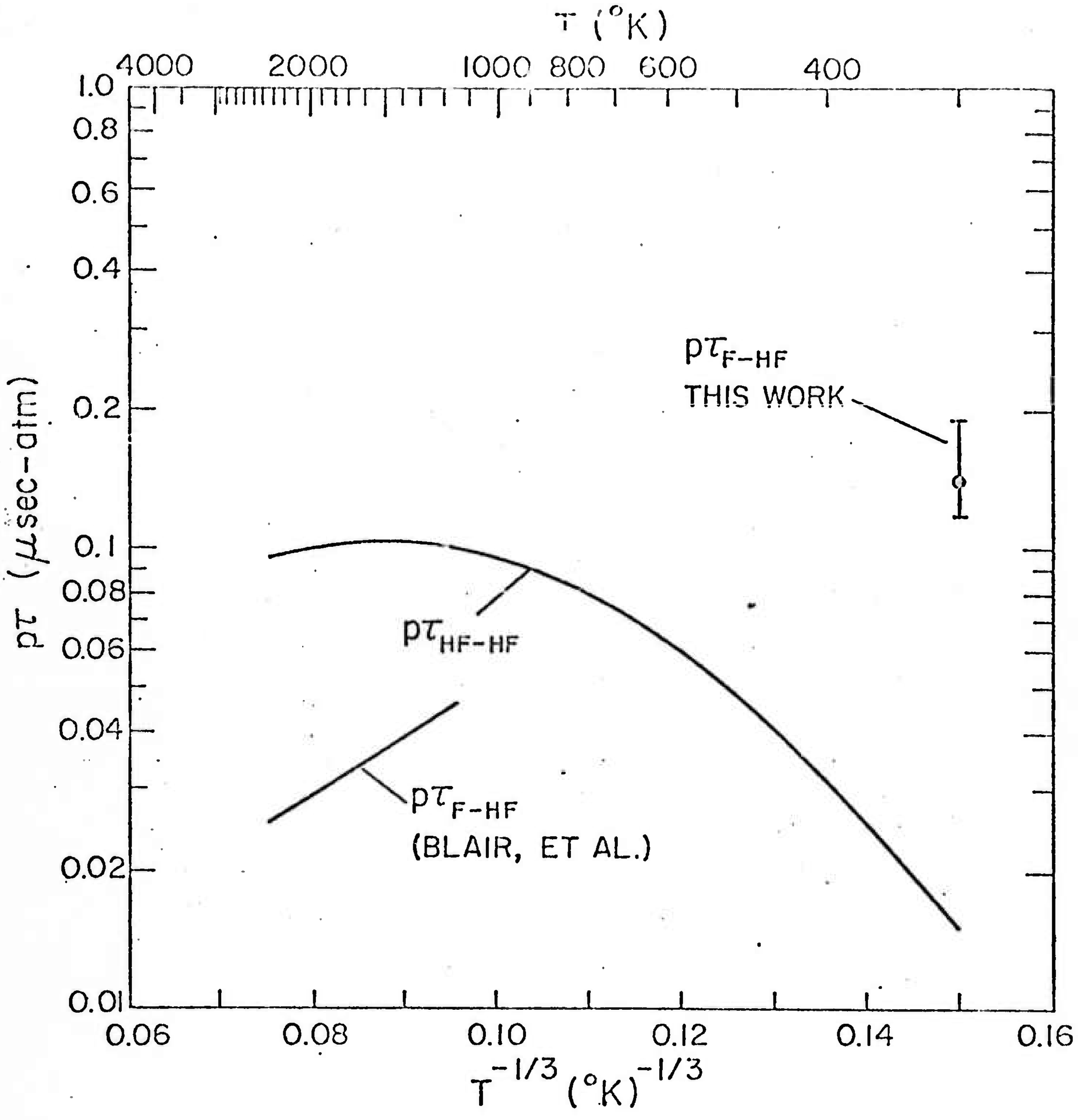
0
0
0.1
0.2
0.3
P_O (Torr)


T (°K)
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2000
1000
800
600
400
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
pτ (μsec-atm)
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THIS WORK
$p\tau_{HF-HF}$
$p\tau_{F-HF}$
(BLAIR, ET AL.)
0.06
0.08
0.10
0.12
0.14
0.16
$T^{-1/3}$ (°K)$^{-1/3}$

B. Studies of Deactivation of Vibrationally Excited CO Molecular Molecules Upon Collision with Atoms -- R. A. McFarlane

During this reporting period work has been carried out in three areas and these will be discussed separately.

