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INFORMATION THEORY ANALYSIS OF DEACTIVATION RATES IN CHEMICAL LASERS

October 1976

Final Report

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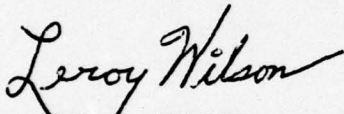
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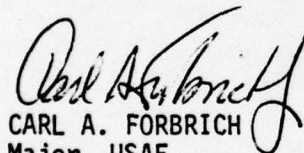
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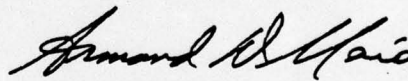


LEROY E. WILSON
Project Officer

FOR THE COMMANDER



CARL A. FORBRICH
Major, USAF
Chief, Chemical Laser Branch



ARMAND D. MAIO
Lt Colonel, USAF
Chief, Advanced Laser Technology Division

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PREFACE

The Surprisal Analysis to determine kinetic information on collisional processes developed by R. D. Levine and coworkers is the most significant development in molecular kinetics in the last decade. J. I. Steinfield of MIT who has implemented the surprisal analysis in several molecular systems gave a series of lectures at AFWL while on a summer faculty term. This inspired Capt. C. Clendening, J. I. Steinfield and L. E. Wilson to apply the Surprisal Analysis to HF chemical lasers.

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SECTION I

BACKGROUND AND INTRODUCTION

Detailed modeling and optimization of the HF (or DF) chemical laser requires the use of a large number of rate constants, from several dozen to over a hundred in the most detailed models. The vibrational deactivation rates, in particular, need to be known over a wide range of initial and final v states and temperatures. Only a handful of the required rates are known experimentally (ref. 1 and 2), and it is customary to guess those rates which are not known. Alternatively, detailed classical or quantum calculations of the unknown rates can be undertaken.

A more systematic approach to this problem is now available in the work of R. D. Levine and co-workers (refs. 3 through 22). These methods are known variously as the Thermodynamic Approach to Collision Processes, the Information-Theoretical Analysis, or the Surprisal Analysis. The latter term, while properly referring to one specialized formulation of the general theory, is a convenient term which we shall use in this report to refer to this entire approach and methodology.

In this report, we have applied Surprisal Theory to the synthesis of the HF-HF $V \leftrightarrow V'$, R, T deactivation rate set. Detailed values for $k(v \rightarrow v')$ have been generated for both $V - (R, T)$ and $V - V$ deactivation channels. This theory also predicts the nature of the temperature dependence of the HF(1) + HF(0) $V - (R, T)$ relaxation rate between 150°K and 4000°K without specific reference to the details of the intermolecular potential.

Among additional problems examined in this report are the use of a "Populations' Evolution in Time" (PET) Approach to generate vibrational level populations without explicitly solving the master equation, and Surprisal Analysis of available rotational relaxation data.

SECTION II

SURPRISAL SYNTHESIS OF HF-HF VIBRATIONAL DEACTIVATION RATES

1. CALCULATION OF PRIOR RATES

Prior rates were calculated for the individual vibrationally and rotationally inelastic collisions.



where v and m are vibrational quantum numbers and J and L are rotational quantum numbers. These have the form (ref. 17)

$$k^0(vJ, mL \rightarrow v'J', m'L') = R (2L' + 1)(2J' + 1) e^{\Delta} |\Delta| K_1(|\Delta|) (kT)^{1/2} \quad (1)$$

where $K_1(x)$ is the modified Bessel Function of the first order and second kind, and

$$\Delta = \frac{[(E_v + E_m) + (E_J + E_L) - (E_{v'} + E_{m'}) + (E_{J'} + E_{L'})]}{2kT} \quad (2)$$

Since small energy defects are important for these calculations, we cannot use the rigid-rotor-harmonic-oscillator (RRHO) approximations, but instead

$$E_v = (v + 1/2) [\omega_e - (v + 1/2) \omega_e x_e] \quad (3a)$$

and

$$E_J = J(J + 1) [B_e - \alpha_e (v + 1/2)] \quad (3b)$$

with similar expressions for E_m and E_L .

The individual prior rates then need to be averaged over rotational states, since we wish to retain only the vibrational information. The expression for this is

$$k^{\circ}(vm \rightarrow v'm') = \frac{\sum_{J'L'} \sum_{JL} (2J+1)(2L+1) e^{-E_J/kT} e^{-E_L/kT} k^{\circ}(vJ, mL \rightarrow v'J', m'L')}{\sum_J e^{-E_J/kT} (2J+1) \sum_L e^{-E_L/kT} (2L+1)} \quad (4)$$

This k° would then be multiplied by the Surprisal factor, $\exp(-\lambda|\Delta|)$, to furnish values of $k(vm \rightarrow v'm')$. In practice, λ was found as described below, and $k(vm \rightarrow v'm')$ calculated as

$$k(vm \rightarrow v'm') = \frac{[\sum_J e^{-E_J/kT} (2J+1)]^{-1} [\sum_L e^{-E_L/kT} (2L+1)]^{-1} \sum_{J'L'} \sum_{JL} (2J+1)(2L+1) e^{-(E_J+E_L)/kT} k^{\circ}(vJ, mL \rightarrow v'J', m'L') e^{-\lambda|E_{v'}+E_{m'}-E_v-E_m|}}{\sum_{J'L'} \sum_{v'm'} k^{\circ}(vJ, mL \rightarrow v'J', m'L') e^{-\lambda|E_{v'}+E_{m'}-E_v-E_m|}} \quad (5)$$

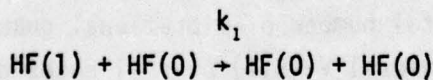
The results of using equation (4) or equation (5) appear to be numerically indistinguishable.

2. DETERMINATION OF SURPRISAL PARAMETERS

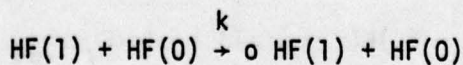
The prior and actual rates are related by the "Surprisal" factor,

$$k(vm \rightarrow v'm') = e^{(-\lambda_0 - \lambda_1|\Delta|)} k^{\circ}(vm \rightarrow v'm') \quad (6)$$

If sufficient data are available, λ_1 can be found by a Surprisal Analysis (refs. 15 through 17); otherwise, various sum rules can be employed. Another method relies on the conservation of probability. We have calculated the rates for the two processes of "V - T" deactivation,



and purely elastic scattering or exchange,



or

$$HF(0) + HF(1)$$

The ratio of these rates depends only on $\lambda_1 |\Delta|$. Since the "collision number" for deactivation is known, namely,

$$Z_v = k_0/k_1 \approx 75$$

we have used this to determine a value of $(\lambda_1/kT) = 0.0021 \text{ l}/(\text{cm}^{-1})$. This corresponds to a $\lambda_1 = 0.438$, or $\Lambda_v = (hc\omega_e/kT)\lambda_1 = 8.69$. This value appears to be rather high (in many systems, Λ_v is of order 1), but is consistent with analysis of the $HF(v) + H \rightarrow HF(v-1) + H$ rates, carried out in reference 17, which gives $\lambda_1 \approx 0.39$, and with our own analysis of $(v,0 \rightarrow v-1, 1)$ rates in HF.

