AD-A099 189 AEROSPACE CORP EL SEGUNDO CA AEROPHYSICS LAB F/G 20/5
INVESTIGATION OF DF KINETICS IN THE PRESENCE OF BF3.(U)
APR 81 J F BOTT, M EPSTEIN F04701-80-C-0081
UNCLASSIFIED TR-0081(6940-01)-5 SD-TR-81-29 NL

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Investigation of DF Kinetics in the Presence of BF_3

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2 April 1981

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Prepared for

SPACE DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, Calif. 90009

This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-80-C-0081 with the Space Division, Deputy for Technology. P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by W. R. Warren, Jr., Director, Aerophysics Laboratory. Lieutenant James C. Garcia, SD/YLXT, was the project officer for Mission-Oriented Investigation and Experimentation (MOIE) Programs.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: SD-TR-81-29	2. GOVT ACCESSION NO.: AD-A099 789
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): INVESTIGATION OF DF KINETICS IN THE PRESENCE OF BF_3	5. TYPE OF REPORT & PERIOD COVERED
	6. PERFORMING ORG. REPORT NUMBER: TR-0081(6940-01)-5
7. AUTHOR(s): J. F. Bott and M. Epstein	8. CONTRACT OR GRANT NUMBER(s): F04701-80-C-0081
9. PERFORMING ORGANIZATION NAME AND ADDRESS: The Aerospace Corporation, El Segundo, Calif. 90245	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS: Space Division, Air Force Systems Command, Los Angeles, Calif. 90009	12. REPORT DATE: 2 April 1981
	13. NUMBER OF PAGES: 13
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Chemical Laser
Deuterium Fluoride
Vibrational Deactivation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Laser modeling calculations have been performed for a helium-free DF laser operating on solid-grain reactants. The laser calculations include deactivation kinetics for BF_3 that are based on measurements at 295 K. Reasonable estimates have been made for the scaling of the deactivation rates to higher vibrational levels and for the temperature dependence. The calculations show that the BF_3 degrades the laser performance about 4% because of the deactivation kinetics.

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I. INTRODUCTION

The technology for helium-free DF lasers is being examined to determine if the operational advantages afforded by solid-grain reactants and closed-system operation can be exploited. All of the required reactants can be produced from storable solid-grain compounds. One solid-grain formulation designed to produce fluorine utilizes NF_4BF_4, which results in the appearance of BF_3 by product in the combustion products. The development of solid-grain compounds and auxiliaries to remove all BF_3 would add cost, complexity, and bulk to the solid-grain system. The object of the present study is to assess the effect of BF_3 on laser performance, with emphasis on the deactivation of DF by BF_3. The study includes a review of the deactivation of DF(v) by BF_3, calculation of combustor products, and DESALE calculations to determine laser power outputs with and without BF_3.

II. DEACTIVATION OF DF(v) by BF_3

The rate coefficient for the deactivation process

$$DF(v = 1) + BF_3 \xrightarrow{k(1)} DF(v = 0) + BF_3(1)$$

has been measured at T = 295 K by the technique of laser-induced fluorescence.[1] Although the temperature dependence is not known, the deactivation rate coefficients for the deactivation of DF(v = 1) by other molecules depend rather weakly on temperature in the 300- to 500-K range.[2] We have chosen a temperature-independent rate for the modeling calculations given by

$$K(1) = 1.25 \times 10^{11} \text{ cm}^3/\text{mol sec}$$

The rate coefficients for the high vibrational levels have been estimated on the basis of the v^2 scaling that holds for DF(v) deactivation by diatomic molecules.[3] The remainder of the kinetics package used in the laser modeling calculations are reactions and rate coefficients recommended by Cohen of The Aerospace Corporation.[4] These reactions are periodically reviewed and updated for consistency with the latest literature.[5] Cohen has estimated rate coefficients for the upper vibrational levels where no data are available.

III. CALCULATIONS

A. PRIMARY- AND SECONDARY-FLOW CALCULATIONS

Typical gas-flow conditions are shown in Table 1 (taken from statement of work). Adiabatic flame-temperature calculations were performed for the primary flow at a total pressure of 2 atm. The results of this calculation are shown in Table 2. The combustion produces a temperature of 2291 K, with the only species of any concentration being fluorine, HF, BF_3, and N_2. The large bond strengths of HF, BF_3, and N_2 make this result quite understandable. Although an adiabatic flame temperature of 2291 K is predicted, the actual temperature of the gas at the entrance to the expansion nozzles is probably closer to 1800 K after heat loss to the walls of the combustor.