I. The excitation of fluorescence in the CO molecule on a transition in the fundamental band ($v = o \leftrightarrow v = 1$) is conveniently carried out using the second harmonic of a high pressure TEA laser operating on a particular rotational transition of the $00^\circ1 \rightarrow 02^\circ0$ band of CO_2. The following coincidences excite the CO v = 1 level.

CO_2		CO	
2 x P(24)	$00^\circ1 \rightarrow 02^\circ0$	P(14)	$1 \rightarrow 0$
2 x R(18)	$00^\circ1 \rightarrow 02^\circ0$	R(2)	$1 \rightarrow 0$

A u.v. preionized TEA laser developed with internal funds was modified to provide a more uniform distribution of ionization and is now producing output on selected rotational lines in both the $00^\circ1 \rightarrow 10^\circ0$ band and the $00^\circ1 \rightarrow 02^\circ0$ band. The particular line is selected by a diffraction grating and the system produces typical power levels of 5 Mw. in a 200 nanosecond pulse. It was found that the substitution of a Maxwell 0.2 μFd capacitor for the series of Sprague ceramic units previously employed substantially shortened the output pulse and increased peak power. Switching is accomplished with an HY-5 hydrogen thyratron at a one p.p.s. rate.

II. Second harmonic generation is accomplished using a Tellurium crystal. Phase matching requires that the fundamental and harmonic signals propagate at an angle of about 15° from the crystalline optic axis. Further, since the crystal structure is trigonal but grows with a hexagonal cross section it is necessary to polarize the beam in the correct quadrant to have the polarization components at the second harmonic frequency add correctly rather than subtract. Prior to cutting and polishing the crystal

X-ray diffraction photographs were taken to determine the correct x and y axes. A crystal of 1 cm. in length was cut and polished with the normal to the entrance and exit faces at 15° to the outer axis. This crystal was found to produce second harmonic output when pumped with the TEA laser. To check on the accuracy of the axis determination a second crystal was cut oriented with the other choice of quadrants. As expected no S. H. G. was found for this orientation.

To reduce the 1" beam diameter of the TEA laser to something less than the 7 mm. transverse dimension of the Te crystal, a folded optical system was set up using convex mirrors to converge the beam and provide an energy density at the Te crystal surface somewhat less than the surface damage threshold. By placing the Te crystal almost in contact with the fluorescence cell no additional optical elements are required in the second harmonic beam.

The fluorescence cell is made from a stainless steel tee which is a standard vacuum fitting by incorporating three sapphire windows: two to permit the second harmonic beam to traverse the cell and a third for observing fluorescence at right angles to the beam direction. The cell is one of a series of elements in a vacuum line through which gas is flowed first past a microwave discharge cavity and then prior to entering the cell through a high Q E.P.R. cavity to be employed for absolute species concentration determination. Stainless steel and teflon materials have been used throughout the system for cleanliness and the vacuum integrity is such as to permit sealed-off operation over several hours if this is required. Pressure measurements are made by a Pirani gauge, thermocouple and oil manometer. A two stage Roots blower with a pumping speed of 100 c.f.m. is used to exhaust the system. This is backed by a 15 c.f.m. Precision Scientific forepump. The blower is rated at an ultimate pressure of less than 10^{-5} Torr.

To observe the fluorescence decay signal an InSb photoconductive detector is mounted above the fluorescence cell adjacent to the third sapphire window. We have just received delivery of the Perry preamplifier and video amplifier to use with this detector. The video amplifier was specified to provide across its entire bandwidth a peak signal of 1 volt into a 50 ohm load. This amplifier drives a Model 8100 Transient Digitizer the 2000 data points from which are transferred each pulse to a Northern Scientific Model 575 Signal Averager. Very significant improvement in this system was recently achieved by going to a digital transfer mode from the analog mode used earlier. Output from the averager is recorded with print out on paper and onto a magnetic cassette using a T.I. Model 733 ASR data terminal. Computer programs are now operating to derive from the recorded decay curves the time constants for single or multiple exponential decays. Under circumstances where S/N ratios are substantially inferior to those anticipated from the CO measurements it has been found very easy to determine decay constants to a precision of better than one percent. This will be particularly valuable for observing incremental changes in decay constants in the presence of atoms generated by the microwave discharge if such effects are small for a particular species.