The absolute scaling factor $\exp(\lambda_0)$ is found simply by noting that the measured value of $k_1(10^{-00}; 300^\circ\text{K})$ is $1.0 \times 10^{12} \text{ cm}^3/\text{mole-sec}$.

3. TABULATION OF RESULTS

The results of the calculation described in parts (a) and (b) are 74 V-(T,R) and V-V rate coefficients which appear to be significant in the self-relaxation of HF levels $v \leq 5$. [By significant, we mean having a bimolecular rate coefficient $\geq 1 \times 10^9 \text{ cm}^3/\text{mole-sec}$.] These are summarized in table 1. The entire calculation requires only 10 or 20 minutes on a CDC 6600 computer.

Examination of the individual rotational channels for the "V-T" processes [(1)-(9)] reveals that most of the vibrational exothermicity is transferred to nearly resonant rotational levels. Such near-resonant V-R transfer was first suggested by Houston et al., (ref. 23), and agrees with recent trajectory calculations by Wilkins (ref. 24). Multiquantum ($\Delta v > 1$) transitions are not significant contributors to these rates, but are important in the V-V processes [(10)-(74)] in which the total number of vibrational quanta is unchanged or decreases by one. The individual V-(R,T) $\Delta v = -1$ rates do not appear to scale as v^2 or $v^{2.4}$, as has been frequently suggested; the dependence is closer to v . Indeed, the basic sum rule [equation (74), ref. 17], namely,

$$\sum_{v'} (E_{v'} - E_v) k(v \rightarrow v'; T) = \alpha [\langle\langle E_v \rangle\rangle_{\text{eq}} - E_v]$$

Table 1

RATE COEFFICIENTS FOR HF-HF V-(V,R,T) DEACTIVATION
PROCESSES, FROM SURPRISAL-SYNTHESIS METHOD

<u>Process*</u>	$\frac{\Delta E_{\text{vib}}^{**}}{\text{cal/mole}}$	$\frac{k}{\text{cm}^3/\text{mole-sec}}$
1. HF(1)+HF → HF(0)+HF	-11,327	1.00 x 10 ¹²
2. HF(2)+HF → HF(1)+HF	-10,834	2.19 x 10 ¹²
3. HF(3)+HF → HF(2)+HF	-10,356	2.88 x 10 ¹²
4. HF(4)+HF → HF(3)+HF	- 9,889	3.66 x 10 ¹²
5. HF(5)+HF → HF(4)+HF	- 9,433	4.09 x 10 ¹²
6. HF(2)+HF → HF(0)+HF	-22,161	1.30 x 10 ⁹
7. HF(3)+HF → HF(1)+HF	-21,190	4.97 x 10 ⁹
8. HF(4)+HF → HF(2)+HF	-20,245	9.12 x 10 ⁹
9. HF(5)+HF → HF(3)+HF	-19,322	1.47 x 10 ¹⁰
10. HF(1)+HF(1) → HF(2)+HF(0)	- 493	4.93 x 10 ¹³
11. HF(2)+HF(0) → HF(1)+HF(1)	+ 493	1.11 x 10 ¹³
12. HF(2)+HF(1) → HF(3)+HF(0)	- 971	3.88 x 10 ¹³
13. HF(2)+HF(2) → HF(4)+HF(0)	- 1,916	2.94 x 10 ¹³
14. HF(2)+HF(2) → HF(3)+HF(1)	- 478	2.86 x 10 ¹³
15. HF(2)+HF(2) → HF(3)+HF(0)	-11,805	4.9 x 10 ¹¹
16. HF(3)+HF(0) → HF(2)+HF(1)	+ 971	7.97 x 10 ¹²
17. HF(3)+HF(0) → HF(1)+HF(1)	- 9,863	1.88 x 10 ¹²
18. HF(3)+HF(1) → HF(4)+HF(0)	- 1,438	3.54 x 10 ¹³
19. HF(3)+HF(1) → HF(2)+HF(2)	+ 478	5.55 x 10 ¹²
20. HF(3)+HF(2) → HF(5)+HF(0)	- 2,839	2.15 x 10 ¹³
21. HF(3)+HF(2) → HF(4)+HF(1)	- 945	2.67 x 10 ¹³
22. HF(3)+HF(2) → HF(4)+HF(0)	-12,272	3.22 x 10 ¹¹
23. HF(3)+HF(3) → HF(6)+HF(0)	- 4,116	1.62 x 10 ¹³
24. HF(3)+HF(3) → HF(5)+HF(1)	- 1,868	2.39 x 10 ¹³
25. HF(3)+HF(3) → HF(4)+HF(2)	- 467	2.35 x 10 ¹³
26. HF(3)+HF(3) → HF(5)+HF(0)	-13,195	1.66 x 10 ¹¹
27. HF(3)+HF(3) → HF(4)+HF(1)	-11,301	5.21 x 10 ¹¹
28. HF(4)+HF(0) → HF(3)+HF(1)	+ 1,438	2.73 x 10 ¹²
29. HF(4)+HF(0) → HF(2)+HF(2)	+ 1,916	4.48 x 10 ¹¹
30. HF(4)+HF(0) → HF(2)+HF(1)	- 8,918	6.14 x 10 ¹²
31. HF(4)+HF(0) → HF(1)+HF(1)	-19,572	6.26 x 10 ⁹

Table 1 (Continued)

