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BASELINE CHEMISTRY MODEL FOR PLUME
RADIATION PREDICTIONS

Edward R. Fisher, et al

Physical Dynamics, Incorporated

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INTRODUCTION

As part of the DARPA Plume Physics Program, extensive modeling calculations have been performed on both field and test environments. These modeling calculations generally involve fluid dynamical, chemical and radiative inputs, each of which may be subject to certain approximations in order to yield a final value for comparison with observation. The purpose of this paper is to outline four chemistry models which can be used for baseline predictions on the IR radiative characteristics of rocket exhaust plumes.

Although these models were initially generated for use in high altitude plume environments where continuum fluid approximations are still valid, the resulting chemistry is also useful to both lower altitude regimes and test environments. The four models developed to date consist of the following:

- (1) APOLLO model
- (2) RELAXATION model
- (3) HYDROCARBON model
- (4) AMINE model .

Each model consists of a chemical mechanism consisting of a sequence of chemical reactions and energy transfer processes with temperature dependent rate coefficients as well as the radiative lifetimes of appropriate species in the IR region of the spectrum. A preliminary attempt to outline a UV model

has been documented elsewhere [Kummler, Fisher, Boynton (1972)].

The rationale behind the development of these baseline chemistry models stems from the desire to provide a common chemistry for direct comparison between different flow field models. In addition, these baseline models provide a state-of-the-art chemistry package to use in making reasonable predictions of plume radiation as well as the radiation observed from rocket test plumes. As new chemical reactions and improved rate coefficient information becomes available, the chemistry models will be updated.

As will become clear in reviewing the chemistry models, many rate coefficients are poorly known. However, the attempt in these models has been to include as much of the important chemistry as is feasible with rate coefficients estimated either from theory or by comparison with other better known rate processes. The output from model calculations can then provide the basis for the design of experiments aimed at quantifying the important chemical rates. This has already been done in several cases, as will be discussed later.

The chemical processes included in these baseline chemistry models must reflect the highly non-equilibrium state of high altitude plumes. Therefore, the following types of chemistry processes have been included in the current models:

Chemi-excitation processes - these are chemical reactions in which the exothermicity of the reaction is either partly or totally deposited directly into an internal energy state of a product molecule. Generally speaking, interest has been focused on product vibrational states since these excited species can directly or indirectly (by transferring the vibrational energy to another species or mode) contribute to observed IR radiation levels. An example of this type of process is



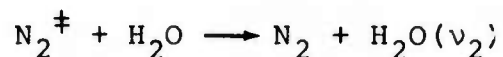
where $\text{H}_2\text{O}^\ddagger$ represents a vibrationally excited molecule. Sufficient reaction energy exists in this process to excite either the stretching or bending modes. As a result of interest generated in this and related processes, experiments have been performed on the quantum yield of these reactions [Trainor (1973)].

Relaxation processes - these are energy transfer processes in which vibrational energy is exchanged with translational or rotational energy (VT) in a collision, or vibrational energy is exchanged directly between vibrational modes (VV). As an example of the former case (VT), the process



is thought to be important in the mixing layer of high altitude plumes. Since vibrational relaxation processes involving atomic species are known to be important in cases where direct experiment has been performed, plume radiation by O atoms is believed to be of major importance in the mixing layer of high altitude plumes. The rates for several of these O atom relaxation processes have

been measured as part of the Plume Physics Program and the results are included in the models. As an example of a VV process



may contribute to the excitation of H_2O by atmospheric N_2 which is vibrationally excited in passing through the air shock prior to entering the mixing layer. Non resonance in vibrational energy in VV processes is supplied or absorbed by the local kinetic and rotational energy depending on the direction of the reaction. For both VT and VV processes, a significant amount of rate coefficient information was obtained from the results of past laser studies.

Excited state processes - these are chemical reactions in which the reactants are in excited internal energy states. By detailed balance arguments based on chemi-excitation reactions, excited state processes are expected to be important in the plume environment. A particularly significant excited state process is



This reaction between atmospheric O atoms and vibrationally excited H_2 may be the source reaction for the vibrationally excited OH observed in APOLLO at high altitudes. This reaction also generates ground state OH which can subsequently react with more H_2 to generate H_2O as outlined under chemi-excitation reactions above. The ground state reaction



has been extensively measured and is well known over the temperature range of interest in plume modeling. The activation energy of 9.5 kcal/mole represents a substantial barrier to the generation of OH in low temperature environments such as rocket plumes. However, if the $\text{H}_2(v=1)$ state, with an energy of 13 kcal/mole above $\text{H}_2(v=0)$, can provide this activation energy then the excited state reaction might proceed with near gas kinetic rate providing an important production reaction for OH. Unfortunately, this excited state reaction is not easily amenable to experimental determination, but current theoretical efforts underway at Wayne State University in collaboration with Brookhaven National Laboratory may permit evaluation of the rate and energy flow in this excited state reaction.

Fuel afterburning reactions - these are generally highly exothermic chemical reactions between atmospheric O atoms and partially reacted or unreacted fuel fragments which find their way into the plume gas through boundary layer flow, peripheral flows (turbine and exhaustorator flows), or incomplete combustion processes. Although the fraction of fuel fragments in the plume flow is generally small (of order 1%) the rate and energetics of fuel species make even this small amount significant in an overall radiation energy balance. An example of a fuel afterburning reaction is the the reaction



which proceeds very rapidly with an exothermicity of about 90 kcal/mole. As discussed in a later section of

this report, the H_2O molecule is likely to be highly vibrationally excited and this provides a substantial source of IR radiation.

DISCUSSION OF MODELS

It is not the intention of this paper to provide an exhaustive review of the four plume chemistry models, but to indicate their availability, to provide some measure of their reliability, and to present some preliminary calculations performed using these models. Although reports have been prepared detailing the four models [Fisher (1973a); Kummeler, Fisher, Boynton (1972, 1973)], a summary tabulating the reactions, rate coefficients and references are given in Appendix I.

Relaxation Model

In this section, we will present a calculation using the RELAXATION model on a TITAN core streamline. This calculation will indicate the detail included in the model as well as the methodology of reducing the size of the chemistry package for specific applications. A report detailing these TITAN core calculations is being prepared [Fisher (1973b)].

In Figure 1, the effective vibrational temperatures of important modes on an outermost TITAN core streamline are shown.

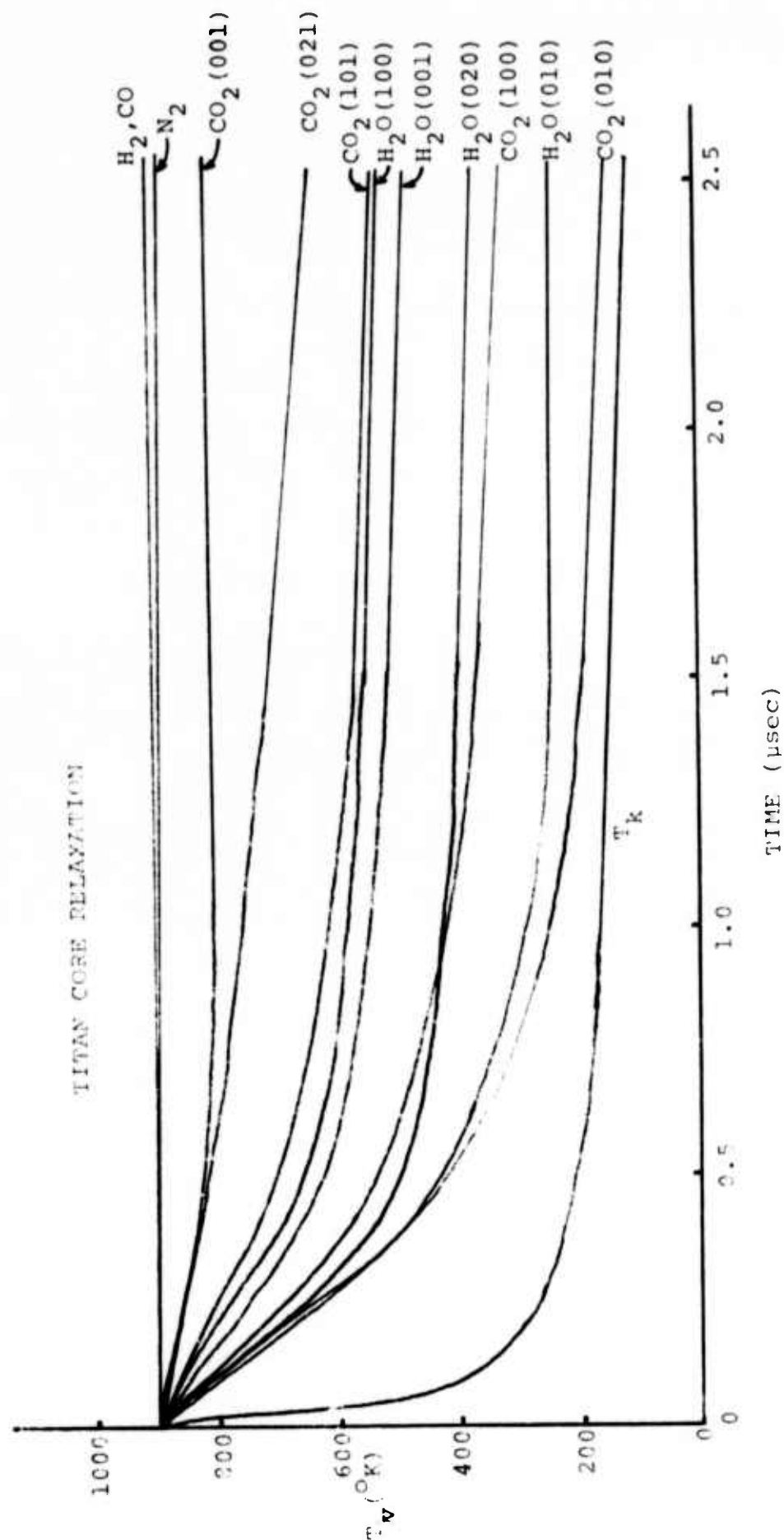


FIGURE 1. Vibrational temperatures in an "outermost" streamline of a TITAN core flow calculated using the RELAXATION Model [Fisher (1973b)].

The calculation was done using a Runge-Kutta-Merson integration procedure with algebraic subroutine for treating the chemistry which is in a quasi steady state. These quasi steady state reactions generally force the system of chemical reactions into a "stiff" condition which greatly increases integration time for standard integrations packages. The algebraic subroutine provides a mechanism to bypass this complication as has been extensively discussed before [Fisher, Kummler (1968)].

The general features that emerge from this calculation are that the diatomic molecules are vibrationally frozen at rear exit conditions; the bending modes of CO_2 and H_2O are nearly in equilibrium with the translational temperature while the stretching modes are partially frozen depending on the extent of VV coupling to the diatomic species. Due to the rapid VV transfer with $\text{N}_2(v=1)$, $\text{CO}_2(001)$ is rather vibrationally hot along this streamline. The modes of CO_2 which depend on $\text{CO}_2(001)$ as a source, i.e., $\text{CO}_2(021)$ and $\text{CO}_2(101)$ are also rather vibrationally hot but reflect the fact that the bending modes of CO_2 are rather vibrationally cold.

The RELAXATION model maintains the Fermi resonance between $\text{CO}_2(100)$ and $\text{CO}_2(020)$ as a VT process with nearly gas kinetic efficiency independent of the collision species, while the $\text{H}_2\text{O}(100)$ and (001) modes are assumed to be in quasi equi-

librium at the local kinetic temperature. This latter assumption stems from the closeness in energy resonance between these modes as well as the sparcity of data regarding the relaxation of higher vibrational levels in H_2O .

The code used in these calculations also provides a "picture" of the important rate processes involving each excited species. This output, called HISTORY, is provided at arbitrary time intervals in the calculation and permits evaluation of the significant reactions both supplying and destroying any particular level. Two such reaction profiles are shown in Tables I and II for two times. Note that the rate coefficients are not generally the same for the two tables reflecting the change in temperature while the difference in rates reflect not only the change in excited species density due to relaxation but also due to pressure. Both the translational temperature and pressure are printed at the top of the respective tables. By using these rate profiles, it is anticipated that the number of relaxation processes can be reduced for subsequent calculations in similar environments.

Since the hydrocarbon afterburning model has been discussed previously [Kummler, Fisher, Boynton (1972)], the amine afterburning model will be more extensively detailed here. Further background information can be obtained in report form [Kummler, Fisher, Boynton (1973)].

TABLE I

Chemical reactions, rate coefficients and separate rates at beginning of relaxation calculation in TITAN core flow as obtained from subroutine HISTORY [Fisher (1973b)].