The combustor gas was assumed to expand adiabatically from 2 atm at 1800 K to a velocity of 1.75×10^5 cm/sec (Mach No. = 5.0) with T = 282 K, and P = 2.86 Torr. These conditions were used as input conditions for the laser modeling calculations. The mole fractions leaving the combustor are shown in Table 2 to be fluorine, 0.161; HF, 0.356; N_2, 0.379; and BF_3, 0.104.

The secondary flow of D_2 is assumed to undergo a small expansion to a velocity of 1.1×10^5 cm/sec corresponding to a Mach number of 1.25. If the D_2 is initially at room temperature, this expansion leads to a final static temperature of 225 K.

B. DESALE CALCULATIONS OF LASER PERFORMANCE

DESALE[6] calculations were performed for a laser with the following configuration: nozzle heights = 0.5 cm; primary nozzle width = 0.08936 cm; secondary nozzle width = 0.01064 cm; total length of nozzle bank = 100 cm; and an unstable cavity with a magnification M = 2. The DESALE calculations take into account finite mixing rates of the primary and secondary flows in the laser cavity, reaction rates, and laser radiation. The mirrors have one edge at x = 0, the nozzle exit, and the other edge at position x downstream. The optimum

Table 1. Typical Gas Flow Conditions

Primary Flows	
Gas	Molar Amount
F_2	1.0
NF_3	1.0
BF_3	0-1.0
N_2	3.16
H_2	1.72
Secondary Flow	
D_2	5.5
Static Pressure = 2-10 Torr Initial Static Temperature = 200-400 K Initial Total Temperature = 1800 K	

Table 2. Primary Flow Calculations

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PRESSURE (ATM) .200000E+01
TEMPERATURE (DEG K) 2291.09
AVERAGE MOLECULAR WEIGHT (GM/MOLES) .278274E+02
AVAILABLE NON-HEATED SYSTEM ENTHALPY (KCAL/GM) .9571
SYSTEM ENTHALPY (KCAL/GM) .9571
SYSTEM ENTROPY (CAL/GM-DEG) 2.2334
COMPRESSIBILITY FACTOR 1.22577
H / RT -6.89707
SYSTEM GAS CP .32652

PRODUCT	MOLE FRACTION	MOLES	PARTIAL PRESSURE	CP	ATOMS/CC	ENTROPY	H-TS
H	.118755E-06	.42675519E-08	.23751008E-06	4.9680	.760918E+12	37.5235	10.7542
B	.208361E-22	.74876153E-24	.41672232E-22	4.9680	.133507E-03	46.7815	210.5980
N	.153405E-07	.55127248E-09	.30681003E-07	4.9719	.982936E+11	46.7457	17.6542
F	.161320E+00	.57971613E-02	.32264030E+00	4.9942	.103365E+19	48.4466	-50.4565
BH	.269341E-27	.96789555E-29	.53868109E-27	8.9423	.172579E-08	56.8781	203.1549
HN	.347479E-11	.12486919E-12	.69495794E-11	8.6422	.222646E+08	58.5577	-2.8264
FH	.356161E+00	.12799620E-01	.71236129E+00	9.3256	.228221E+19	56.4057	-112.7551
H2	.333125E-09	.11971097E-10	.66624996E-09	8.4272	.213448E+10	46.1336	-21.1835
BH2	.248366E-29	.89252071E-31	.49673131E-29	14.0669	.159139E-10	65.9555	165.7987
H2N	.144599E-15	.51962565E-17	.28919702E-15	12.5269	.926509E+03	65.0475	-15.5926
H2N2	.390591E-20	.14036165E-21	.78118103E-20	16.3611	.250269E-01	80.0702	-29.8093
H2F2	.198986E-05	.71507230E-07	.39797261E-05	18.2552	.127500E+14	86.9611	-171.9859
BH3	.309333E-35	.11116113E-36	.61666593E-35	18.1346	.198204E-16	71.3934	169.0084
H3N	.813630E-19	.29238422E-20	.16272608E-18	17.4693	.521330E+00	71.1726	-40.2161
H3F3	.126866E-10	.45590292E-12	.25373221E-10	30.0102	.812889E+08	119.3833	-231.8180
N2H4	.162182E-32	.58281435E-34	.32436461E-32	28.9627	.103918E-13	100.1394	-16.3892
H4F4	.211305E-15	.75933677E-17	.42260907E-15	41.3381	.135392E+04	153.4160	-296.0222
H5F5	.313106E-20	.11251703E-21	.62621217E-20	52.6659	.200621E-01	187.0655	-359.6941
B2H6	.106485E-73	.38266060E-75	.21296929E-73	40.7831	.682296E-55	113.4354	372.1366
B3H6N3	.331480E-91	.11911981E-92	.66295387E-91	63.0718	.212394E-72	163.1507	346.3139
H6F6	.754438E-25	.27111293E-26	.15088757E-24	63.9938	.483403E-06	220.4554	-425.5796
B5H9	.129460-150	.46522413-152	.25891992-150	74.8116	.829509-132	173.4434	930.3273
B10H14	.413023-275	.14842276-276	.82604504-275	131.8924	.264642-256	280.4325	1821.9002
BN	.104649E-26	.37606321E-28	.20929752E-26	8.9672	.670533E-08	67.1645	194.5575
BF	.333298E-12	.11977325E-13	.66659658E-12	8.9854	.213559E+07	64.4992	48.0163
BF2	.293448E-06	.10545289E-07	.58689678E-06	13.7353	.188026E+13	84.1627	-69.9125
BF3	.103527E+00	.37203066E-02	.20705321E+00	19.4920	.663342E+18	95.0392	-183.6774
B2	.564386E-44	.20281639E-45	.11287721E-43	9.1065	.361628E-25	65.3822	412.6737
B2F4	.116555E-15	.41884788E-17	.23310928E-15	30.2361	.746819E+03	129.3058	-106.5965
NF	.106233E-06	.38176503E-08	.21247086E-06	9.1049	.680699E+12	68.5037	-46.7635
NF2	.162876E-07	.58530824E-09	.32575259E-07	13.7601	.104362E+12	85.1513	-93.8326
NF3	.472560E-10	.16981803E-11	.94512018E-10	19.6407	.302731E+09	98.0294	-122.8386
N2	.378905E+00	.13616241E-01	.75781024E+00	8.7002	.242782E+19	61.3974	-120.9579
N2F4	.113659E-22	.40844088E-24	.22731727E-22	31.3745	.728263E-04	128.1155	-107.2651
F2	.649367E-04	.23335482E-05	.12987334E-03	9.3638	.416079E+15	66.0235	-70.4699
B COND	0.	0.	0.	7.2699	0.	12.4522	158.7005
BN SOLID	0.	0.	0.	11.7000	0.	22.5057	86.2061