RATE COEFFICIENTS FOR HF-HF V-(V,R,T) DEACTIVATION
PROCESSES, FROM SURPRISAL-SYNTHESIS METHOD

Process*	$\frac{\Delta E_{vib}^{**}}{\text{cal/mole}}$	$\frac{k}{\text{cm}^3/\text{mole-sec}}$
32. HF(4)+HF(1) → HF(5)+HF(0)	- 1,894	3.47 x 10 ¹³
33. HF(4)+HF(1) → HF(3)+HF(2)	+ 945	4.12 x 10 ¹²
34. HF(4)+HF(1) → HF(2)+HF(2)	- 9,411	1.13 x 10 ¹²
35. HF(4)+HF(2) → HF(6)+HF(0)	- 3,743	1.62 x 10 ¹³
36. HF(4)+HF(2) → HF(5)+HF(1)	- 1,401	2.69 x 10 ¹³
37. HF(4)+HF(2) → HF(3)+HF(3)	+ 467	4.32 x 10 ¹²
38. HF(4)+HF(2) → HF(5)+HF(0)	-12,728	2.42 x 10 ¹¹
39. HF(4)+HF(2) → HF(3)+HF(1)	-20,723	2.3 x 10 ⁹
40. HF(4)+HF(3) → HF(7)+HF(0)	- 5,554	6.72 x 10 ¹²
41. HF(4)+HF(3) → HF(6)+HF(1)	- 2,772	1.92 x 10 ¹³
42. HF(4)+HF(3) → HF(5)+HF(2)	- 923	2.40 x 10 ¹³
43. HF(4)+HF(3) → HF(5)+HF(1)	-11,757	3.81 x 10 ¹¹
44. HF(4)+HF(4) → HF(8)+HF(0)	- 7,335	2.61 x 10 ¹²
45. HF(4)+HF(4) → HF(7)+HF(1)	- 4,116	1.20 x 10 ¹³
46. HF(4)+HF(4) → HF(6)+HF(2)	- 1,827	2.29 x 10 ¹³
47. HF(4)+HF(4) → HF(5)+HF(3)	- 456	2.25 x 10 ¹³
48. HF(4)+HF(4) → HF(6)+HF(1)	-12,661	2.12 x 10 ¹¹
49. HF(4)+HF(4) → HF(5)+HF(2)	-10,812	6.54 x 10 ¹¹
50. HF(4)+HF(4) → HF(5)+HF(1)	-21,646	1.1 x 10 ⁹
51. HF(4)+HF(4) → HF(3)+HF(3)	-19,778	1.9 x 10 ⁹
52. HF(5)+HF(0) → HF(4)+HF(1)	+ 1,894	8.34 x 10 ¹¹
53. HF(5)+HF(0) → HF(3)+HF(2)	+ 2,839	8.43 x 10 ¹⁰
54. HF(5)+HF(0) → HF(3)+HF(1)	- 7,995	8.68 x 10 ¹²
55. HF(5)+HF(0) → HF(2)+HF(2)	- 7,512	5.50 x 10 ¹²
56. HF(5)+HF(0) → HF(2)+HF(1)	-18,351	2.75 x 10 ¹⁰
57. HF(5)+HF(1) → HF(6)+HF(0)	- 2,342	3.28 x 10 ¹³
58. HF(5)+HF(1) → HF(4)+HF(2)	+ 1,401	1.50 x 10 ¹²
59. HF(5)+HF(1) → HF(3)+HF(3)	+ 1,868	2.51 x 10 ¹¹
60. HF(5)+HF(1) → HF(3)+HF(2)	- 8,488	3.78 x 10 ¹²
61. HF(5)+HF(2) → HF(2)+HF(0)	- 4,631	1.23 x 10 ¹³
62. HF(5)+HF(2) → HF(6)+HF(1)	- 1,849	2.80 x 10 ¹³

Table 1 (Continued)

RATE COEFFICIENTS FOR HF-HF V-(V,R,T) DEACTIVATION
PROCESSES, FROM SURPRISAL-SYNTHESIS METHOD

Process*	$\Delta E_{\text{vib}}^{**}$ cal/mole	k cm ³ /mole-sec
63. HF(5)+HF(2) → HF(4)+HF(3)	+ 923	3.45 x 10 ¹²
64. HF(5)+HF(2) → HF(3)+HF(3)	- 8,966	1.16 x 10 ¹²
65. HF(5)+HF(3) → HF(8)+HF(0)	- 6,879	3.55 x 10 ¹²
66. HF(5)+HF(3) → HF(7)+HF(1)	- 3,660	1.52 x 10 ¹³
67. HF(5)+HF(3) → HF(6)+HF(2)	- 1,371	2.53 x 10 ¹³
68. HF(5)+HF(3) → HF(4)+HF(4)	+ 456	4.09 x 10 ¹²
69. HF(5)+HF(4) → HF(8)+HF(1)	- 5,441	6.57 x 10 ¹²
70. HF(5)+HF(4) → HF(7)+HF(2)	- 2,715	1.88 x 10 ¹³
71. HF(5)+HF(4) → HF(6)+HF(3)	- 904	2.35 x 10 ¹³
72. HF(5)+HF(5) → HF(8)+HF(2)	- 4,040	1.19 x 10 ¹³
73. HF(5)+HF(5) → HF(7)+HF(3)	- 1,792	2.26 x 10 ¹³
74. HF(5)+HF(5) → HF(6)+HF(4)	- 448	2.22 x 10 ¹³

*In processes (1)-(9), the vibrational state of the second HF is not explicitly stated, although calculations indicate that the rate of the V-(R,T) process does depend to some extent on HF(v'). Also, both forward and reverse processes are listed separately; processes (21) and (33), for example, are of course related by detailed balancing.

** ΔE_{vib} is written so that $\Delta E_{\text{vib}} < 0$ corresponds to an exothermic process, i.e., net conversion of vibrational energy to translation and rotation, and $\Delta E_{\text{vib}} > 0$ to an endothermic process.

would seem to preclude v^r scaling with $r > 1$. Consider the following simple demonstration.

For $v=1$, the only significant rate is to $v' = 0$, so we have

$$\begin{aligned}(E_0 - E_1)k(1 \rightarrow 0) &= \alpha[E_0 + (E_1 - E_0)e^{-(E_1 - E_0)/kT} - E_1] \\ &= \alpha[(E_0 - E_1)(1 - e^{-hc\omega_e/kT})]\end{aligned}$$

The $(E_0 - E_1)$ cancels, leaving the usual definition of the vibrational relaxation time,

$$\alpha = \frac{k(1 \rightarrow 0)}{1 - e^{-hc\omega_e/kT}}$$

for $v=2$, we have

$$(E_0 - E_2)k(2 \rightarrow 0) + (E_1 - E_2)k(2 \rightarrow 1) = \alpha[\langle E_V \rangle_{eq} - E_2] \approx \alpha(E_0 - E_2)$$

From table 1, we note that $k(2 \rightarrow 0)$ is almost 10^3 times smaller than $k(2 \rightarrow 1)$. We may thus write

$$(E_1 - E_2)k(2 \rightarrow 1) \approx \alpha(E_0 - E_2)$$

or

$$k(2 \rightarrow 1) \approx \frac{E_0 - E_2}{E_1 - E_2} k(1 \rightarrow 0)$$

for $hc\omega_e/kT \gg 1$. For a harmonic oscillator this would require $k(2 \rightarrow 1) = 2k(1 \rightarrow 0)$; even including the HF anharmonicity, we have only $k(2 \rightarrow 1) \approx 2.05 k(1 \rightarrow 0)$, not $4k(1 \rightarrow 0)$ as v^2 scaling would predict.