KINETICS OF THE REACTIONS					
TIME = 0.0	SEC	PRES = 1.51E-01 ATM	TEMP = 898.00 K	CONSTANT	RATE
NO.	REACTIONS				
1.	H2* + H	= H2	+ H	6.731E-12	0.0
2.	H2 + H	= H2*	+ H	8.343E-15	0.0
3.	H2* + C	= H2	+ C	8.990E-12	0.0
4.	H2 + C	= H2*	+ C	1.114E-14	0.0
5.	H2* + H2	= H2	+ H2	8.271E-14	7.085E 18
6.	H2 + H2	= H2*	+ H2	1.025E-16	6.920E 18
7.	H2* + H2O	= H2	+ H2O	9.271E-14	1.040E 19
8.	H2 + H2O	= H2*	+ H2O	1.025E-16	1.015E 19
9.	H2* + H	= N2	+ H	2.889E-18	0.0
10.	N2 + H	= N2*	+ H	6.791E-20	0.0
11.	N2* + C	= N2	+ C	1.106E-14	0.0
12.	N2 + C	= N2*	+ C	2.598E-16	0.0
13.	N2* + H2	= N2	+ H2	1.610E-15	3.665E 18
14.	N2 + H2	= N2*	+ H2	3.785E-17	3.617E 18
15.	N2* + H2O	= N2	+ H2O	1.610E-15	5.378E 18
16.	N2 + H2O	= N2*	+ H2O	3.785E-17	5.307E 18
17.	OH* + H	= OH	+ H	3.000E-11	0.0
18.	OH + H	= OH*	+ H	9.603E-14	0.0
19.	OH* + O	= OH	+ O	3.000E-11	0.0
20.	OH + O	= OH*	+ O	9.603E-14	0.0
21.	OH* + H2	= OH	+ H2	1.000E-11	1.028E 14
22.	OH + H2	= OH*	+ H2	3.201E-14	1.008E 14
23.	OH* + H2O	= OH	+ H2O	3.000E-12	4.526E 13
24.	OH + H2O	= OH*	+ H2O	9.603E-15	4.436E 13
25.	H2O + C	= H2O	+ C	2.000E-10	0.0
26.	H2O + H	= H2O	+ H	1.536E-11	0.0
27.	H2O + O	= H2O	+ O	1.000E-11	0.0
28.	H2O + O	= H2O	+ O	7.679E-13	0.0
29.	H2O + H2	= H2O	+ H2	1.000E-11	7.071E 22
30.	H2O + H2	= H2O	+ H2	7.679E-13	7.008E 22
31.	H2O + H2O	= H2O	+ H2O	1.000E-11	1.038E 23
32.	H2O + H2O	= H2O	+ H2O	7.679E-13	1.028E 23
33.	H2O + H	= H2O	+ H	1.000E-11	0.0
34.	H2O + H	= H2O	+ H	2.372E-14	0.0
35.	H2O + O	= H2O	+ O	1.000E-11	0.0
36.	H2O + O	= H2O	+ O	2.372E-14	0.0
37.	H2O + H2	= H2O	+ H2	2.000E-13	4.423E 19

TABLE I (cont'd)

38.	H2O	000+	H2	=	H2O	001+	H2	4.744E-16	4.330E 19
39.	H2O	001+	H2O	=	H2O	000+	H2O	1.000E-12	3.245E 20
40.	H2O	000+	H2O	=	H2O	001+	H2O	2.372E-15	3.177E 20
41.	H2O	001+	H	=	H2O	020+	H	1.000E-11	0.0
42.	H2O	020+	H	=	H2O	001+	H	3.781E-12	0.0
43.	H2O	001+	O	=	H2O	020+	O	1.000E-11	0.0
44.	H2O	020+	O	=	H2O	001+	O	3.781E-12	0.0
45.	H2O	001+	H2	=	H2O	020+	H2	1.000E-11	2.212E 21
46.	H2O	020+	H2	=	H2O	001+	H2	3.781E-12	2.204E 21
47.	H2O	001+	H2O	=	H2O	020+	H2O	1.000E-11	3.245E 21
48.	H2O	020+	H2O	=	H2O	001+	H2O	3.781E-12	3.234E 21
49.	CO*	+	H	=	CO	+	H	2.889E-17	0.0
50.	CO	+	H	=	CO*	+	H	9.181E-19	0.0
51.	CO*	+	O	=	CO	+	O	4.759E-13	0.0
52.	CO	+	O	=	CO*	+	O	1.512E-14	0.0
53.	CO*	+	H2	=	CO	+	H2	3.947E-14	3.841E 19
54.	CO	+	H2	=	CO*	+	H2	1.254E-15	3.795E 19
55.	CO*	+	H2O	=	CO	+	H2O	3.947E-14	5.636E 19
56.	CO	+	H2O	=	CO*	+	H2O	1.254E-15	5.568E 19
57.	CO2	010+	H	=	CO2	000+	H	1.839E-12	0.0
58.	CO2	000+	H	=	CO2	010+	H	6.284E-13	0.0
59.	CO2	010+	O	=	CO2	000+	O	7.848E-13	0.0
60.	CO2	000+	O	=	CO2	010+	O	2.682E-13	0.0
61.	CO2	010+	H2	=	CO2	000+	H2	3.678E-12	2.258E 22
62.	CO2	000+	H2	=	CO2	010+	H2	1.257E-12	2.250E 22
63.	CO2	010+	H2O	=	CO2	000+	H2O	1.000E-11	9.009E 22
64.	CO2	000+	H2O	=	CO2	010+	H2O	3.417E-12	8.975E 22
65.	CO2	010+	CO2	=	CO2	000+	CO2	1.570E-13	4.459E 20
66.	CO2	000+	CO2	=	CO2	010+	CO2	5.363E-14	4.442E 20
67.	CO2	001+	H	=	CO2	000+	H	2.889E-17	0.0
68.	CO2	000+	H	=	CO2	001+	H	6.590E-19	0.0
69.	CO2	001+	O	=	CO2	000+	O	4.759E-13	0.0
70.	CO2	000+	O	=	CO2	001+	O	1.086E-14	0.0
71.	CO2	001+	H2	=	CO2	000+	H2	3.947E-14	1.633E 19
72.	CO2	000+	H2	=	CO2	001+	H2	9.002E-16	1.612E 19
73.	CO2	001+	H2O	=	CO2	000+	H2O	3.947E-14	2.396E 19
74.	CO2	000+	H2O	=	CO2	001+	H2O	9.002E-16	2.365E 19
75.	CO2	001+	H	=	CO2	030+	H	5.084E-14	0.0
76.	CO2	030+	H	=	CO2	001+	H	2.600E-14	0.0
77.	CO2	001+	O	=	CO2	030+	O	2.892E-13	0.0
78.	CO2	030+	O	=	CO2	001+	O	1.479E-13	0.0

TABLE I (cont'd)

79.	C02 C01+ H2	= C02 C30+ H2	1.019E-13	4.218E 19
80.	C02 C30+ H2	= C02 C01+ H2	5.212E-14	4.208E 19
81.	C02 C01+ H2O	= C02 C30+ H2O	2.870E-13	1.743E 20
82.	C02 C30+ H2O	= C02 C01+ H2O	1.468E-13	1.738E 20
83.	C02 C01+ C02	= C02 C30+ C02	5.760E-14	1.103E 19
84.	C02 C30+ C02	= C02 C01+ C02	2.945E-14	1.100E 19
85.	C02 C01+ C0	= C02 C30+ C0	4.320E-14	8.270E 18
86.	C02 C30+ C0	= C02 C01+ C0	2.209E-14	8.250E 18
87.	C02 C01+ N2	= C02 C30+ N2	4.320E-14	2.589E 19
88.	C02 C30+ N2	= C02 C01+ N2	2.209E-14	2.583E 19
89.	H2* + H2O C02	= H2 + H2O C01	3.189E-13	3.577E 19
90.	H2 + H2O C01	= H2* + H2O C02	1.666E-13	3.569E 19
91.	H2* + OH	= H2 + OH*	1.000E-12	3.869E 12
92.	H2 + OH*	= H2* + OH	3.872E-13	3.856E 12
93.	N2* + H2O C01	= N2 + H2O C01	3.000E-13	6.929E 19
94.	N2 + H2O C01	= N2* + H2O C02	2.282E-13	6.922E 19
95.	N2* + H2O C02	= N2 + H2O C01	1.235E-13	3.680E 20
96.	N2 + H2O C02	= N2* + H2O C02	3.779E-14	3.665E 20
97.	H2O C01+ H2O C02	= H2O C02+ H2O C02	2.997E-11	2.150E 22
98.	H2O C02+ H2O C02	= H2O C01+ H2O C02	2.816E-11	2.150E 22
99.	C02 C01+ H2O C02	= C02 C01+ H2O C01	1.000E-13	5.419E 19
100.	C02 C01+ H2O C01	= C02 C01+ H2O C02	8.694E-14	5.417E 19
101.	N2* + C02 C02	= N2 + C02 C01	2.965E-13	1.734E 20
102.	N2 + C02 C01	= N2* + C02 C02	3.055E-13	1.734E 20
103.	N2* + C0	= N2 + C0*	4.911E-14	4.854E 19
104.	N2 + C0*	= N2* + C0	3.633E-14	4.849E 19
105.	C02 C01+ C0	= C02 C02+ C0*	6.884E-13	1.237E 20
106.	C02 C02+ C0*	= C02 C01+ C0	4.942E-13	1.236E 20
107.	C02 C01+ H2O C02	= C02 C02+ H2O C01	5.993E-12	3.629E 20
108.	C02 C02+ H2O C01	= C02 C01+ H2O C02	6.390E-12	3.630E 20
109.	C02 C01+ H2O C02	= C02 C02+ H2O C01	5.993E-12	4.309E 20
110.	C02 C02+ H2O C01	= C02 C01+ H2O C02	7.590E-12	4.312E 20
111.	C02 C01+ C02 C02	= C02 C02+ C02 C01	5.993E-10	7.119E 21
112.	C02 C02+ C02 C01	= C02 C01+ C02 C02	6.205E-10	7.120E 21
113.	C02 C02+ C02 C02	= C02 C02+ C02 C01	1.199E-11	7.016E 21
114.	C02 C01+ C02 C02	= C02 C02+ C02 C02	1.297E-11	7.018E 21
115.	H2O C02+ H	= H2O C01+ H	4.000E-10	0.0

TABLE I (cont'd)

116.	H2O	O10+ H	= H2O	O20+ H	3.268E-11	0.0
117.	H2O	O20+ O	= H2O	O10+ O	2.000E-11	0.0
118.	H2O	O10+ O	= H2O	O20+ O	1.634E-12	0.0
119.	H2O	O20+ H2	= H2O	O10+ H2	2.000E-11	1.166E 22
120.	H2O	O10+ H2	= H2O	O20+ H2	1.634E-12	1.156E 22
121.	H2O	O20+ H2O	= H2O	O10+ H2O	2.000E-11	1.711E 22
122.	H2O	O10+ H2O	= H2O	O20+ H2O	1.634E-12	1.696E 22
123.	CO2	O20+ H	= CO2	O10+ H	3.678E-12	0.0
124.	CO2	O10+ H	= CO2	O20+ H	1.360E-12	0.0
125.	CO2	O20+ O	= CO2	O10+ O	1.570E-12	0.0
126.	CO2	O10+ O	= CO2	O20+ O	5.804E-13	0.0
127.	CO2	O20+ H2	= CO2	O10+ H2	7.260E-12	1.654E 22
128.	CO2	O10+ H2	= CO2	O20+ H2	2.685E-12	1.648E 22
129.	CO2	O20+ H2O	= CO2	O10+ H2O	2.000E-11	6.686E 22
130.	CO2	O10+ H2O	= CO2	O20+ H2O	7.396E-12	6.663E 22
131.	CO2	O20+ CO2	= CO2	O10+ CO2	3.139E-13	3.309E 20
132.	CO2	O10+ CO2	= CO2	O20+ CO2	1.161E-13	3.297E 20
133.	CO2	O30+ H	= CO2	O20+ H	5.808E-12	0.0
134.	CO2	O20+ H	= CO2	O30+ H	2.050E-12	0.0
135.	CO2	O30+ O	= CO2	O20+ O	2.354E-12	0.0
136.	CO2	O20+ O	= CO2	O30+ O	8.312E-13	0.0
137.	CO2	O30+ H2	= CO2	O20+ H2	1.113E-11	8.987E 21
138.	CO2	O20+ H2	= CO2	O30+ H2	3.930E-12	8.954E 21
139.	CO2	O30+ H2O	= CO2	O20+ H2O	3.000E-11	3.554E 22
140.	CO2	O20+ H2O	= CO2	O30+ H2O	1.059E-11	3.541E 22
141.	CO2	O30+ CO2	= CO2	O20+ CO2	4.777E-13	1.784E 20
142.	CO2	O20+ CO2	= CO2	O30+ CO2	1.687E-13	1.778E 20
143.	H2O	O20+ HV	= H2O	O30+ HV	1.400E-01	1.386E 14
144.	H2O	O10+ HV	= H2O	O20+ HV	4.500E-02	1.205E 15
145.	H2O	O00+ HV	= H2O	O00+ HV	1.400E-02	1.173E 13
146.	H2O	O20+ HV	= H2O	O10+ HV	2.200E-02	4.858E 13
147.	CO2	O10+ HV	= CO2	O00+ HV	3.300E-01	7.676E 15
148.	CO2	O00+ HV	= CO2	O00+ HV	2.500E-03	3.919E 12
149.	CO2	O00+ HV	= CO2	O00+ HV	9.100E-02	1.594E 13
150.	OH*	+ HV	= OH	+ HV	3.000E-01	1.169E 07
151.	CO2	O20+ M	= CO2	O20+ M	1.000E-10	9.029E 23
152.	CO2	O20+ M	= CO2	O20+ M	8.475E-11	9.024E 23

TABLE II

Chemical reactions, rate coefficients and individual rates at 1.62 μ sec in TITAN core flow as obtained from subroutine HISTORY [Fisher (1973b)].