sized mirrors are those that produce the maximum power (Fig. 1). The calculations were performed for the conditions listed in Table 3, and the results of output power versus mirror width are shown in Figs. 1 and 2.

A maximum power of 4700 W was calculated for Run 1, which contained the full amount of BF_3 and the deactivation kinetics for DF(v)-BF_3. The calculation for Run 2 was performed for exactly the same conditions except the deactivation kinetics for DF(v)-BF_3 were deleted. The output power in Run 2 increased to 4875 W from 4700 W in Run 1, a change of only about 4%. The BF_3 was removed from the primary flow for Run 3 with a consequent 10.4% decrease in the static pressure. In order to match the pressures in the primary and secondary flows, the D_2 flow rate was reduced by 10.4%. The resulting power of 4750 W falls between the powers of Runs 1 and 2. The lower pressure allows mixing to occur sooner, but the lower D_2 concentration tends to stretch out the reaction zone.

In order to check the sensitivity of the results to uncertainties in the deactivation rate coefficient, a calculation was performed in which the rate coefficients for DF(v) deactivation by BF_3 were arbitrarily increased by a factor of 2. The calculated peak power in this case was 4515 W, about 4% below the power for Run 1 with the most probable rates and about 8% below that of Run 2 where the deactivation rates are set equal to zero. The decrease in laser power is roughly proportional to the increase in the deactivation rate. The temperature in the laser cavity increased from about 280 to 380 K at the peak power in all cases so that the average temperature was 330 K, only about 12% above the temperature of the DF(1)-BF_3 rate measurements. A calculation performed with the standard rate coefficients, but with a v^3 scaling for the DF(v)-BF_3 rates gave 4370 W, compared to 4700 W for the v^2 scaled calculation.

The most important deactivators in the system are HF and D_2. Instead of taking BF_3 out of the primary flow, an alternative is to reduce heat losses in the combustor and use 10% less H_2, which makes HF. Run 4 shows that the power is increased about 5% by a 10% reduction in HF.