We have also noted that the suggestion that multiquantum $V-(R,T)$ rates scale as $1/\Delta v$ (ref. 25) is not borne out either. This is compensated, however, by the appearance of very rapid $V-V$ rates for the higher v levels.

The only available experimental data with which to compare these results are the flow-tube experiments of Kwok and Wilkins (ref. 26), which measure the total rate of deactivation of $HF(v)$ by $HF(0)$. This comparison is shown in table 2.

Table 2

DEACTIVATION RATES FOR HF(v) by HF(0)

v/	k(x 10 ¹² cm ³ /mole-sec)*	
	expt. (ref. 26)	Calculated
1	1.0	1.0**
2	12	13.3
3	11	12.7
4	16	13.0
5	35	19.1
6	59	31
7	--	45

*k is the sum of V-(T,R) [e.g., HF(3) + HF(0) → HF(2) + HF(0)] and V-V [e.g., HF(3) + HF(0) → HF(2) + HF(1)] processes.

**k(1 + 0 → 0 + 0) chosen for normalization.

The agreement is quite good; in particular, the slight decrease in overall deactivation rate, observed from ($v=2$) to ($v=3$), is predicted by the Surprisal Method. The rapid increase in experimental values for $v > 3$ is mirrored by the Surprisal results, although the rise is not quite as fast as in the experimental results.

Very recently, measurements have been carried out of the v -dependence of the HF V-R, T deactivation rates (ref. 27). These results indicate that the scaling rule is something like $v^{1.5}$, which is much closer to the Surprisal results than the results of a $v^{2.4}$ scaling would be.

SECTION III

TEMPERATURE DEPENDENCE OF $k(10 \rightarrow 00)$

The temperature dependence of the deactivation rate for



has been extensively studied (ref. 1). Its most notable feature is an inverse temperature dependence below 1000°K, followed by a broad minimum which then rises again to an asymptotic Landau-Teller $\exp(-T^{-1/3})$ form at high temperatures. If the Information-Theoretical analysis is to be useful, it must reproduce this behavior.

The form of the rate constant in equation (6) is derived from minimization of the Lagrangian (ref. 6).

$$\begin{aligned} \mathcal{L} = & \sum_{v, m'} k(vm \rightarrow v'm') \log \frac{k(vm \rightarrow v'm')}{k^o(vm \rightarrow v'm')} \\ & + (\lambda_0 - 1) \sum_{v, m'} k(vm \rightarrow v'm') + \lambda \sum_{v, m'} k(vm \rightarrow v'm') \\ & \times [(E_{v'} + E_{m'}) - (E_v + E_m)] \end{aligned} \quad (8)$$

Detailed balancing requires that the reverse reactions be given by

$$\begin{aligned} k(vm \rightarrow v'm') &= e^{-[(E_{v'} + E_{m'}) - (E_v + E_m)]/kT} k(v'm' \rightarrow vm) \\ &= e^{\Delta E/kT} k(v'm' \rightarrow vm) \end{aligned} \quad (9)$$

These reactions will become important at high temperatures, especially as many of the V-V processes have an overall $\Delta E < 1000^\circ\text{K}$. Incorporating equation (9) in equation (8) gives

$$\begin{aligned} \mathcal{L} = & \sum_{v'm'} k(vm \rightarrow v'm') \log \left[\frac{k(vm \rightarrow v'm')}{k^0(vm \rightarrow v'm')} (1 + e^{-\Delta E/kT}) \right] \\ & + (\lambda_0 - 1) \sum_{v'm'} k(vm \rightarrow v'm') (1 + e^{-\Delta E/kT}) \\ & + \lambda_1 \sum_{v'm'} k(vm \rightarrow v'm') (\Delta E - e^{-\Delta E/kT} \Delta E) \end{aligned} \quad (10)$$

Taking variations of \mathcal{L} with respect to all $k(vm \rightarrow v'm')$ gives

$$\begin{aligned} (1 + e^{\Delta E/kT}) \left[\log \frac{k(vm \rightarrow v'm')}{k^0(vm \rightarrow v'm')} + 1 \right] + (\lambda_0 - 1)(1 + e^{-\Delta E/kT}) \\ + \lambda_1 \Delta E (1 - e^{-\Delta E/kT}) = 0 \end{aligned} \quad (11)$$

Dividing through by $(1 + e^{-\Delta E/kT})$,

$$\log \frac{k(vm \rightarrow v'm')}{k^0(vm \rightarrow v'm')} + 1 - 1 + \lambda_0 + \lambda_1 \Delta E \tanh \left(\frac{\Delta E}{2kT} \right) = 0 \quad (12)$$

Thus, the deactivation rate constant is given by the expressions

$$k(vm \rightarrow v'm'; T) = k^0(vm \rightarrow v'm'; T) e^{-\lambda_0} e^{-\lambda_1 \Delta E \tanh \left(\frac{\Delta E}{2kT} \right)} \quad (13)$$

In general, we expect that both λ_0 and λ_1 may be temperature-dependent (ref. 17). The former may be eliminated from the calculation by using, instead of equation (13),

$$k(vm \rightarrow v'm'; T) = \frac{k_0(vm \rightarrow v'm'; T) e^{-\lambda_1 \Delta E \tanh \left(\frac{\Delta E}{2kT} \right)}}{\sum_{v'm'} k_0(vm \rightarrow v'm'; T) e^{-\lambda_1 \Delta E \tanh \left(\frac{\Delta E}{2kT} \right)}} \quad (14)$$

Let us assume, provisionally, that λ_1 is independent of temperature and equal to $0.0021 \text{ l}/(\text{cm}^{-1})$, as found for $T = 300^\circ\text{K}$. We can then calculate $k(10 \rightarrow 00; T)$ from equation (14) for a range of temperatures, with $\Delta E = \omega_0$ (HF). The results of doing so are shown in figure 1. The most striking observation is that we do find the inverse temperature dependence at low T , the minimum around 1000°K , and the rapid increase in k at high T . The Information-Theoretic results