KINETICS OF THE REACTIONS						
TIME = 1.620E-06 SEC		PRES = 1.861E-04 ATM		TEMP = 140.26 K		
NO.	REACTIONS	CONSTANT	RATE			
1.	H2* + H	1.480E-15	0.0	H2 + H	1.480E-15	0.0
2.	H2 + H	3.628E-34	0.0	H2 + H	3.628E-34	0.0
3.	H2* + O	3.553E-12	0.0	H2 + O	3.553E-12	0.0
4.	H2 + O	8.710E-31	0.0	H2 + O	8.710E-31	0.0
5.	H2* + H2	3.593E-19	3.050E 13	H2 + H2	3.593E-19	3.050E 13
6.	H2 + H2	8.809E-38	5.946E-03	H2 + H2	8.809E-38	5.946E-03
7.	H2* + H2O	3.593E-19	4.475E 13	H2 + H2O	3.593E-19	4.475E 13
8.	H2 + H2O	8.809E-38	8.725E-03	H2 + H2O	8.809E-38	8.725E-03
9.	N2* + H	2.735E-26	0.0	N2 + H	2.735E-26	0.0
10.	N2 + H	1.019E-36	0.0	N2 + H	1.019E-36	0.0
11.	N2* + O	1.433E-15	0.0	N2 + O	1.433E-15	0.0
12.	N2 + O	5.340E-26	0.0	N2 + O	5.340E-26	0.0
13.	N2* + H2	7.594E-22	1.671E 12	N2 + H2	7.594E-22	1.671E 12
14.	N2 + H2	2.829E-32	2.706E 03	N2 + H2	2.829E-32	2.706E 03
15.	N2* + H2O	7.594E-22	2.451E 12	N2 + H2O	7.594E-22	2.451E 12
16.	N2 + H2O	2.829E-32	3.970E 03	N2 + H2O	2.829E-32	3.970E 03
17.	OH* + H	3.000E-11	0.0	OH + H	3.000E-11	0.0
18.	OH + H	3.197E-27	0.0	OH + H	3.197E-27	0.0
19.	OH* + O	3.000E-11	0.0	OH + O	3.000E-11	0.0
20.	OH + O	3.197E-27	0.0	OH + O	3.197E-27	0.0
21.	OH* + H2	1.000E-11	2.902E 12	OH + H2	1.000E-11	2.902E 12
22.	OH + H2	1.066E-27	3.365E 00	OH + H2	1.066E-27	3.365E 00
23.	OH* + H2O	3.000E-12	1.278E 12	OH + H2O	3.000E-12	1.278E 12
24.	OH + H2O	3.197E-28	1.481E 00	OH + H2O	3.197E-28	1.481E 00
25.	H2O + H	2.000E-10	0.0	H2O + H	2.000E-10	0.0
26.	H2O + H	1.459E-17	0.0	H2O + H	1.459E-17	0.0
27.	H2O + O	1.000E-11	0.0	H2O + O	1.000E-11	0.0
28.	H2O + O	7.296E-19	0.0	H2O + O	7.296E-19	0.0
29.	H2O + H2	1.000E-11	6.659E 19	H2O + H2	1.000E-11	6.659E 19
30.	H2O + H2	7.296E-19	7.232E 16	H2O + H2	7.296E-19	7.232E 16
31.	H2O + H2O	1.000E-11	9.770E 19	H2O + H2O	1.000E-11	9.770E 19
32.	H2O + H2O	7.296E-19	1.061E 17	H2O + H2O	7.296E-19	1.061E 17
33.	H2O + H	1.000E-11	0.0	H2O + H	1.000E-11	0.0
34.	H2O + H	1.565E-28	0.0	H2O + H	1.565E-28	0.0
35.	H2O + O	1.000E-11	0.0	H2O + O	1.000E-11	0.0
36.	H2O + O	1.565E-28	0.0	H2O + O	1.565E-28	0.0
37.	H2O + H2	2.000E-13	4.949E 17	H2O + H2	2.000E-13	4.949E 17

TABLE II (cont'd)

38.	H2O	COO + H2	= H2O	COO + H2	3.130E-32	3.102E 05
39.	H2O	COO + H2O	= H2O	COO + H2O	1.000E-12	3.631E 18
40.	H2O	COO + H2O	= H2O	COO + H2O	1.565E-29	2.276E 06
41.	H2O	COO + H	= H2O	COO + H	1.000E-11	0.0
42.	H2O	COO + H	= H2O	COO + H	1.975E-14	0.0
43.	H2O	COO + O	= H2O	COO + O	1.000E-11	0.0
44.	H2O	COO + O	= H2O	COO + O	1.975E-14	0.0
45.	H2O	COO + H2	= H2O	COO + H2	1.000E-11	2.475E 19
46.	H2O	COO + H2	= H2O	COO + H2	1.975E-14	2.105E 16
47.	H2O	COO + H2O	= H2O	COO + H2O	1.000E-11	3.631E 19
48.	H2O	COO + H2O	= H2O	COO + H2O	1.975E-14	3.089E 16
49.	CO*	CO + H	= CO*	CO + H	2.735E-25	0.0
50.	CO	CO + H	= CO*	CO + H	7.026E-35	0.0
51.	CO*	CO + O	= CO*	CO + O	9.425E-17	0.0
52.	CO	CO + O	= CO*	CO + O	2.421E-26	0.0
53.	CO*	CO + H2	= CO	CO + H2	1.013E-18	9.918E 14
54.	CO	CO + H2	= CO*	CO + H2	2.602E-28	7.873E 06
55.	CO*	CO + H2O	= CO	CO + H2O	1.013E-18	1.455E 15
56.	CO	CO + H2O	= CO*	CO + H2O	2.602E-28	1.155E 07
57.	CO2	COO + H	= CO2	COO + H	9.876E-13	0.0
58.	CO2	COO + H	= CO2	COO + H	1.020E-15	0.0
59.	CO2	COO + O	= CO2	COO + O	8.403E-16	0.0
60.	CO2	COO + O	= CO2	COO + O	8.681E-19	0.0
61.	CO2	COO + H2	= CO2	COO + H2	1.975E-12	2.873E 20
62.	CO2	COO + H2	= CO2	COO + H2	2.040E-15	5.859E 19
63.	CO2	COO + H2O	= CO2	COO + H2O	1.000E-11	2.134E 21
64.	CO2	COO + H2O	= CO2	COO + H2O	1.033E-14	4.352E 20
65.	CO2	COO + CO2	= CO2	COO + CO2	1.681E-16	1.131E 16
66.	CO2	COO + CO2	= CO2	COO + CO2	1.736E-19	2.306E 15
67.	CO2	COO + H	= CO2	COO + H	2.735E-25	0.0
68.	CO2	COO + H	= CO2	COO + H	8.413E-36	0.0
69.	CO2	COO + O	= CO2	COO + O	9.425E-17	0.0
70.	CO2	COO + O	= CO2	COO + O	2.899E-27	0.0
71.	CO2	COO + H2	= CO2	COO + H2	1.013E-18	4.369E 14
72.	CO2	COO + H2	= CO2	COO + H2	3.116E-29	8.948E 05
73.	CO2	COO + H2O	= CO2	COO + H2O	1.013E-18	6.411E 14
74.	CO2	COO + H2O	= CO2	COO + H2O	3.116E-29	1.313E 06
75.	CO2	COO + H	= CO2	COO + H	3.278E-15	0.0
76.	CO2	COO + H	= CO2	COO + H	4.473E-17	0.0
77.	CO2	COO + O	= CO2	COO + O	7.598E-15	0.0
78.	CO2	COO + O	= CO2	COO + O	1.037E-16	0.0

TABLE II (cont'd)

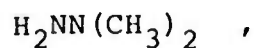
79.	CO2 001+ H2	= CO2 030+ H2	6.571E-15	2.833E 18
80.	CO2 030+ H2	= CO2 001+ H2	8.966E-17	1.406E 14
81.	CO2 001+ H2O	= CO2 030+ H2O	9.852E-14	6.234E 19
82.	CO2 030+ H2O	= CO2 001+ H2O	1.344E-15	3.094E 15
83.	CO2 001+ CO2	= CO2 030+ CO2	1.513E-15	3.018E 17
84.	CO2 030+ CO2	= CO2 001+ CO2	2.065E-17	1.498E 13
85.	CO2 001+ CO	= CO2 030+ CO	1.135E-15	2.264E 17
86.	CO2 030+ CO	= CO2 001+ CO	1.548E-17	1.123E 13
87.	CO2 001+ N2	= CO2 030+ N2	1.135E-15	7.088E 17
88.	CO2 030+ N2	= CO2 001+ N2	1.548E-17	3.518E 13
89.	H2* + H2O 000	= H2 + H2O 001	4.684E-15	5.655E 17
90.	H2 + H2O 001	= H2* + H2O 000	7.337E-17	1.759E 14
91.	H2* + OH*	= H2 + OH*	1.000E-12	3.846E 12
92.	H2 + OH*	= H2* + OH	2.300E-15	6.467E 08
93.	N2* + H2O 010	= N2 + H2O 001	3.000E-13	6.306E 16
94.	N2 + H2O 001	= N2* + H2O 010	5.211E-14	1.770E 17
95.	N2* + H2O 000	= N2 + H2O 010	4.194E-16	1.313E 18
96.	N2 + H2O 010	= N2* + H2O 000	2.141E-19	1.957E 12
97.	H2O 010+ H2O 010	= H2O 020+ H2O 000	1.184E-11	7.535E 15
98.	H2O 020+ H2O 000	= H2O 010+ H2O 010	7.957E-12	1.207E 19
99.	CO2 001+ H2O 000	= CO2 010+ H2O 010	1.000E-13	6.134E 19
100.	CO2 010+ H2O 010	= CO2 001+ H2O 000	4.581E-14	5.671E 14
101.	N2* + CO2 000	= N2 + CO2 001	1.154E-12	1.046E 21
102.	N2 + CO2 001	= N2* + CO2 000	1.398E-12	8.274E 20
103.	N2* + CO	= N2 + CO*	5.554E-15	4.828E 18
104.	N2 + CO*	= N2* + CO	7.330E-16	9.849E 17
105.	CO2 001+ CO	= CO2 000+ CO*	4.750E-14	8.893E 18
106.	CO2 000+ CO*	= CO2 001+ CO	5.688E-15	2.294E 18
107.	CO2 001+ H2O 000	= CO2 000+ H2O 001	2.369E-12	7.698E 18
108.	CO2 000+ H2O 001	= CO2 001+ H2O 000	3.569E-12	3.639E 18
109.	CO2 001+ H2O 000	= CO2 000+ H2O 001	2.369E-12	6.143E 19
110.	CO2 000+ H2O 001	= CO2 001+ H2O 000	1.075E-11	1.096E 19
111.	CO2 001+ CO2 000	= CO2 000+ CO2 001	2.369E-10	2.230E 20
112.	CO2 000+ CO2 001	= CO2 001+ CO2 000	2.959E-10	2.184E 20
113.	CO2 020+ CO2 000	= CO2 010+ CO2 010	4.737E-12	3.700E 19
114.	CO2 010+ CO2 010	= CO2 020+ CO2 000	7.856E-12	2.385E 18
115.	H2O 020+ H	= H2O 010+ H	4.000E-10	0.0

TABLE II (cont'd)

116.	H2O	010+ H	= H2O	020+ H	4.344E-17	0.0
117.	H2O	020+ O	= H2O	010+ O	2.000E-11	0.0
118.	H2O	010+ O	= H2O	020+ O	2.172E-18	0.0
119.	H2O	020+ H2	= H2O	010+ H2	2.000E-11	2.132E 19
120.	H2O	010+ H2	= H2O	020+ H2	2.172E-18	1.446E 13
121.	H2O	020+ H2O	= H2O	010+ H2O	2.000E-11	3.128E 19
122.	H2O	010+ H2O	= H2O	020+ H2O	2.172E-18	2.122E 13
123.	CO2	020+ H	= CO2	010+ H	1.975E-12	0.0
124.	CO2	010+ H	= CO2	020+ H	3.384E-15	0.0
125.	CO2	020+ O	= CO2	010+ O	1.681E-15	0.0
126.	CO2	010+ O	= CO2	020+ O	2.879E-18	0.0
127.	CO2	020+ H2	= CO2	010+ H2	3.898E-12	7.389E 19
128.	CO2	010+ H2	= CO2	020+ H2	6.679E-15	9.715E 17
129.	CO2	020+ H2O	= CO2	010+ H2O	2.000E-11	5.562E 20
130.	CO2	010+ H2O	= CO2	020+ H2O	3.427E-14	7.313E 18
131.	CO2	020+ CO2	= CO2	010+ CO2	3.361E-16	2.947E 15
132.	CO2	010+ CO2	= CO2	020+ CO2	5.759E-19	3.875E 13
133.	CO2	030+ H	= CO2	020+ H	3.119E-12	0.0
134.	CO2	020+ H	= CO2	030+ H	3.971E-15	0.0
135.	CO2	030+ O	= CO2	020+ O	2.521E-15	0.0
136.	CO2	020+ O	= CO2	030+ O	3.210E-18	0.0
137.	CO2	030+ H2	= CO2	020+ H2	5.977E-12	9.374E 18
138.	CO2	020+ H2	= CO2	030+ H2	7.612E-15	1.443E 17
139.	CO2	030+ H2O	= CO2	020+ H2O	3.000E-11	6.903E 19
140.	CO2	020+ H2O	= CO2	030+ H2O	3.820E-14	1.062E 18
141.	CO2	030+ CO2	= CO2	020+ CO2	5.115E-16	3.711E 14
142.	CO2	020+ CO2	= CO2	030+ CO2	6.513E-19	5.711E 12
143.	H2O	100	= H2O	000+ HV	1.400E-01	3.655E 12
144.	H2O	010	= H2O	000+ HV	4.500E-02	1.135E 12
145.	H2O	001	= H2O	000+ HV	1.400E-02	1.312E 11
146.	H2O	020	= H2O	010+ HV	2.200E-02	8.884E 10
147.	CO2	010	= CO2	000+ HV	3.300E-01	1.818E 14
148.	CO2	001	= CO2	000+ HV	2.500E-03	4.084E 12
149.	CO2	101	= CO2	000+ HV	9.100E-02	7.876E 11
150.	OH*		= OH	+ HV	3.000E-01	3.298E 05
151.	CO2	100+ M	= CO2	020+ M	1.000E-10	4.397E 20
152.	CO2	020+ M	= CO2	100+ M	3.468E-11	2.423E 19