Table 3. Calculated Laser Performance

	Run No.			
	1	2	3	4
Pressure, atm	0.003776	0.003776	0.0033835	0.003248
Primary Flow				
F, %	16.1	16.1	18.0	18.75
HF, %	35.6	35.6	39.7	37.19
BF_3, %	10.4	10.4	0	0
N_2, %	37.9	37.9	42.3	44.06
Comments	With deactivation by BF_3	Without deactivation by BF_3	No BF_3, HF	No BF_3, reduced by 10%
Max Power, W	4700	4875	4750	5000

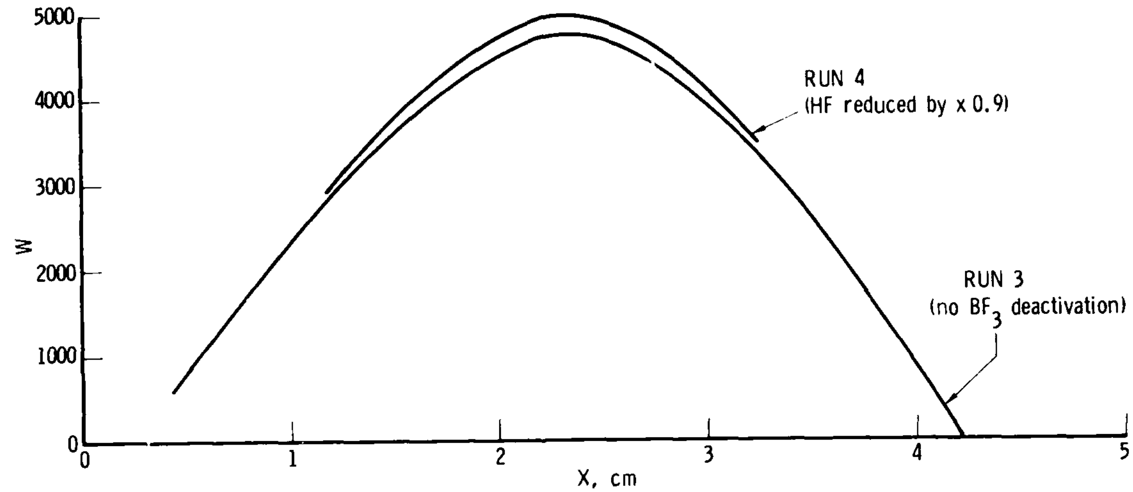

Fig. 1. Power Output Versus Mirror Length

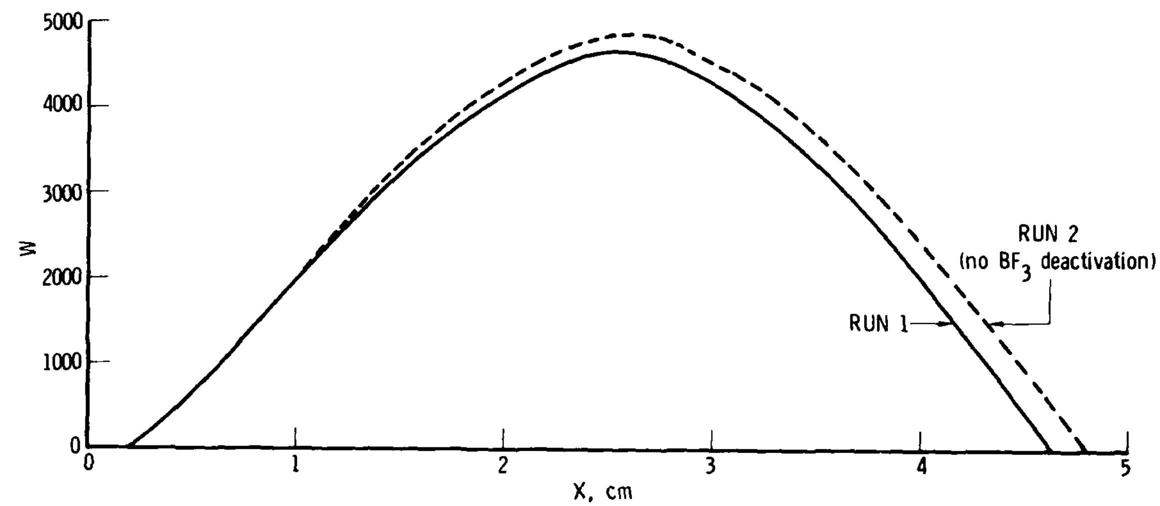

Fig. 2. Power Output Versus Mirror Length

IV. CONCLUSIONS

Laser modeling calculations have been performed for a helium-free DF laser based on solid-grain reactants. The presence of BF_3, a combustion by-product, in the laser cavity, degrades the laser performance by about 4% for reasonable estimates of the temperature dependence of the deactivation rate coefficient and for its scaling to higher vibrational levels. It is concluded, on the basis of our DESALE calculations, that laser performance degradation is not severe enough to warrant the removal of BF_3 from a combustor flow that utilizes an NF_4BF_4 solid-grain formulation.

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