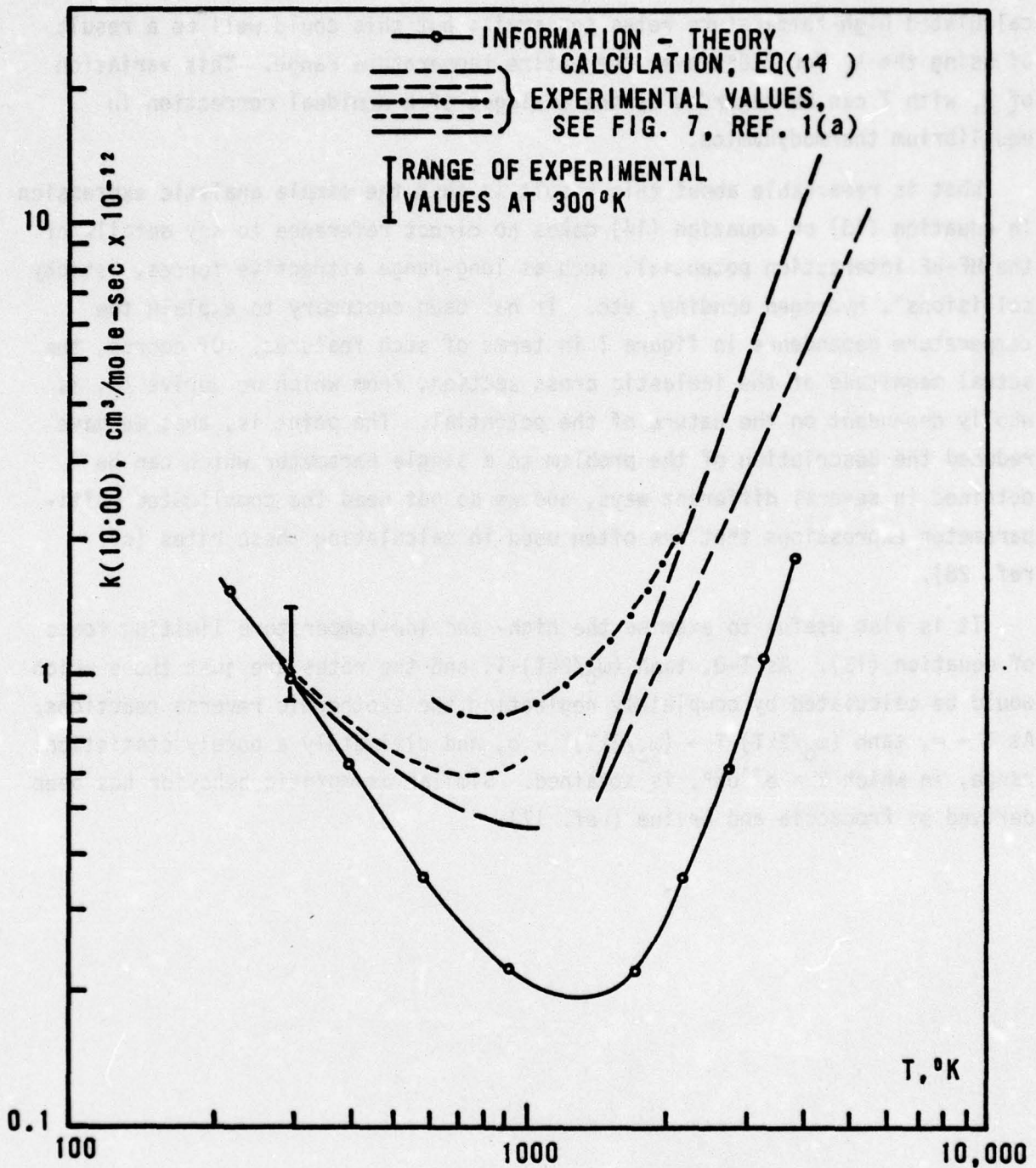


Figure 1. Temperature Dependence of the $\text{HF}(v = 1) + \text{HF}(v = 0) \rightarrow 2\text{HF}(v = 0)$ Deactivation Rate, as Calculated from the Surprisal Theory. Also, shown are several recent experimental measurements of this quantity, taken from reference 1. The Surprisal calculation is normalized to the measured value of the rate coefficient at 300°K.

appear to have a deeper minimum than is found experimentally, making the calculated high-temperature rates too small; but this could well be a result of using the λ_1 for 300°K over the entire temperature range. This variation of λ_1 with T can be regarded as the analogue of a nonideal correction in equilibrium thermodynamics.

What is remarkable about this result is that the simple analytic expression in equation (13) or equation (14) makes no direct reference to any details of the HF-HF interaction potential, such as long-range attractive forces, "sticky collisions", hydrogen bonding, etc. It has been customary to explain the temperature dependence in figure 1 in terms of such features. Of course, the actual magnitude of the inelastic cross section, from which we derive λ_1 , is wholly dependent on the nature of the potential. The point is, that we have reduced the description of the problem to a single parameter which can be obtained in several different ways, and we do not need the complicated multi-parameter expressions that are often used in calculating these rates (cf. ref. 28).

It is also useful to examine the high- and low-temperature limiting forms of equation (13). As $T \rightarrow 0$, $\tanh(\omega_0/2kT) \rightarrow 1$, and the rates are just those which would be calculated by completely neglecting the exothermic reverse reactions. As $T \rightarrow \infty$, $\tanh(\omega_0/2kT) \rightarrow (\omega_0/2kT)T \rightarrow 0$, and ultimately a purely statistical range, in which $k = e^{-\lambda} \omega_0$, is attained. Similar asymptotic behavior has been derived by Procaccia and Levine (ref. 17).

SECTION IV

OTHER APPLICATIONS OF THE THEORY

Several other aspects of Surprisal methods, which may be of use in laser kinetics problems, have been investigated briefly.

1. REMAINING PROBLEM AREAS IN VIBRATIONAL SURPRISAL

Although the approach described in the preceding sections has been quite successful in reproducing the known behavior of HF-HF relaxation rates, there still remains a number of questions to be explored. The most important seems to be the accurate formulations of sum rules, analogous to equation (11) of reference 17 for V-V' and VR-V'R' exchanges. This is especially the case for collisions between dissimilar pairs, such as HF-DF, HF-H₂, etc. which form an important part of real laser systems. In the latter cases, it may be necessary to introduce as many as four independent Surprisal parameters, one for the vibrational and rotational degrees of freedom of each species. Hopefully, information from one-component relaxation experiments can be used to determine values of these individual parameters.