Chemical Models: Substituted Hydrazine

The chemistry of $\text{RHNNR}'\text{R}''$ compounds is quite different from the hydrogen and hydrocarbon chemistry reviewed previously [Kummler, Fisher, Boynton (1972)] because of the characteristic strong NN bonding. In addition, the different chemical behavior of unsymmetrical dimethyl hydrazine (UDMH),

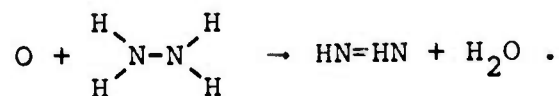


and hydrazine or monomethyl hydrazine (MMH),

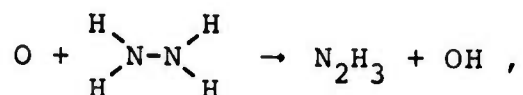


precludes some of the simplicity of the generalizations inherent in the lumped parameter approach to the hydrocarbon oxidation. Major radiating steps in the plume appear to be associated with the initial attack of O atoms on the fuel-like species, rather than the secondary reactions of products of the initial attack as in hydrocarbon oxidation.

Oxygen atom attack on hydrazine has been studied using high intensity crossed molecular beams [Gehring, et al (1970), Foner and Hudson (1970)]. The products of the reaction have been found to be $\text{N}_2\text{H}_2 + \text{H}_2\text{O}$, via the elementary reaction:

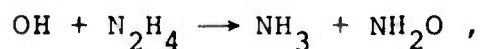


This reaction is highly exothermic (90 kcal) and forms a completely new water molecule by simultaneously abstracting two hydrogen atoms. The expected (from, for example, the analogous O attack on ethylene) atom transfer reaction,



which is 26 kcal exothermic, is about 1/25 as probable [Foner and Hudson (1970)]. The reaction of O + UDMH can only produce OH.

Once significant quantities of OH become available through the latter reactions, additional processes are possible. Again, high intensity molecular beams [Gehring, et al (1970)] have been used to identify the products of the reaction:



which is the key reaction in severing the N-N bond.

The likely mechanism for oxidation of substituted hydrazine compounds is illustrated schematically in Figure 2. The reaction rate constants for the principal reactions are given in Table III. A more complete literature review of pertinent reactions has been given by Kummeler, Fisher and Boynton (1973), while a summary of the Amine model is given in Appendix I.

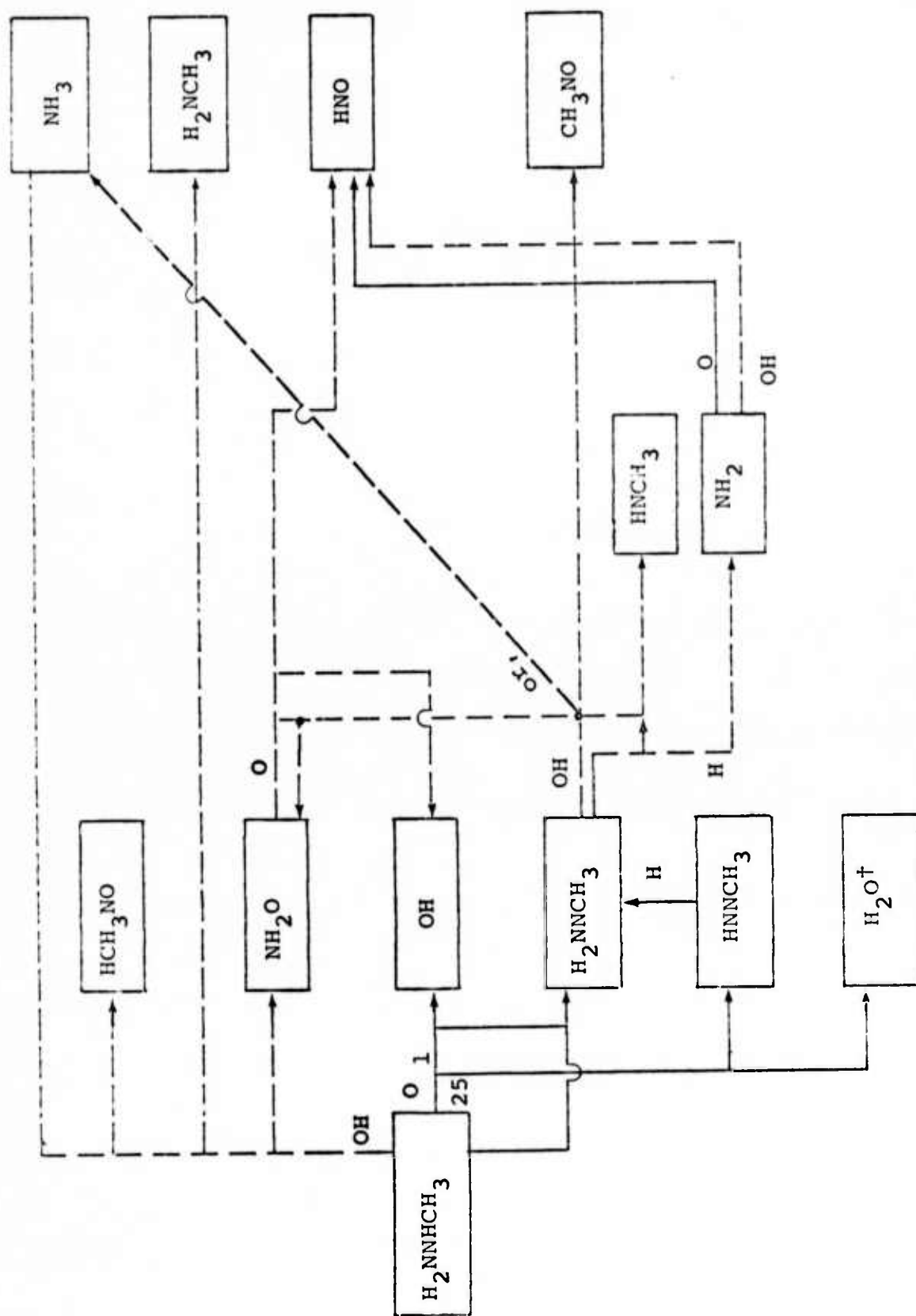


FIGURE 2. Simplified O atom oxidation mechanism for NNH (UDMH and N_2H_4 are similar) illustrating the stable species which can form in this system as intermediates. The dotted lines represent reactions which are probable, but which have not yet been experimentally observed.

TABLE III
INFRARED HYDRAZINE MODEL A

FUEL CHEMI-EXCITATION REACTIONS

<u>Reaction</u>	<u>Assumed Products*</u>	<u>Forward Rate Constant cc/sec</u>	<u>Reaction Energy kcal/gmole</u>	<u>Reference</u>
O + MMH $\rightarrow$ NH ₂ CH ₃ + H ₂ O(001)	(100)	2×10^{-11}	-102	Foner and Hudson (1970)
	H ₂ O(020)			
	(010)			
O + N ₂ H ₄ $\rightarrow$ N ₂ H ₂ + H ₂ O(001)	(100)	1.8×10^{-11}	-90	Gehring, <u>et al</u> (1969)
	H ₂ O(020)			
	(010)			
O + UDMH $\rightarrow$ HN ₂ (CH ₃) ₂ + OH		1×10^{-12}	-25	Analogy
OH + N ₂ H ₄ $\rightarrow$ NH ₃ + NH ₂ O		2×10^{-11}	?	Gehring, <u>et al</u> (1970)

* This puts about 40% of the reaction energy into the stretching modes of product H₂O. (For purposes of computational convenience, we have treated a molecule excited to the second level as two singly-excited molecules; the quenching is thus somewhat more efficient than it should be.)

The salient features of Figure 2 have been examined experimentally in the Wayne State University discharge flow system. Comparative results for $O + N_2H_4$ chemiluminescence are presented in Figure 3. The reaction of $H + NO_2$ produces OH, but is not sufficiently exothermic to produce more than $v=2$ in the product molecule. Hence, the OH fundamental between 2.7μ and 3.0μ is broader than the overtone at 1.5μ . (The instrumental response has not been taken out of Figure 2, so that the overtone appears larger than the fundamental. Calibration with the $NO + O$ glow reverses this effect and gives excellent agreement with observed values of the overtone to fundamental intensity ratio.) For the reaction of $O + C_2H_4$ the overtone shows hot bands consistent with the greater available energy. The CO overtone at 2.3μ also appears and the intensity ratio of the overtone to fundamental ratio under these conditions indicates that some $H_2O(100)$ and $H_2O(001)$ radiation may be present. The reaction of $O + N_2H_4$ exhibits a much broader peak at 2.7μ indicative of $H_2O(100)$ and (001) radiation and a band at 1.9μ also indicative of H_2O emission is present. The emission of these systems will be analyzed in detail elsewhere.

In order to assess the potential magnitude of the resulting infrared emission, we have taken the mechanism of Figure 2 and reduced it to the simplest form consistent with the production and loss of vibrationally excited H_2O . We have also

included a number of VT and VV excitation and de-excitation reactions for H_2O in order to have a basis for comparing calculations with and without chemi-excitation and to provide for quenching of excited species produced by reaction. The mechanism is presented in Appendix I; rate data for the H_2O VV and VT processes are the same as we have used in calculations on the Apollo system [Boynton (1973)] and follow the recommendations of the Plume Chemistry Workshop held at Physical Dynamics, Berkeley, in January 1973 [Fisher (1973a)].

The rate equations for the above mechanism were integrated through a flow field simulating the mixing layer of a Titan II exhaust plume at 120 km. Details of the flow field calculation will be presented in a separate report, but a brief outline is presented here. The exit plane conditions are taken from an unpublished nozzle flow calculation by D. Thomas (Aerospace Corp.) who included finite-rate chemistry and film cooling effects. External flow calculations were performed with the MULTITUBE and BOW codes [Boynton (1971)]. Unburned fuel concentrations of 5% in the film cooling layer and 1% in the interior exhaust gases were assumed; reactions of N_2H_4 and UDMH with O were included in the flow field calculation, so that depletion of these species would be properly accounted for in a subsequent (overlay) chemistry calculation.

Figure 3. A comparison of the infrared emission spectra for the reactions $O + N_2H_4$, $O + C_2H_4$ and $H + NO_2$. Concentrations of O and H were approximately 10μ and the concentrations of N_2H_4 , C_2H_4 and NO_2 were approximately 2μ , 10μ and 4.5μ respectively. All spectra were taken at a contact time of less than 2 msec. Both O and H were diluted in a stream consisting primarily of He.

$H + NO_2 \rightarrow$; 2000 μ slits, 50 μ vFS, 100 μ FS, $\tau = 10$, 1 RPM, $\frac{5 \text{ min}}{\text{in}}$,
800 μ He, 200 μ H_2 , 5 μ NO_2 , 5 μ H, 1st window.

$O + C_2H_4 \rightarrow$; 1000 μ slits, 50 μ vFS, 100 μ FS, $\tau = 10$, 1 RPM, $\frac{5 \text{ min}}{\text{in}}$,
10 μ C_2H_4 , 800 μ He, 200 μ O_2 , 1st window.

$O + N_2H_4 \rightarrow$; 2000 μ slits, 20 μ vFS, 100 μ FS, $\tau = 3, 4$ RPM, $\frac{2 \text{ min}}{\text{in}}$,
2 μ N_2H_4 , 900 μ He, 90 μ O_2 , 11 μ O, 1st window.