III. To determine absolute atom concentrations, an E.P.R. system has been set up using a 10 mw. Gunn oscillator operating at 9450 MHz. During operation this oscillator is frequency locked to the resonant frequency of the TE_{011} mode cavity which monitors the atom concentration. This is accomplished by using the fact that the Gunn oscillator output frequency depends slightly on the current supplied to the diode. A feedback stabilizer was designed and built to provide a small frequency modulation at 70 kHz and to phase detect the a.c. component at this frequency in the signal reflected from the E.P.R. cavity. A low noise integrated circuit preamplifier is used to amplify the signal to a level appropriate to drive a precision multiplier (Analog Devices Model AD530J) and the output is integrated in a low drift integrator (Analog Devices Model 43J). The other input to the multiplier is derived from the 70 kHz oscillator through a variable phase shifter. Level set, modulation and correction signals then drive a high power operational amplifier which provides the Gunn oscillator current.

The magnet is supplied from a Hewlett Packard 0 - 600 V, 0 - 20 Amp. power supply. The basic stability of this supply was approximately 1:3000 and it was found to be inadequate for the E.P.R. measurements intended. A secondary regulation system referenced to a low temperature coefficient 0.04 ohm resistor which passes the total magnet current was built and is now operating. This is driven from a level set and field scan circuit to provide selected ΔH increments in selectable time periods. E.P.R. spectra of atomic oxygen have been recorded and more than adequate resolution is available for the concentration measurements planned. Some difficulty is being experienced with the microwave discharge causing interference with the magnet power supply and secondary stabilizer. Inductors are being installed in all correction signal lines and it is expected that this problem will be corrected directly.

When the E.P.R. system is operational it will be incorporated into the gas flow system described above. Initial measurements of O on CO^* will employ NO_2 titration for atom concentration determination. Our first efforts to observe CO^* fluorescence have begun.

C. Study of Chemical Laser Systems -- S. A. Bauer

During the first quarter of this year the experimental part of our project on laser induced fluorescence from the bending mode of CO_2 was completed. The results of this study were presented at the April ACS Meeting in Los Angeles. The 2.8μ laser emission from $HF^\dagger$ [$SF_6 + H_2 + He$, electrically pulsed] is partially absorbed by carbon dioxide. HF lines at 3622.71, 3577.8 and 3644.16 μm pump the ($02^\circ1$) level, that at 3693.50 μ pumps the (11^11) level, and both 3593.80 and 3577.80 pump the (03^11) level of CO_2. Line center frequency mismatching is rectified partially by pressure broadening with argon, or with mixtures which incorporate other collision partners of interest. At CO_2 concentrations above 2%, collisions with the ($00^\circ0$) state rapidly degrade the pumped states to overpopulate the ($00^\circ1$) and ($0n^\ell0$) states, from which fluorescence is observed at 4.3μ and 15.0μ, respectively. The latter showed an early growth, followed by a fluorescence decay such that the total fluorescence intensity could be represented by a superposition of two exponentials. The longer period was associated with v-T de-excitation of CO_2 for which the values:

$$k(CO_2Ar) = 41\ \mathrm{sec}^{-1}\mathrm{torr}^{-1},\ \text{and}\ k(CO_2\text{-}CO_2) = 227\ \mathrm{sec}^{-1}\mathrm{torr}^{-1}$$

were deduced. These check reasonably well with extrapolated shock tube measurements and ultrasonic data. The rate constants for pumping ($0n^\ell0$) proved to be about twice the literature values for the ($00^\circ1$) de-excitation: ≈ 120 $\mathrm{sec}^{-1}\mathrm{torr}^{-1}$ for CO_2 - Ar and 660 $\mathrm{sec}^{-1}\mathrm{torr}^{-1}$ for CO_2 - CO_2. As yet the explanation for this is not clear. Corresponding values were also measured for two additional collision partners, CS_2 and COS.

The assembly of data and the preparation of a complete computer program for the CS_2 - O_2 - He chemical laser model system was completed. This was also reported at the Los Angeles meeting. While there is general concensus that the dominant pumping reaction which produces CO lasing is:

$$CS^{(o)}[{}^1\Sigma^+] + O[{}^3P_2] \rightarrow S[{}^3P_2] + CO^{(v)}[{}^1\Sigma^+],$$

and that in the chain reaction, CS radicals are produced via a rapid S atom abstraction by O from CS_2, with the oxygen atoms regenerated in the reaction $S + O_2 \rightarrow SO + O$, to develop a tractable mechanism we sought a minimum set of auxiliary steps; that is, those reactions which if omitted would affect to a measurable extent the concentrations of the important species: $CO^{(v)}$, O, S, and CS. After a thorough search of literature and the introduction of plausible rate parameters for all possible reactions, a sequence of computer trials were run with our fully developed kinetics program, which incorporates v-T and v-v transfer rates as well as the adiabatic condition, for the time evolution of the state and species populations, following the pulsed discharge. Then, by successive approximations some of the reactions were eliminated and others inserted until a self consistent set of steps was developed. Time-concentration histograms for the various species and for the evolving populations of $CO^{(v)}$ have been plotted. These agreed quite well with our experimental observations. A complete report is now being prepared.