A second issue is that of the temperature dependence of the λ 's, as discussed in the previous section. In terms of the thermodynamic formulation of Surprisal theory, treatments to date have treated all reacting species as ideal gases. As in equilibrium thermodynamics, nonideal effects modify this behavior. Temperature- and density-dependent Surprisal parameters may be encountered, and it will be necessary for the theory to treat these effects.

2. ROTATIONAL NONEQUILIBRIUM

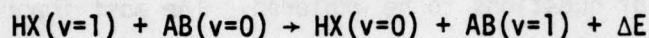
The importance of nonequilibrium distributions over rotational states in HF or DF laser active media has recently been suggested by several groups (refs. 29 through 31). If rotational deactivation processes have to be explicitly included in performance codes, the dimensionality of the problem is measured to a frightening extent. Instead of a few dozen rates connecting 5 or 6 vibrational levels, we would have 50 or 60 vibrotational levels, with some tens of thousands of reactions to be considered!

It seems evident that Information-Theoretical methods will be essential in managing and coordinating this mass of data. A formulation of Surprisal

Theory for rotational energy transfer is available (refs. 18 and 19). We have applied this analysis to the available data on rotational energy transfer in HF (refs. 32 and 33). Hitchen finds that this data can best be fit by the expression $k(ij \rightarrow kl) \propto e^{-\alpha |(E_j - E_i) + (E_l - E_k)|/kT}$, with $\alpha = 0.96$. This is of course just the Surprisal form of the rate, $k \sim \exp(\theta |\Delta|/2kT)$, with $\theta = 1.92$. While more work needs to be done on that analysis, it does appear that most of the data can be represented by a single rotational Surprisal parameter.

3. V-V CORRELATION RULES

Bott (ref. 34) has carried out an empirical correlation of available single-quantum V-V' energy exchange, that is, for processes of the type



He finds that the data are best represented by

$$P_{VV'} \propto (\mu_1 \mu_2) e^{-c\Delta E/h\nu_1} \quad (15)$$

where the energy transfer probability $P_{VV'}$ is defined as the ratio of the transfer rate $k_{VV'}$ to the gas-kinetic collision rate; μ_1 and μ_2 are the permanent dipole moments of molecules HX and AB; ν_1 is the vibration frequency of HX; and ΔE is the energy defect.

It is quite easy to see how the main features of equation (15) arise from the Surprisal form of the rate constant, equation (6). The $\exp(-\Delta E)$ dependence is self-evident. This is to be multiplied by the Surprisal factor λ_V . Now, for $h\nu_1 \gg kT$, we can write $\lambda_V = \Lambda_V kt/h\nu_1$, where Λ_V is a constant of order unity (ref. 17). We thus obtain the $\exp(1/h\nu_1)$ dependence as well. It would be of interest to carry out a more rigorous derivation of this result, particularly to see how the $(\mu_1 \mu_2)$ dependence enters into the pre-exponential (A_T or e^{λ_0}) factor.

4. POPULATIONS' EVOLUTION IN TIME APPROACH

Recently, Procaccia and Levine (ref. 20) have indicated a method whereby the populations in a multi-level system relaxing toward equilibrium may be explicitly calculated without reference to detailed rate constants. In this "Populations' Evolution in Time (PET)" Approach, the populations are given as

$$n_v(t) = e^{-\beta(t)E_v - \lambda_0(t)} \quad (16)$$

The time-dependent parameter β is found by using a type of sum rule, which requires that

$$R[\beta(t)] = \langle V(t) \rangle \quad (17)$$

with

$$\langle V(t) \rangle = \langle V(\infty) \rangle + [\langle V(t_0) \rangle - \langle V(\infty) \rangle] e^{-(t-t_0)/\tau} \quad (18)$$

and

$$R[\beta] = \frac{\sum_v E_v e^{-\beta(t)E_v}}{\sum_v e^{-\beta(t)E_v}} \quad (19)$$

The normalization parameter $\lambda_0(t)$ is then found simply as

$$\lambda_0(t) = \ln \left[\sum_v e^{-\beta(t)E_v} \right] \quad (20)$$

Thus, the only inputs required are the initial departure of the system from equilibrium at time t_0 , $[\langle V(t_0) \rangle - \langle V(\infty) \rangle]$, and the bulk relaxation time τ .

We have applied the PET method to a simple model of relaxation in pure HF following an injection of population at some specified v' , such as would occur in pumping a $v' \rightarrow 0$ transition with a pulsed laser. A full master equation (for $0 \leq v \leq 5$), using the deactivation rate constants in table 1, was solved by numerical integration. Equations (16) through (19) were then solved for the same initial conditions, and with a relaxation time τ consistent with the rates used in the model. The comparison is shown in figure 2. We see that the PET method gives essentially perfect agreement with the full master equation for each vibrational level, as had been previously noted (ref. 20). The only quantity that is not well determined is the relative proportions in higher v states following the excitation pulse, which is determined by $V \leftrightarrow V$ exchanges. Levine suggests that these can also be calculated by adding an additional VV constraint to equation (16) to give