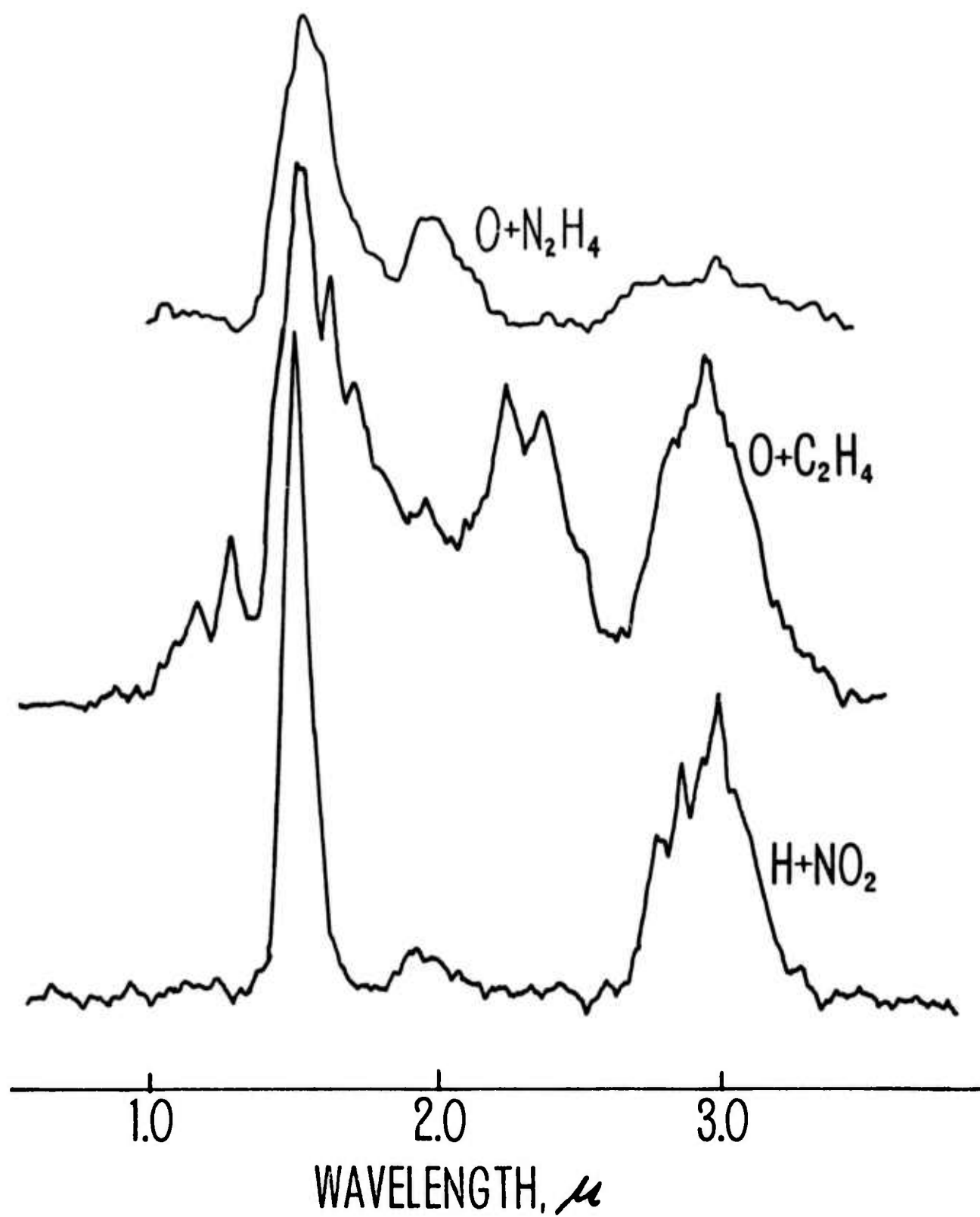


FIGURE 3.

Results of these exploratory calculations are shown in Figure 4. We show cumulative radiant intensity as a function of distance behind the vehicle for the sum of the H_2O (100) and (001) bands and the OH band (which is negligible in this calculation because important formation mechanisms such as $\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$ have not been included). The lower curve is for the H_2O excitation processes alone, and the upper curve includes the effects of the simplified chemi-excitation mechanism.

With the assumption of product energy distribution together with those about initial fuel concentrations, there is a substantial difference in calculated radiant intensity with and without chemiluminescent reaction.

These calculations may overestimate the contribution of chemiluminescence to the plume signature for any or all of the following reasons:

- 1) The exhaust-gas concentrations of N_2H_4 and UDMH may be too high. In that connection, note that N_2H_4 (the major reacting species in this system) is a good mono-propellant and decomposes spontaneously at elevated temperatures to give less reactive NH_3 , N_2 , and H_2 . The amount of external reaction may depend on the extent of such decomposition as well as the overall unburned fuel level. This should not be the case with MMH, which is more stable.

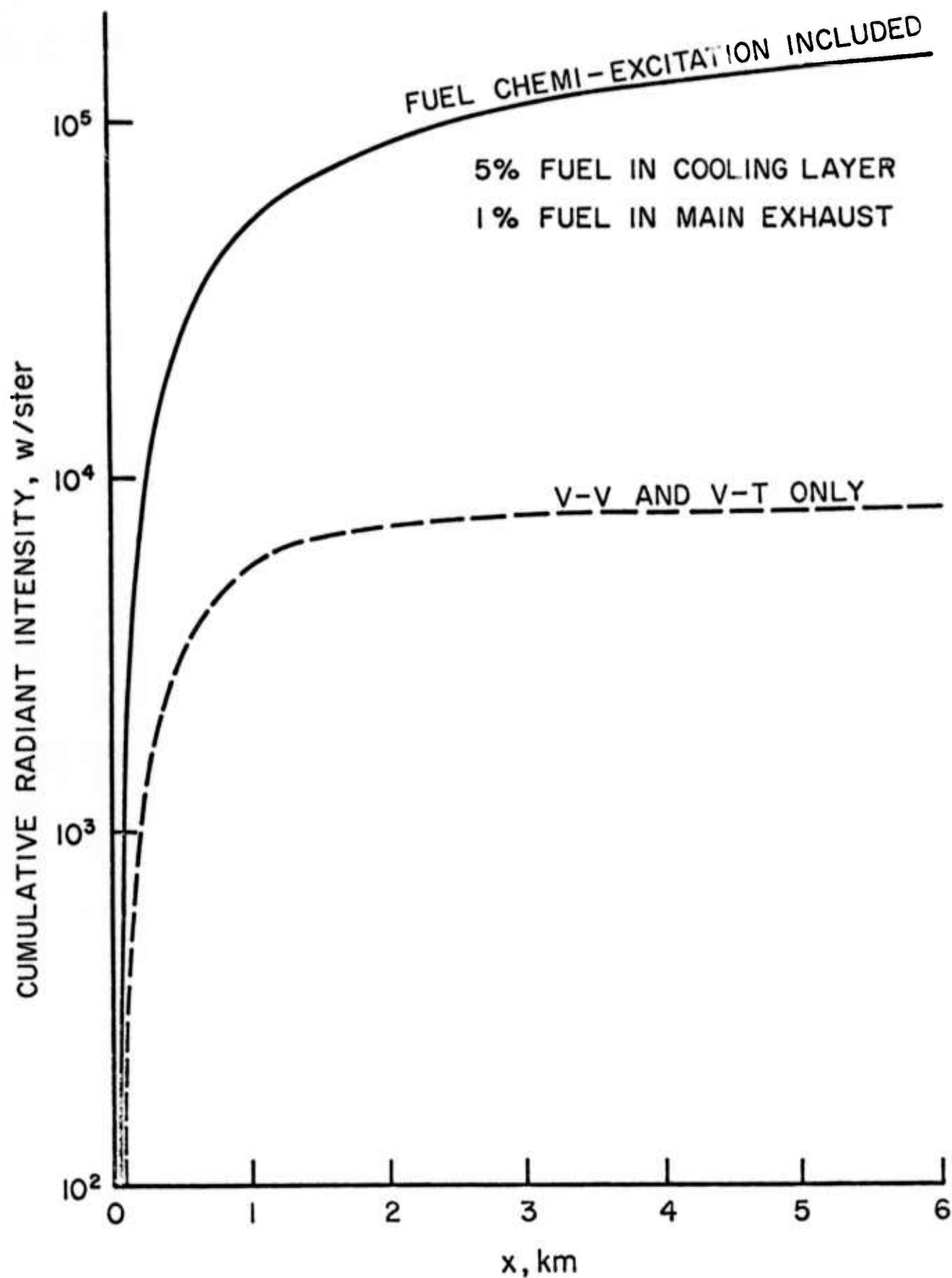


FIGURE 4. The effect of chemi-excitation on predicted cumulative radiant intensity.

- 2) The photon yields may be optimistic, although a rather drastic decrease would still allow substantial chemi-excitation relative to VT and VV excitation.
- 3) Unburned fuel could be ejected from the engine or turbine exhaust in the form of droplets which would have to be vaporized in the plume before reacting. [Webber, et al (1972), using a detailed combustion code to evaluate the external surface contamination potential due to unburned propellants from two small engines, indicates that essentially all unburned propellant leaving these engines is in the form of small droplets.]

However, even with these qualifications, it is evident that there is a distinct possibility that external chemiluminescence of unburned fuel species comprises a substantial fraction of amine-fueled missile plume signatures. This possibility should not be ignored in studies aimed at elucidating plume emission mechanisms.

SUMMARY

The availability of baseline chemistry models for four rocket plume environments has been established. The mechanism for determining the important relaxation processes in systems involving non-equilibrium distributions of N_2 , H_2 , CO , O , H , H_2O and CO_2 has been presented and preliminary calculations shown. An amine/substituted hydrazine model has been detailed and calculations appropriate to the TITAN mixing layer presented. As was found in the case of hydrocarbon afterburning in the ATLAS vehicle [Fisher (1973c)], minor quantities of unreacted amine or hydrazine in the plume flow can lead to a significant amount of plume radiation in the IR.

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APPENDIX I
BASELINE CHEMISTRY MODELS

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(1) APOLLO MODEL

<u>Reaction</u>	<u>Reference</u>	<u>Rate Constant (cc/molecule-sec)</u>
1) $O + H_2 \rightarrow OH + H$	(a,b)	$1.65^{-13} \exp(-2500/T)$
2) $H + OH \rightarrow O + H_2$	(c)	$6.9^{-14} \exp(-1425/T)$
3) $O + H_2(v=1) \rightarrow OH + H$	(d)	$1.3^{-10} \alpha \ (\alpha = 0.9, 0.5)$
4) $H + OH \rightarrow O + H_2(v=1)$	(c)	$5.5^{-11} \alpha \exp(-4925/T)$
5) $O + H_2(v=1) \rightarrow OH(v=1) + H$	(d)	$1.3^{-10} (1 - \alpha)$
6) $H + OH(v=1) \rightarrow O + H_2(v=1)$	(c)	$5.5^{-11} (1 - \alpha) \exp(215/T)$
7) $OH + H_2 \rightarrow H_2O + H$	(d)	$3.8^{-11} \exp(-2600/T)$
8) $H + H_2O \rightarrow OH + H_2$	(c)	$1.5^{-10} \exp(-10075/T)$
9) $OH + H_2(v=1) \rightarrow H_2O + H$	(e)	1.5^{-10}
10) $H + H_2O \rightarrow OH + H_2(v=1)$	(c)	$5.8^{-10} \exp(-13475/T)$
11) $OH(v=1) + H_2 \rightarrow H_2O + H$	(e)	1.5^{-11}
12) $H + H_2O \rightarrow OH(v=1) + H_2$	(c)	$5.8^{-11} \exp(-12475/T)$
13) $OH + OH \rightarrow H_2O + O$	(a)	$9.6^{-12} \exp(-390/T)$
14) $O + H_2O \rightarrow OH + OH$	(a)	$9.5^{-11} \exp(-9000/T)$
15) $O + OH \rightarrow O_2 + H$	(f)	4^{-11}
16) $H + O_2 \rightarrow O + OH$	(c)	$6.9^{-10} \exp(-8400/T)$
17) $O + OH(v=1) \rightarrow O_2 + H$	(f)	4^{-11}
18) $H + O_2 \rightarrow O + OH(v=1)$	(c)	$6.9^{-10} \exp(-13400/T)$

ENERGY TRANSFER REACTIONS*

Vibration-Translation Processes:

19) $H_2(v=1) + H \rightarrow H_2 + H$	(g)	$3.2^{-11} \exp(-1400/T)$
20) $H_2(v=1) + O \rightarrow H_2 + O$	(e)	$3.0^{-13} \sqrt{T}$
21) $H_2(v=1) + H_2 \rightarrow H_2 + H_2$	(h,i)	$1.5^{-7} \exp(-139/T^{1/3})$
22) $H_2(v=1) + H_2O \rightarrow H_2 + H_2O$	(e,j)	$1.5^{-7} \exp(-139/T^{1/3})$
23) $N_2(v=1) + H \rightarrow N_2 + H$	(u)	$1.9^{-6} \exp(-164/T^{1/3})$
24) $N_2(v=1) + O \rightarrow N_2 + O$	(k,l,m)	$1.2^{-13} \exp(-23/T^{1/3})$
25) $N_2(v=1) + H_2 \rightarrow N_2 + H_2$	(n)	$3.9^{-8} \exp(-164/T^{1/3})$
26) $N_2(v=1) + H_2O \rightarrow N_2 + H_2O$	(e,j)	$3.9^{-8} \exp(-164/T^{1/3})$
27) $OH(v=1) + H \rightarrow OH + H$	(e)	3^{-11}
28) $OH(v=1) + O \rightarrow OH + O$	(e)	3^{-11}
29) $OH(v=1) + H_2 \rightarrow OH + H_2$	(e)	1^{-11}
30) $OH(v=1) + H_2O \rightarrow OH + H_2O$	(e)	3^{-12}
31) $H_2O(010) + H \rightarrow H_2O(000) + H$	(e)	1^{-11}
32) $H_2O(010) + O \rightarrow H_2O(000) + O$	(e)	1^{-11}
33) $H_2O(010) + H_2 \rightarrow H_2O(000) + H_2$	(e,o)	1^{-11}
34) $H_2O(010) + H_2O \rightarrow H_2O(000) + H_2O$	(p)	1^{-11}
35) $H_2O(020) + H \rightarrow H_2O(010) + H$	(t)	2^{-11}
36) $H_2O(020) + O \rightarrow H_2O(010) + O$	(t)	2^{-11}
37) $H_2O(020) + H_2 \rightarrow H_2O(010) + H_2$	(t)	2^{-11}
38) $H_2O(020) + H_2O \rightarrow H_2O(010) + H_2O$	(t)	2^{-11}

* Note that the reverse rate coefficient can be calculated directly from detailed balance.