We reported on our extensions of our prior investigation of the C_3O_2 chemical laser at the Philadelphia Meeting of the APS. Our studies of the $C_3O_2 + O_2$+He pulsed laser consist of four parts. First, both literature and experimental surveys were made of preparative methods, in search for an efficient route for generating substantial quantities of the suboxide. In this we were only partially successful. Yields of up to 15% were obtained, compared to conventional yields of about 8%. The second part consisted of a parametric study of reagent composition and of discharge conditions to maximize laser output for an axial discharge configuration, and the recording of relative lasing intensities and delays for onset of lasing as a function of upper vibrational state. The effect of added cold CO was also investigated. In the third part, relative populations of excited states, as present at a sequence of delays after pulse initiation, were obtained from chemiluminescence data, in the absence of lasing. A set of 25 reactions with corresponding rate constants was selected such that the computed time evolution of the chemiluminescence intensity reproduced the observed distribution over the interval 40 - 400 μs. Finally, visible and UV spectra emitted during the induction period for lasing were recorded. A complete report is being prepared.

We also discovered conditions for operating our axially excited $CS_2 + O_2$ + He laser so as to obtain stimulated emission for the $(1 \rightarrow 0)$ CO transition. These studies have been summarized in a brief paper which will be submitted to Chemical Physics Letters.

A detailed report on the use of H_2CO and D_2DO polymers as sources for hydrogen (or deuterium) in HF (or DF) TEA pulsed lasers has been prepared. On a mole/mole basis formaldehyde, which can be readily generated from the solid polymer by gentle heating, is approximately 10 times more effective for HF laser generation than a comparable quantity of hydrogen (or deuterium). This is a very practical development which liberates the user from carrying hydrogen at high pressures in massive cylinders. Further work with the CW configuration is underway.

Finally, the high powered CO_2 TEA laser has been completed and is in process of being checked out. It will be used for the rapid pyrolysis of boron containing species in mixtures consisting of boron compound with compatible oxidizers.

D. Laser Double Resonance Studies of Vibration to Rotation Energy Transfer -- Professor T. A. Cool

Apparatus are being assembled for the laser double resonance experiment schematically outlined in Figure 1. The experiment is designed to record the temporal variations in rotational populations of the ground vibrational state of HF following the laser excitation of a selected rotational state of the HF ($v = 1$) level. Rotational population changes are determined from observations of the absorption of an HF probe laser capable of operation on transitions ranging from P(4) to P(15) on the $1 \rightarrow 0$ vibration-rotation band.

Two boxcar signal averagers are used to accomplish the recording of incident and transmitted probe laser intensities. The boxcar arrangement also provides a means for automatic scanning of the variable time interval between pump and probe laser pulses. A logarithmic amplifier provides the logarithm of the ratio of incident to transmitted intensities, a quantity which is proportional to the population of the absorbing rotational state.

The major objective of the experiment is the determination of the rate constants for vibration to rotation energy transfer by the processes

$$HF(v=1, J_1) + HF(v=0, J_2) \rightarrow HF(v=0, J_1') + HF(v=0, J_2') \quad . \qquad (1)$$

The experimental measurements will provide the temporal variations in J_1' and J_2' rotational state populations. The rotational relaxation of these populations will be described empirically in terms of the Polanyi-Woodall relaxation model (modified where appropriate). Once the rotational relaxation behavior can be successfully modeled, it will then be possible to recover the nascent rotational populations produced by the processes (1).

The experimental apparatus have been assembled in preliminary form to establish the feasibility of the technique. Further development of the probe laser must be accomplished before experiments can begin.

DOUBLE RESONANCE ROTATIONAL RELAXATION EXPERIMENT

$$\ln\left[\frac{\langle A(t)\rangle_{\Delta t'}}{\langle B(t+\Delta t)\rangle_{\Delta t'}}\right] \propto \langle N_J(t+\Delta t)\rangle_{\Delta t'}$$