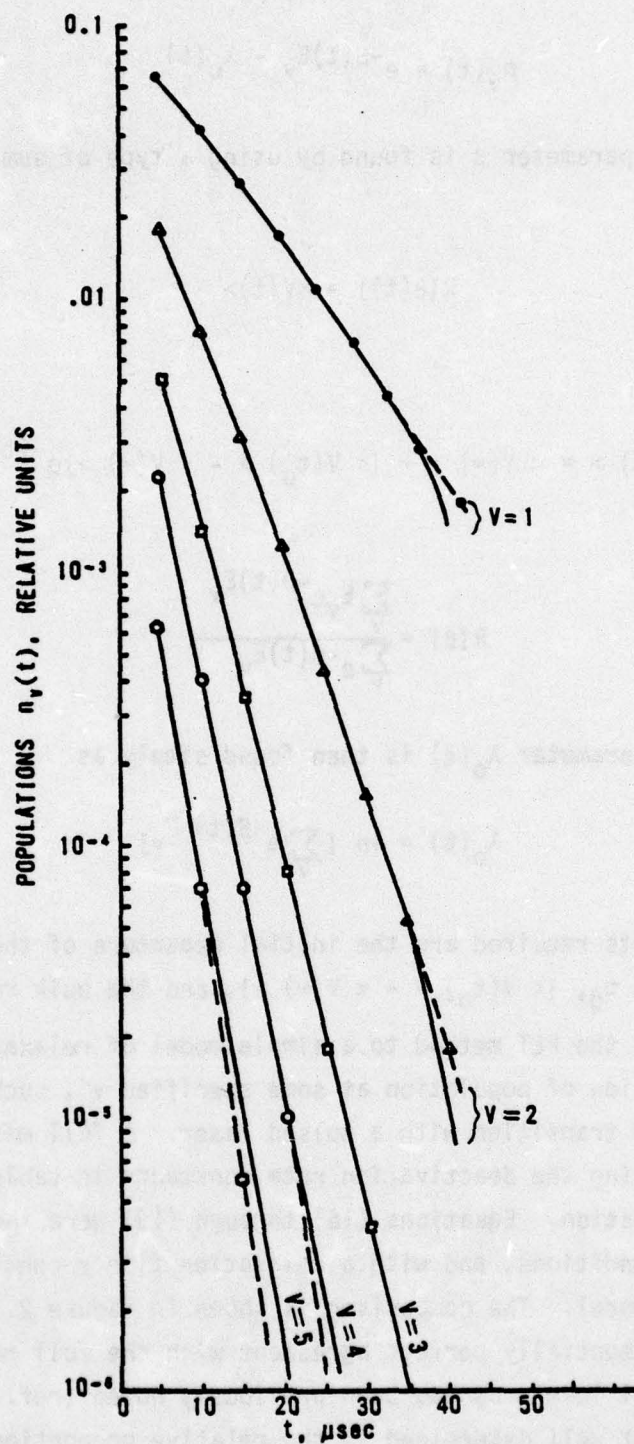


Figure 2. Comparison of Master-Equation and PET Solutions for $n_v(t)$, $v = 0$ to $v = 5$. Initial conditions: $p[\text{HF}(v = 0)] = 1.9$ torr, $p[\text{HF}(v = 4)] = 0.2$ Torr, all other $n_v = 0$. Relaxation time $\tau = 9.1$ μsec . Solid curves, PET solution [equations (16)-(19)]; symbols and dashed curves, explicit integration with rate package in table 1. Populations normalized to initial $t = 5$ μsec .

$$n_v(t) = e^{-\beta(t)E_v + \lambda(t)|E_v - E_i| - \lambda_0(t)} \quad (21)$$

where $v=i$ is the level initially displaced from equilibrium.

On a more profound level, major simplifications may be possible in the way in which we model complex chemical laser systems, beyond merely generating sets of rate constants. When using the modeling codes, after all, we are not really interested in the detailed values of these rate constants; the information we actually require is $[n(x,t)]$, the time and space variation of the concentrations of particular species, such as $HF(v)$. We need the rate constants only as input to a kinetic master equation which must then be coupled to optics and gas-dynamic equations to find these concentrations. The whole idea of the Information-Theoretic approach is to find expressions only for the data we want to know, while avoiding detailed consideration of large masses of unnecessary data. It may be possible to apply the PET approach to the gas-dynamic chemical laser problem, in an attempt to find a direct route to $[n(x,t)]$ while bypassing as much of the detailed kinetics as possible. This problem has been treated in a general way by Ben-Shaul and Hofacker (ref. 22), and further analysis of specific systems would be highly desirable. If it were indeed possible to streamline performance codes by eliminating much of the detailed kinetics, a much more thorough modeling of the optics and gas-dynamic parameters would then be both possible and practical.

SECTION V
CONCLUSIONS

Our initial experience in applying Surprisal Theory to the HF relaxation problem has been that a great deal of insight may be obtained with the theory as it exists, but that a number of questions remain to be answered. These questions pertain both to fundamental aspects of the theory, its range of validity, etc., and to practical aspects of its implementation. Among the problems that need to be investigated are the best methods for finding the λ_V parameter, proper formulation of sum rules for coupled vibration-rotation systems, and so on. Asymptotic forms of the rate constants for limiting high- and low-temperature τ would also be useful.

The Surprisal Theory has at this point received an impressive number of validations, both from experimental and computed data bases, in HF and many other systems. If we accept the point of view that this theory is an essentially correct description of Nature, then our entire approach to state-to-state chemical kinetics needs to be revised. The present approach is to carry out ever more sophisticated and detailed calculations, and to validate these with ever more marginal experiments. The Information-Theoretical approach states that essentially all microscopic rate data for a given system is interrelated, and determined by one or two parameters. The purpose of an experiment is then to establish the value of these parameters by very careful measurements of a basic system property, such as the relaxation time. A calculation is deemed to be correct once it is done carefully enough to reproduce the Surprisal-synthesized results, and all theoretical methods -- classical trajectories, close-coupled quantum states, R-matrix theory, etc. -- should converge to these results if properly done. In applying kinetic information to the analysis and modeling of real systems, Surprisal Methods again offer the prospect of much more rapid and efficient modeling procedures than are presently being used, and also make it possible to bypass much of the detailed information now required.

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APPENDIX

COMPUTER PROGRAMS FOR CALCULATING PRIOR RATES, EQUATIONS (4) AND (5)

```

PROGRAM RATE
      T=76      OPT=1
      ETN 6,7+23

      PROGRAM RATE(INPUT,TAPE5=INPUT,OUTPUT,TAPE6=OUTPUT,PUNCH)
      REAL V, L, V1, M1
      DIMENSION I(2,50), J(14,14,2)
      DO 10 I=1,2
      DO 10 J=1,50
100    Z(I, J)=0
      READ(5,100) M1, J1, AE1, WX1, M2, J2, AE2, WX2
      WRITE(6,100) M1, J1, AE1, WX1, M2, J2, AE2, WX2
110    FORMAT(2(F9.2, F7.3, F6.2, F9.3))
      A(1,1)=M1
      A(1,2)=J1
      A(1,3)=AE1
      A(1,4)=WX1
      A(2,1)=M2
      A(2,2)=J2
      A(2,3)=AE2
      A(2,4)=WX2
      READ(5,100) V, L, V1, M
      WRITE(6,100) V, L, V1, M
130    FORMAT(F15.4)
      READ(5,100) TEM
      WRITE(6,100) TEM
150    FORMAT(F3.2)
11    CONTINUE
      READ(5,100) J, M
      WRITE(6,100) J, M
170    FORMAT(2F9.1)
      EXT=(V+J*.5)*(A(1,1)-A(1,4)*(V+J*.5))+(M+J*.5)*(A(2,1)-A(2,4)*(M+J*.5))
11
      CALL CAN(1,3,TEM,J,M,L,V,M)
      DO 20 I=1,14
      DO 20 J1=1,14
      DO 20 J2=1,2
20    Z(I, J1, J2)=0.0
      DO 1 J=1,14
      DO 1 L=1,14
      DO 1 M=1,14
      DO 1 I1=1,14
      X0=(Z(I1,1)+Z(I1,2)+Z(I1,3)+Z(I1,4)+Z(I1,5)+Z(I1,6)+Z(I1,7)+Z(I1,8)+Z(I1,9)+Z(I1,10)+Z(I1,11)+Z(I1,12)+Z(I1,13)+Z(I1,14))/14
      X1A=100*(X0)
      X2A=200*(X0)
      IF(X1A,GT,2.2150) GOTO 7
      IF(X2A,GT,5.41) GOTO 3
      I1=I1-1
      M2=M2-1
      EXT=(V+J*.5)*(A(1,1)-A(1,4)*(V+J*.5))+(M+J*.5)*(A(2,1)-A(2,4)*(M+J*.5))
11
  