39) $\text{H}_2\text{O}(001) + \text{H} \rightarrow \text{H}_2\text{O}(000) + \text{H}$	(e)	1^{-11}
40) $\text{H}_2\text{O}(001) + \text{O} \rightarrow \text{H}_2\text{O}(000) + \text{O}$	(e)	1^{-11}
41) $\text{H}_2\text{O}(001) + \text{H}_2 \rightarrow \text{H}_2\text{O}(000) + \text{H}_2$	(o)	2^{-13}
42) $\text{H}_2\text{O}(001) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}(000) + \text{H}_2\text{O}$	(q)	1^{-12}
43) $\text{H}_2\text{O}(001) + \text{H} \rightarrow \text{H}_2\text{O}(020) + \text{H}$	(e)	1^{-11}
44) $\text{H}_2\text{O}(001) + \text{O} \rightarrow \text{H}_2\text{O}(020) + \text{O}$	(e)	1^{-11}
45) $\text{H}_2\text{O}(001) + \text{H}_2 \rightarrow \text{H}_2\text{O}(020) + \text{H}_2$	(e)	1^{-11}
46) $\text{H}_2\text{O}(001) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}(020) + \text{H}_2\text{O}$	(e)	1^{-11}

Vibration-Vibration Processes

47) $\text{H}_2(v=1) + \text{H}_2\text{O}(000)$ $\rightarrow \text{H}_2(v=0) + \text{H}_2\text{O}(001)$	(r)	$2.5^{-14} T^{5/6} \exp(-30.1/T^{1/3})$
48) $\text{H}_2(v=1) + \text{OH}(v=0)$ $\rightarrow \text{H}_2(v=0) + \text{OH}(v=1)$	(e)	1^{-12}
49) $\text{N}_2(v=1) + \text{H}_2\text{O}(010)$ $\rightarrow \text{N}_2(v=0) + \text{H}_2\text{O}(001)$	(e)	3^{-13}
50) $\text{N}_2(v=1) + \text{H}_2\text{O}(000)$ $\rightarrow \text{N}_2(v=0) + \text{H}_2\text{O}(010)$	(s)	$9.4^{-11} \exp(-64/T^{1/3})$
51) $\text{H}_2\text{O}(010) + \text{H}_2\text{O}(010)$ $\rightarrow \text{H}_2\text{O}(020) + \text{H}_2\text{O}(000)$	(e)	$1^{-12} \sqrt{T}$
52) $\text{H}_2\text{O}(001)$ and $\text{H}_2\text{O}(100)$ assumed in quasi-equilibrium at the local translational temperature.		

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- q) estimate based on analogy to HF VT relaxation

- r) estimate based on the modified Rapp model, J. Chem. Phys. 40, 573(1964); Fisher unpublished results.
- s) estimate based on data of C.W. Von Rosenberg, K.N.C. Bray and N.H. Pratt, J. Chem. Phys. 56, 3230(1972) and 13th Symp. (Intern.) on combustion p. 89, (1971).
- t) scaled from the analogous rate constant for exciting the lowest bending mode.
- u) estimated based on the rate for $\text{CO} + \text{H}$; see reference (o) under RELAXATION MODEL (2).

(2) RELAXATION MODEL

<u>Vibration-Translation Processes</u>	<u>Reference</u>	<u>Rate Constant (cc/molecule-sec)</u>
1) $\text{H}_2(v=1) + \text{H} \rightarrow \text{H}_2 + \text{H}$	(a)	$3.2^{-11} \exp(-1400/T)$
2) $\text{H}_2(v=1) + \text{O} \rightarrow \text{H}_2 + \text{O}$	(b)	$3.0^{-13} \sqrt{T}$
3) $\text{H}_2(v=1) + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_2$	(c,d)	$1.5^{-7} \exp(-139/T^{1/3})$
4) $\text{H}_2(v=1) + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{O}$	(b,e)	$1.5^{-7} \exp(-139/T^{1/3})$
5) $\text{N}_2(v=1) + \text{H} \rightarrow \text{N}_2 + \text{H}$	(y)	$1.9^{-6} \exp(-164/T^{1/3})$
6) $\text{N}_2(v=1) + \text{O} \rightarrow \text{N}_2 + \text{O}$	(f,g,h)	$1.2^{-13} \exp(-23/T^{1/3})$
7) $\text{N}_2(v=1) + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2$	(i)	$3.9^{-8} \exp(-164/T^{1/3})$
8) $\text{N}_2(v=1) + \text{H}_2\text{O} \rightarrow \text{N}_2 + \text{H}_2\text{O}$	(b,e)	$3.9^{-8} \exp(-164/T^{1/3})$
9) $\text{OH}(v=1) + \text{H} \rightarrow \text{OH} + \text{H}$	(b)	3^{-11}
10) $\text{OH}(v=1) + \text{O} \rightarrow \text{OH} + \text{O}$	(b)	3^{-11}
11) $\text{OH}(v=1) + \text{H}_2 \rightarrow \text{OH} + \text{H}_2$	(b)	1^{-11}
12) $\text{OH}(v=1) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2\text{O}$	(b)	3^{-12}
13) $\text{H}_2\text{O}(010) + \text{H} \rightarrow \text{H}_2\text{O}(000) + \text{H}$	(b)	1^{-11}
14) $\text{H}_2\text{O}(010) + \text{O} \rightarrow \text{H}_2\text{O}(000) + \text{O}$	(b)	1^{-11}
15) $\text{H}_2\text{O}(010) + \text{H}_2 \rightarrow \text{H}_2\text{O}(000) + \text{H}_2$	(b,j)	1^{-11}
16) $\text{H}_2\text{O}(010) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}(000) + \text{H}_2\text{O}$	(k)	1^{-11}
17) $\text{H}_2\text{O}(001) + \text{H} \rightarrow \text{H}_2\text{O}(000) + \text{H}$	(b)	1^{-11}
18) $\text{H}_2\text{O}(001) + \text{O} \rightarrow \text{H}_2\text{O}(000) + \text{O}$	(b)	1^{-11}
19) $\text{H}_2\text{O}(001) + \text{H}_2 \rightarrow \text{H}_2\text{O}(000) + \text{H}_2$	(j)	2^{-13}
20) $\text{H}_2\text{O}(001) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}(000) + \text{H}_2\text{O}$	(l)	1^{-12}

21)	$\text{H}_2\text{O}(001) + \text{H} \rightarrow \text{H}_2\text{O}(020) + \text{H}$	(b)	1^{-11}
22)	$\text{H}_2\text{O}(001) + \text{O} \rightarrow \text{H}_2\text{O}(020) + \text{O}$	(b)	1^{-11}
23)	$\text{H}_2\text{O}(001) + \text{H}_2 \rightarrow \text{H}_2\text{O}(020) + \text{H}_2$	(b)	1^{-11}
24)	$\text{H}_2\text{O}(001) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}(020) + \text{H}_2\text{O}$	(b)	1^{-11}
25)	$\text{CO}(v=1) + \text{H} \rightarrow \text{CO}(v=0) + \text{H}$	(o)	$5.3^{-7} \exp(-119/T^{1/3})$
26)	$\text{CO}(v=1) + \text{O} \rightarrow \text{CO}(v=0) + \text{O}$	(p)	$1^{-8} \exp(-96/T^{1/3})$
27)	$\text{CO}(v=1) + \text{H}_2 \rightarrow \text{CO}(v=0) + \text{H}_2$	(q)	$9^{-9} \exp(-119/T^{1/3})$
28)	$\text{CO}(v=1) + \text{H}_2\text{O} \rightarrow \text{CO}(v=0) + \text{H}_2\text{O}$	(b)	$9^{-9} \exp(-119/T^{1/3})$
29)	$\text{CO}_2(010) + \text{H} \rightarrow \text{CO}_2(000) + \text{H}$	(b)	$3.8^{-12} \exp(-7/T^{1/3})$
30)	$\text{CO}_2(010) + \text{O} \rightarrow \text{CO}_2(000) + \text{O}$	(p)	$2.3^{-9} \exp(-77/T^{1/3})$
31)	$\text{CO}_2(010) + \text{H}_2 \rightarrow \text{CO}_2(000) + \text{H}_2$	(r)	$7.6^{-12} \exp(-7/T^{1/3})$
32)	$\text{CO}_2(010) + \text{H}_2\text{O} \rightarrow \text{CO}_2(000) + \text{H}_2\text{O}$	(s)	1^{-11}
33)	$\text{CO}_2(010) + \text{CO}_2 \rightarrow \text{CO}_2(000) + \text{CO}_2$	(r)	$4.6^{-10} \exp(-77/T^{1/3})$
34)	$\text{CO}_2(001) + \text{H} \rightarrow \text{CO}_2(000) + \text{H}$	(t)	$6.7^{-8} \exp(-208/T^{1/3})$
35)	$\text{CO}_2(001) + \text{O} \rightarrow \text{CO}_2(000) + \text{O}$	(t)	$1^{-8} \exp(-96/T^{1/3})$
36)	$\text{CO}_2(001) + \text{H}_2 \rightarrow \text{CO}_2(000) + \text{H}_2$	(t)	$9^{-9} \exp(-119/T^{1/3})$
37)	$\text{CO}_2(001) + \text{H}_2\text{O} \rightarrow \text{CO}_2(000) + \text{H}_2\text{O}$	(t)	$9^{-9} \exp(-119/T^{1/3})$
38)	$\text{CO}_2(001) + \text{H} \rightarrow \text{CO}_2(030) + \text{H}$	(b)	$2.13^{17} T^{-6.34} \exp(-3013/T$ $-378.7/T^{1/3} + 1416/T^{2/3})$
39)	$\text{CO}_2(001) + \text{O} \rightarrow \text{CO}_2(030) + \text{O}$	(u)	$4.6^{24} T^{-5.89} \exp(-4223/T$ $-672.7/T^{1/3} + 2683/T^{2/3})$
40)	$\text{CO}_2(001) + \text{H}_2 \rightarrow \text{CO}_2(030) + \text{H}_2$	(v)	$4.27^{17} T^{-6.34} \exp(-3013/T$ $-378.7/T^{1/3} + 1416/T^{2/3})$

- 41) $\text{CO}_2(001) + \text{H}_2\text{O} \rightarrow \text{CO}_2(030) + \text{H}_2\text{O}$ (v) $4.71^{-40} T^{4.54} \exp(2081/T + 454/T^{1/3} - 1729/T^{2/3})$
- 42) $\text{CO}_2(001) + \text{CO}_2 \rightarrow \text{CO}_2(030) + \text{CO}_2$ (v) $9.16^{23} T^{-5.89} \exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$
- 43) $\text{CO}_2(001) + \text{CO} \rightarrow \text{CO}_2(030) + \text{CO}$ (v) $6.87^{23} T^{-5.89} \exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$
- 44) $\text{CO}_2(001) + \text{N}_2 \rightarrow \text{CO}_2(030) + \text{N}_2$ (v) $6.87^{23} T^{-5.89} \exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$

Vibration-Vibration Processes

- 45) $\text{H}_2(v=1) + \text{H}_2\text{O}(000) \rightarrow \text{H}_2(v=0) + \text{H}_2\text{O}(001)$ (m) $2.5^{-14} T^{5/6} \exp(-30.1/T^{1/3})$
- 46) $\text{H}_2(v=1) + \text{OH}(v=0) \rightarrow \text{H}_2(v=0) + \text{OH}(v=1)$ (b) 1^{-12}
- 47) $\text{N}_2(v=1) + \text{H}_2\text{O}(010) \rightarrow \text{N}_2(v=0) + \text{H}_2\text{O}(001)$ (b) 3^{-13}
- 48) $\text{N}_2(v=1) + \text{H}_2\text{O}(000) \rightarrow \text{N}_2(v=0) + \text{H}_2\text{O}(010)$ (n) $9.4^{-11} \exp(-64/T^{1/3})$
- 49) $\text{H}_2\text{O}(010) + \text{H}_2\text{O}(010) \rightarrow \text{H}_2\text{O}(020) + \text{H}_2\text{O}(000)$ (b) $1^{-12} \sqrt{T}$
- 50) $\text{CO}_2(001) + \text{H}_2\text{O}(000) \rightarrow \text{CO}_2(010) + \text{H}_2\text{O}(010)$ (b) 1^{-13}

- 51) $N_2(v=1) + CO_2(000)$
 $\rightarrow N_2(v=0) + CO_2(001)$ (r) Take the largest value $\begin{cases} 1.71^{-6} \exp(-175.3/T^{1/3}) \\ 6.07^{-14} \exp(15.3/T^{1/3}) \end{cases}$
- 52) $N_2(v=1) + CO(v=0)$
 $\rightarrow N_2(v=0) + CO(v=1)$ (v) Take the largest value $\begin{cases} 1.78^{-6} \exp(-210/T^{1/3}) \\ 6.98^{-13} \exp(-25.6/T^{1/3}) \end{cases}$
- 53) $CO_2(001) + CO(v=0)$
 $\rightarrow CO_2(000) + CO(v=1)$ (b) $1.56^{-11} \exp(-30.1/T^{1/3})$
- 54) $CO_2(101) + H_2O(000)$
 $\rightarrow CO_2(000) + H_2O(001)$ (b) $2^{-13} \sqrt{T}$
- 55) $CO_2(021) + H_2O(000)$
 $\rightarrow CO_2(000) + H_2O(001)$ (b) $2^{-13} \sqrt{T}$
- 56) $CO_2(101) + CO_2(000)$
 $\rightarrow CO_2(100) + CO_2(001)$ (b) $2^{-11} \sqrt{T}$
- 57) $CO_2(020) + CO_2(000)$
 $\rightarrow CO_2(010) + CO_2(010)$ (b) $4^{-13} \sqrt{T}$
- 58) $H_2O(020) + H \rightarrow H_2O(010) + H$ (w) 2^{-11}
- 59) $H_2O(020) + O \rightarrow H_2O(010) + O$ (w) 2^{-11}
- 60) $H_2O(020) + H_2 \rightarrow H_2O(010) + H_2$ (w) 2^{-11}
- 61) $H_2O(020) + H_2O \rightarrow H_2O(010) + H_2O$ (w) 2^{-11}
- 62) $CO_2(020) + H \rightarrow CO_2(010) + H$ (w) $7.6^{-12} \exp(-7/T^{1/3})$
- 63) $CO_2(020) + O \rightarrow CO_2(010) + O$ (w) $4.6^{-9} \exp(-77/T^{1/3})$
- 64) $CO_2(020) + H_2 \rightarrow CO_2(010) + H_2$ (w) $1.5^{-11} \exp(-7/T^{1/3})$
- 65) $CO_2(020) + H_2O \rightarrow CO_2(010) + H_2O$ (w) 2^{-11}

- 66) $\text{CO}_2(020) + \text{CO}_2 \rightarrow \text{CO}_2(010) + \text{CO}_2$ (w) $9.2^{-10} \exp(-77/T^{1/3})$
- 67) $\text{CO}_2(030) + \text{H} \rightarrow \text{CO}_2(020) + \text{H}$ (w) $1.2^{-11} \exp(-7/T^{1/3})$
- 68) $\text{CO}_2(030) + \text{O} \rightarrow \text{CO}_2(020) + \text{O}$ (w) $6.9^{-9} \exp(-77/T^{1/3})$
- 69) $\text{CO}_2(030) + \text{H}_2 \rightarrow \text{CO}_2(020) + \text{H}_2$ (w) $2.3^{-11} \exp(-7/T^{1/3})$
- 70) $\text{CO}_2(030) + \text{H}_2\text{O} \rightarrow \text{CO}_2(020) + \text{H}_2\text{O}$ (w) 3^{-11}
- 71) $\text{CO}_2(030) + \text{CO}_2 \rightarrow \text{CO}_2(020) + \text{CO}_2$ (w) $1.4^{-9} \exp(-77/T^{1/3})$
- 72) $\text{H}_2\text{O}(100)$ and $\text{H}_2\text{O}(001)$ assumed in quasi-equilibrium at the local translational temperature.
- 73) $\text{CO}_2(100) + \text{M} \rightarrow \text{CO}_2(020) + \text{M}$ (x) 1^{-10}

References (Vibrational Relaxation Model)

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- (e) past measurements involving water presumably measure both VV and VT processes.
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- (g) R.J. McNeal, M.E. Whitson Jr. and G.R. Cook, preprint of work submitted to Chem. Phys. Letters (1972). Aerospace Report SPL 3303, July(1972).
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- (j) estimate based on Marriott's cross section values see E.R. Fisher, AFCRL Special Report, 72-0539, August (1972).
- (k) estimate based on all available data
- (l) estimate based on analogy to HF VT relaxation
- (m) estimate based on the modified Rapp model, J. Chem. Phys. 40, 573(1964) Fisher unpublished results.
- (n) estimate based on data of C.W. Von Rosenberg, K.N.C. Bray and N.H. Pratt, J. Chem. Phys. 56, 3230(1972) and 13th Symp. (Intern.) on combustion p. 89, (1971).
- (o) C.N. Rosenberg, R. Taylor and D. Teare, J. Chem. Phys. 54, 1974(1971). Also assuming the $\text{CO}_2 + \text{H}_2$ activation energy, as shown in reaction 27).
- (p) unpublished data from AVCO.

- (q) W. J. Hoche and R. C. Millikan, J. Chem. Phys. 38, 214 (1963); and R. C. Millikan, J. Chem. Phys. 38, 2855 (1963).
- (r) R. Taylor and S. Bitterman, Rev. Mod. Phys. 41, 26 (1969).
- (s) M.I. Buckwald and S. H. Bauer, J. Phys. Chem. 76, 3108 (1972).
- (t) since direct VT relaxation of $\text{CO}_2(v_3)$ to ground state has not been unambiguously determined without competing VV processes, $\text{CO}_2(v_3)$ was assumed to relax like $\text{CO}(v=1)$.
- (u) estimate based on analogy with reaction 35).
- (v) estimate based on AVCO suggestion.
- (w) scaled from the analogous rate constant for exciting the lowest bending mode.
- (x) the Fermi resonance in CO_2 is assumed to couple the (100) and (020) modes with a gas kinetic efficiency independent of collision partner.
- (y) estimated based on the rate for $\text{CO} + \text{H}$, under (o) above.

(3) HYDROCARBON MODEL

LUMPED PARAMETER
IR REACTION SCHEME

<u>Reaction</u>	<u>Rate Constant, cc/sec</u>	<u>Photon Yield</u>
1. $A + O \rightarrow R + OH$	$1.3 \times 10^{-10} e^{-4840/RT}$	--
2. $A + OH \rightarrow R + H_2O$	$1.2 \times 10^{-11} e^{-850/RT}$	1
3. $R + O \rightarrow Ol + OH$	1×10^{-11}	6
4. $R + OH \rightarrow Ol + H_2O$	1×10^{-11}	7
5. $Ol + O \rightarrow (80\%) R + CHO$	1×10^{-11}	--
$\rightarrow (20\%) C_2H_5 + CHO$	1×10^{-11}	--
6. $C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	$1.8 \times 10^{-11} e^{-2480/RT}$	1
7. $C_2H_5 + O \rightarrow C_2H_4 + OH$	1×10^{-11}	5
8. $C_2H_5 + OH \rightarrow C_2H_4 + H_2O$	1×10^{-11}	5
9. $C_2H_4 + O \rightarrow CH_3 + CHO$	$5 \times 10^{-12} e^{-1040/RT}$	--
10. $C_2H_4 + OH \rightarrow CH_3 + CH_2O$	$1 \times 10^{-11} e^{+900/RT}$	--
11. $CH_4 + OH \rightarrow CH_3 + H_2O$	$4.0 \times 10^{-12} e^{-5000/RT}$	1
12. $CH_3 + O_2 \rightarrow CH_2O + OH$	1.7×10^{-13}	1
13. $CHO + O \rightarrow CO + OH$	5×10^{-11}	8
14. $CH_2O + OH \rightarrow CHO + H_2O$	$4 \times 10^{-14} e^{-1000/RT}$	2
15. $CH_2O + O \rightarrow CHO + OH$	$1 \times 10^{-12} e^{-1000/RT}$	1
16. $CHO + OH \rightarrow CO + H_2O$	1×10^{-12}	9
17. $OH + O \rightarrow O_2 + H$	2.2×10^{-11}	--

(3) HYDROCARBON MODEL

(cont'd)

18.	$\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$	$9.3 \times 10^{-13} e^{-1080/RT}$	--
19.	$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	$3.7 \times 10^{-11} e^{-5150/RT}$	1
20.	$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	$9.5 \times 10^{-12} e^{-780/RT}$	1
21.	$\text{OH} + \text{H} \rightarrow \text{H}_2 + \text{O}$	$1.2 \times 10^{-11} e^{-7300/RT}$	--
22.	$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	$3.7 \times 10^{-10} e^{-16,800/RT}$	--
23.	$\text{H} + \text{CO}_2 \rightarrow \text{CO} + \text{OH}$	$9.3 \times 10^{-11} e^{-23,500/RT}$	--
24.	$\text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2$	$1.4 \times 10^{-9} e^{-20,100/RT}$	--
25.	$\text{O} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	$9.5 \times 10^{-11} e^{-18,000/RT}$	--
26.	$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$	$2.9 \times 10^{-11} e^{-9450/RT}$	--
27.	$\text{CH}_3 + \text{O} \rightarrow \text{CH}_2\text{O} + \text{H}$	3.3×10^{-11}	--
28.	$\text{CHO} + \text{H} \rightarrow \text{CO} + \text{H}_2$	3.3×10^{-11}	--

"A" is a saturated hydrocarbon, $\text{C}_n\text{H}_{2n+2}$, with $n \geq 3$

"R" is an alkyl radical, $\text{C}_n\text{H}_{2n+1}$, with $n \geq 3$

"Ol" is an olefinic hydrocarbon, C_nH_{2n} , with $n \geq 3$

(4) AMINE MODEL

INFRARED HYDRAZINE MODEL A

FUEL CHEMI-EXCITATION REACTIONS

<u>Reaction</u>	<u>Forward Rate Constant cc/sec</u>	<u>Reaction Energy kcal/gmole</u>
$O + MMH \rightarrow HN_2CH_3 + H_2O$ (001) (100) H_2O (020) (010)	2×10^{-11}	-102
$O + N_2H_4 \rightarrow N_2H_2 + H_2O$ (001) (100) H_2O (020) (010)	1.8×10^{-11}	-90
$O + UDMH \rightarrow HN_2(CH_3)_2 + OH$	1×10^{-12}	-25
$OH + N_2H_4 \rightarrow NH_3 + NH_2O$	2×10^{-11}	

(4) AMINE MODEL

(cont'd)

REACTIONS OF OH AND H₂O

<u>Reaction</u>	<u>Rate Constant</u> <u>cc/molecule-sec</u>
$O + OH \rightarrow O_2 + H$	4.0×10^{-11}
$H_2 + O \rightarrow$ +	$2.9 \times 10^{-11} e^{-4725/T}$
$OH + H \rightarrow H_2 + O$	$1.22 \times 10^{-11} e^{-3650/T}$
$H_2^* + O \rightarrow OH + H$	0.65×10^{-10}
$OH + H \rightarrow H_2^* + O$	$2.75 \times 10^{-11} e^{-4925/T}$
$H_2^* + O \rightarrow OH^* + H$	0.65×10^{-10}
$OH^* + H \rightarrow H_2^* + O$	$2.75 \times 10^{-11} e^{215/T}$
$OH + H_2 \rightarrow H_2O$	$3.8 \times 10^{-11} e^{-2600/T}$
$H_2O + H \rightarrow OH + H_2$	$1.5 \times 10^{-10} e^{-10075/T}$
$OH + H_2^* \rightarrow H_2O^* + H$	1.5×10^{-10}
$H_2O^* + H \rightarrow OH + H_2^*$	$5.8 \times 10^{-10} e^{-13475/T}$
$OH^* + H \rightarrow OH + H_2$	1.5×10^{-11}
$H_2O^* + H \rightarrow OH^* + H_2$	$5.8 \times 10^{-11} e^{-12475/T}$
$OH + OH \rightarrow H_2O + O$	$9.6 \times 10^{-12} e^{-390/T}$
$H_2O + O \rightarrow OH + OH$	$9.5 \times 10^{-11} e^{-9000/T}$
$O + OH \rightarrow O_2 + H$	4×10^{-11}
$O_2 + H \rightarrow OH + O$	$6.9 \times 10^{-10} e^{-8400/T}$
$O + OH^* \rightarrow O_2 + H$	4×10^{-11}
$O_2 + H \rightarrow O + OH^*$	$6.9 \times 10^{-10} e^{-13400/T}$

(4) AMINE MODEL
(cont'd)

RELAXATION PROCESSES OF OH AND H₂O

<u>Reaction</u>		<u>Forward Rate Constant (cc/molecule-sec)</u>
OH* + M $\rightleftharpoons$ OH + M	M = H	3×10^{-11}
"	M = O	3×10^{-11}
"	M = H ₂	1×10^{-11}
"	M = H ₂ O	3×10^{-12}
H ₂ O(010) + M $\rightleftharpoons$ H ₂ O(000) + M	M = H	2×10^{-10}
"	M = O	1×10^{-11}
"	M = H ₂	1×10^{-11}
"	M = H ₂ O	1×10^{-11}
H ₂ O(100) + M $\rightarrow$ H ₂ O + M	M = H	1×10^{-11}
"	M = O	1×10^{-11}
"	M = H ₂	2×10^{-13}
"	M = H ₂ O	1×10^{-12}
H ₂ O(001) + M $\rightarrow$ H ₂ O + M	M = H	1×10^{-11}
"	M = O	1×10^{-11}
"	M = H ₂	2×10^{-13}
"	M = H ₂ O	1×10^{-12}

(4) AMINE MODEL

(cont'd)

$\text{H}_2\text{O}(001) + \text{M} \rightarrow \text{H}_2\text{O}(020) + \text{M}$	$\text{M} = \text{H}$	1×10^{-11}
"	$\text{M} = \text{O}$	1×10^{-11}
"	$\text{M} = \text{H}_2$	1×10^{-11}
"	$\text{M} = \text{H}_2\text{O}$	1×10^{-11}
$\text{H}_2\text{O}(100) + \text{M} \rightarrow \text{H}_2\text{O}(020) + \text{M}$	$\text{M} = \text{H}$	1×10^{-11}
"	$\text{M} = \text{O}$	1×10^{-11}
"	$\text{M} = \text{H}_2$	1×10^{-11}
"	$\text{M} = \text{H}_2\text{O}$	1×10^{-11}
$\text{H}_2\text{O}(010) + \text{H}_2\text{O}(010) \rightarrow \text{H}_2\text{O}(020) + \text{H}_2\text{O}$		$1 \times 10^{-12} \sqrt{T}$
$\text{H}_2\text{O}(020) + \text{M} \rightarrow \text{H}_2\text{O}(010) + \text{M}$	$\text{M} = \text{H}$	2×10^{-10}
"	$\text{M} = \text{O}$	1×10^{-11}
"	$\text{M} = \text{H}_2$	1×10^{-11}
"	$\text{M} = \text{H}_2\text{O}$	1×10^{-11}
$\text{H} + \text{N}_2\text{H}_4 \rightarrow \text{N}_2\text{H}_3 + \text{H}_2$		$2.2 \times 10^{-11} e^{-1260/T}$
$\text{H} + \text{N}_2\text{H}_3 \rightarrow 2\text{NH}_2$		
$\text{H} + \text{N}_2\text{H}_2 \rightarrow \text{N}_2\text{H}_3$		1×10^{-10}
$\text{O} + \text{NH}_3 \rightarrow \text{NH}_2 + \text{OH}$		$2.5 \times 10^{-12} e^{-3000/T}$
$\text{OH} + \text{NH}_3 \rightarrow \text{NH}_2 + \text{H}_2\text{O}^{(*)}$		$6.6 \times 10^{-14} e^{-560/T(T)^{.68}}$

(4) AMINE MODEL

(cont'd)

$O + NH_2 \rightarrow HNO + H$		1×10^{-11}
$OH + HNO \rightarrow H_2O(*) + NO$		3×10^{-11}
$H_2^* + M \rightarrow H_2 + M$	$M = H$	$3.2 \times 10^{-11} e^{-1400/T}$
"	$M = O$	$4.4 \times 10^{-13} \sqrt{T}$
"	$M = H_2$	$1.5 \times 10^{-7} e^{-139/T^{1/3}}$
"	$M = H_2O$	$1.5 \times 10^{-7} e^{-139/T^{1/3}}$
$N_2^* + M \rightarrow N_2 + M$	$M = H$	$6.7 \times 10^{-9} e^{-208/T^{1/3}}$
"	$M = O$	$1.2 \times 10^{-13} e^{-23/T^{1/3}}$
"	$M = H_2$	$3.9 \times 10^{-8} e^{-164/T^{1/3}}$
"	$M = H_2O$	$3.9 \times 10^{-8} e^{-164/T^{1/3}}$
$H_2^* + H_2O \rightarrow H_2 + H_2O(100)$		$2.5 \times 10^{-14} T^{5/6} e^{-30.1/T^{1/3}}$
$H_2^* + H_2O \rightarrow H_2 + H_2O(001)$		$2.5 \times 10^{-14} T^{5/6} e^{-30.1/T^{1/3}}$
$H_2^* + OH \rightarrow H_2 + OH^*$		1×10^{-12}
$N_2^* + H_2O(010) \rightarrow N_2 + H_2O(100)$		3×10^{-13}
$N_2^* + H_2O(010) \rightarrow N_2 + H_2O(001)$		3×10^{-13}
$N_2^* + H_2O \rightarrow N_2 + H_2O(010)$		$9.4 \times 10^{-11} e^{-64/T^{1/3}}$

(4) AMINE MODEL

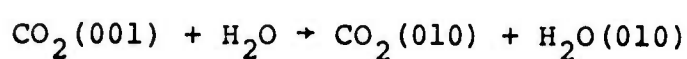
(cont'd)

$\text{CO}^* + \text{M} \rightarrow \text{CO} + \text{M}$	$\text{M} = \text{H}$	$6.7 \times 10^{-8} e^{-208/T^{1/3}}$
"	$\text{M} = \text{O}$	$1 \times 10^{-8} e^{-96/T^{1/3}}$
"	$\text{M} = \text{H}_2$	$9 \times 10^{-9} e^{-119/T^{1/3}}$
"	$\text{M} = \text{H}_2\text{O}$	$1 \times 10^{-8} e^{-96/T^{1/3}}$
$\text{CO}_2(010) + \text{M} \rightarrow \text{CO}_2 + \text{M}$	$\text{M} = \text{H}$	$3.8 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{O}$	$2.3 \times 10^{-9} e^{-77/T^{1/3}}$
"	$\text{M} = \text{H}_2$	$7.6 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{H}_2\text{O}$	1×10^{-11}
"	$\text{M} = \text{CO}_2$	$4.6 \times 10^{-9} e^{-77/T^{1/3}}$
$\text{CO}_2(001) + \text{M} \rightarrow \text{CO}_2 + \text{M}$	$\text{M} = \text{H}$	$6.7 \times 10^{-8} e^{-208/T^{1/3}}$
"	$\text{M} = \text{O}$	$1 \times 10^{-8} e^{-96/T^{1/3}}$
"	$\text{M} = \text{H}_2$	$9 \times 10^{-9} e^{-119/T^{1/3}}$
"	$\text{M} = \text{H}_2\text{O}$	$9 \times 10^{-9} e^{-119/T^{1/3}}$

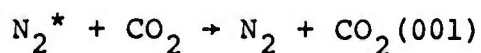
(4) AMINE MODEL

(cont'd)

$\text{CO}_2(001) + \text{M} \rightarrow \text{CO}_2(030) + \text{M}$	$\text{M} = \text{H}$	$2.13 \times 10^{17} T^{-6.34} \exp(-3013/T - 378.7/T^{1/3} + 1416/T^{2/3})$
"	$\text{M} = \text{O}$	$4.6 \times 10^{24} T^{-5.89} \exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$
"	$\text{M} = \text{H}_2$	$4.27 \times 10^{17} T^{-6.34} \exp(-3013/T - 378.7/T^{1/3} + 1416/T^{2/3})$
"	$\text{M} = \text{H}_2\text{O}$	$4.71 \times 10^{-40} T^{4.54} \exp(2081/T + 454/T^{1/3} - 1729/T^{2/3})$
"	$\text{M} = \text{CO}_2$	$9.16 \times 10^{23} T^{-5.89} \exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$
"	$\text{M} = \text{CO}$	$6.87 \times 10^{23} T^{-5.89} \exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$
"	$\text{M} = \text{N}_2$	$6.87 \times 10^{23} T^{-5.89} \exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$



$$1 \times 10^{-13}$$



$$\left\{ \begin{array}{l} 1.72 \times 10^{-6} e^{-175/T^{1/3}} \\ 6 \times 10^{-14} e^{15.3/T^{1/3}} \end{array} \right\} \text{largest}$$

(4) AMINE MODEL

(cont'd)

$N_2^* + CO \rightarrow N_2 + CO^*$		$\left\{ \begin{array}{l} 1.78 \times 10^{-6} e^{-210/T^{1/3}} \\ 7 \times 10^{-13} e^{-25.6/T^{1/3}} \end{array} \right\}$ largest
$CO_2(001) + CO \rightarrow CO_2 + CO^*$		$1.57 \times 10^{-11} e^{-30.1/T^{1/3}}$
$CO_2(101) + H_2O \rightarrow CO_2 + H_2O(100)$		$2 \times 10^{-13} \sqrt{T}$
$CO_2(101) + H_2O \rightarrow CO_2 + H_2O(001)$		$2 \times 10^{-13} \sqrt{T}$
$CO_2(021) + H_2O \rightarrow CO_2 + H_2O(100)$		$2 \times 10^{-13} \sqrt{T}$
$CO_2(021) + H_2O \rightarrow CO_2 + H_2O(001)$		$2 \times 10^{-13} \sqrt{T}$
$CO_2(101) + CO_2 \rightarrow CO_2(001) + CO_2(100)$		$2 \times 10^{-11} \sqrt{T}$
$CO_2(020) + CO_2 \rightarrow CO_2(010) + CO_2(010)$		$2 \times 10^{-13} \sqrt{T}$
$CO_2(100) + M \rightarrow CO_2 + M$	$M = H$	$3.8 \times 10^{-12} e^{-17.6/T^{1/3}}$
"	$M = O$	$2.3 \times 10^{-9} e^{-194/T^{1/3}}$
"	$M = H_2$	$7.6 \times 10^{-12} e^{-17.6/T^{1/3}}$
"	$M = H_2O$	3×10^{-13}
$CO_2(101) + M \rightarrow CO_2(100) + M$	$M = H$	$6.7 \times 10^{-8} e^{-208/T^{1/3}}$
"	$M = O$	$1.0 \times 10^{-8} e^{-96/T^{1/3}}$
"	$M = H_2$	$9.0 \times 10^{-9} e^{-119/T^{1/3}}$
"	$M = H_2O$	$9.0 \times 10^{-9} e^{-119/T^{1/3}}$

(4) AMINE MODEL

(cont'd)

$\text{CO}_2(101) + \text{M} \rightarrow \text{CO}_2(001) + \text{M}$	$\text{M} = \text{H}$	$3.8 \times 10^{-12} e^{-17.6/T^{1/3}}$
"	$\text{M} = \text{O}$	$2.3 \times 10^{-9} e^{-194/T^{1/3}}$
"	$\text{M} = \text{H}_2$	$4.6 \times 10^{-9} e^{-194/T^{1/3}}$
"	$\text{M} = \text{H}_2\text{O}$	3×10^{-13}
$\text{CO}_2(020) + \text{M} \rightarrow \text{CO}_2(010) + \text{M}$	$\text{M} = \text{H}$	$3.8 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{O}$	$2.3 \times 10^{-9} e^{-77/T^{1/3}}$
"	$\text{M} = \text{H}_2$	$7.6 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{H}_2\text{O}$	1.0×10^{-11}
"	$\text{M} = \text{CO}_2$	$4.6 \times 10^{-9} e^{-77/T^{1/3}}$
$\text{CO}_2(021) + \text{M} \rightarrow \text{CO}_2(011) + \text{M}$	$\text{M} = \text{H}$	$3.8 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{O}$	$2.3 \times 10^{-9} e^{-77/T^{1/3}}$
"	$\text{M} = \text{H}_2$	$7.6 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{H}_2\text{O}$	1.0×10^{-11}
"	$\text{M} = \text{CO}_2$	$4.6 \times 10^{-9} e^{-77/T^{1/3}}$

(4) AMINE MODEL

(cont'd)

$\text{CO}_2(011) + \text{M} \rightarrow \text{CO}_2(001) + \text{M}$	$\text{M} = \text{H}$	$3.8 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{O}$	$2.3 \times 10^{-9} e^{-77/T^{1/3}}$
"	$\text{M} = \text{H}_2$	$7.6 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{H}_2\text{O}$	1.0×10^{-11}
"	$\text{M} = \text{CO}_2$	$4.6 \times 10^{-9} e^{-77/T^{1/3}}$
$\text{CO}_2(021) + \text{M} \rightarrow \text{CO}_2(020) + \text{M}$	$\text{M} = \text{H}$	$6.7 \times 10^{-8} e^{-208/T^{1/3}}$
"	$\text{M} = \text{O}$	$1.0 \times 10^{-8} e^{-96/T^{1/3}}$
"	$\text{M} = \text{H}_2$	$9.0 \times 10^{-9} e^{-119/T^{1/3}}$
"	$\text{M} = \text{H}_2\text{O}$	$9.0 \times 10^{-9} e^{-119/T^{1/3}}$
$\text{CO}_2(030) + \text{M} \rightarrow \text{CO}_2(020) + \text{M}$	$\text{M} = \text{H}$	$3.8 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{O}$	$2.3 \times 10^{-9} e^{-77/T^{1/3}}$
"	$\text{M} = \text{H}_2$	$7.6 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{H}_2\text{O}$	1.0×10^{-11}

(5) RADIATIVE LIFETIMES

<u>SPECIES</u>	<u>t(sec)</u>
OH(v=1)	0.3
H ₂ O(100)	0.14
H ₂ O(010)	0.045
H ₂ O(001)	0.014
H ₂ O(020)	0.022
CO ₂ (010)	0.33
CO ₂ (001)	0.0025
CO ₂ (101)	0.091