```

```

C=0.0
DO 1946 J1=1,100
DO 99 L1=1,100
EX=EXT+J*(J-1)*(B1-AE1*(V+0.5))+L*(L-1)*(B2-AE2*(M+0.5))
EY=EY+J1*(J1-1)*(B1-AE1*(V1+0.5))+L1*(L1-1)*(B2-AE2*(M1+0.5))
D=(EX-EY)/(2*TEM)
IF(D.LE.-15) GO TO 2

WX21=ABS(D)
PHO=(2*J1-1)*(2*L1-1)*2.*SQRT(TEM)
PHO=PHO*EXP(D)*FK(WX21)
G=PHO*D
99 CONTINUE
2 CONTINUE
1946 CONTINUE
Z(IM1,IM2,1)=Z(IM1,IM2,1)+G
3 CONTINUE
CALL PED(A,B,Z,J,L,XLAM,V,M,TEM)
1 CONTINUE
DO 7 IM1=1,14
DO 7 IM2=1,14
XD=(IM1-1)*W1+(IM2-1)*W2
XDT=V*W1+M*W2
XD1=(XDT-XD)/TEM
XDA=ABS(XD1*TEM)
XDA1=2*XDA/(W1+W2)
IF(XDA1.GT.2.2) GO TO 31
IF(XD1.LE.-6) GO TO 31
V1=IM1-1
M1=IM2-1
WRITE(6,1900)TEM,V,M,V1,M1,Z(IM1,IM2,2)
1900 FORMAT(2X,F6.0,4F5.1,2X,E15.4)
31 CONTINUE
7 CONTINUE
GO TO 11
END

```

```

SUBROUTINE PED(A,B,Z,J,L,XLAM,V,Y,TEM)
REAL V,M,V1,M1
DIMENSION A(2,50),A(2,4)
DIMENSION Z(14,14,2)
M1=A(1,1)
M2=A(2,1)
S=0.
DO 7 I'2=1,14
DO 3 I'1=1,14
XD=(I'1-1)*M1+(I'2-1)*M2
YDT=V*M1+M*M2
XD1=(YDT-XD)/TEM
XDA=ABS(XD1*TEM)
XDA1=2*XDA/(M1+M2)
IF(XDA1.GT.2.2)GO TO 31
IF(X'1.LE.-5)GO TO 31
V1=I'1-1
M1=I'2-1
EYT=(V+0.5)*(A(1,1)-A(1,4)*(V+0.5))+(M+0.5)*(A(2,1)-A(2,4)*(M+0.5))
EY = (V1+0.5)*(A(1,1)-A(1,4)*(V1+0.5))+(M1+0.5)*(A(2,1)-A(2,4)*(M1+0.5))
S=S+7*(I'1,I'2,1)*EXP(-XLAM*ABS(EYT-EY))
31 CONTINUE
7 CONTINUE
DO 7 I'2=1,14
DO 3 I'1=1,14
XD=(I'1-1)*M1+(I'2-1)*M2
YDT=V*M1+M*M2
XD1=(YDT-XD)/TEM
XDA=ABS(XD1*TEM)
XDA1=2*XDA/(M1+M2)
IF(XDA1.GT.2.2)GO TO 3
IF(X'1.LE.-5)GO TO 3
V1=I'1-1
M1=I'2-1
EYT=(V+0.5)*(A(1,1)-A(1,4)*(V+0.5))+(M+0.5)*(A(2,1)-A(2,4)*(M+0.5))
EY = (V1+0.5)*(A(1,1)-A(1,4)*(V1+0.5))+(M1+0.5)*(A(2,1)-A(2,4)*(M1+0.5))
Z(I'1,I'2,2)=Z(I'1,I'2,2)+7*(I'1,I'2,1)*A(1,J)*A(2,L)*EXP(-XLAM*ABS(EYT-EY))/S
Z(I'1,I'2,1)=0.0
CONTINUE
RETURN
END

```

FTN 4,5+428

76/76 OPT=1

FUNCTION FK

```

FUNCTION FK(X)
C THIS SUBROUTINE COMPUTES THE 1ST ORDER MODIFIED BESSEL FUNCTION
C TIMES Y
IF(X.LE.0.000001) GO TO 2
IF(Y.GT.2) GO TO 1
T=X/3.75
U=T+T
Z=X*(.5+U*(.9789059+.5149887*U+.1505493*U*U))
W=7+X*U+U*U*(.02658733+.00301532*U+.00032411*U*U)
W=X*X/4
Z1=ALOG(X/2)*Z+(1/X)*(1+.1544314*W-.6727852*W*W-.1815690*W*W*W)
FK1 =Z1-(1/X)*W*W*W*W*(.0191940-.00110404*W-.00004686*W*W)
FK=FK1*X
RETURN
1 W=2/Y
Z1=EXP(-X)*(1/SQRT(X))*(1.2533141+.2349952*W-.0365562*W*W+.0150426
13*W**4*W)
FK1 =Z1+EXP(-X)*(1/SQRT(X))*W*W*W*W*(-.00789353+.00325614*W-.0006
18245*W*W)
FK=FK1*X
RETURN
2 FK=1.
RETURN
END
    
```

FTN 4.5+428

SUBROUTINE CAN 76/76 OPT=1

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C SUBROUTINE CAN(A,B,TEM,JM,LM,V,M)
C CANONICAL AVERAGE CALCULATION
C THE RELATIVE POP ARE STORED IN P
C JM AND LM EVALUATE HOW HIGH J AND M TO USE
C TEM = THERMAL ENERGY
C DIMENSION B(2,50),A(2,4)
REAL V,I
Z=0
DO 1 I=1,50
  R(1,I)=(2*I-1)*EXP(-(I-1)*((A(1,2)-A(1,3))*(M+0.5)))/TEM)
  Z=Z+R(1,I)
  Z1=B(1,I)/Z
  IF(Z1.GE.0.01) GO TO 1
  J=I
GO TO 2
1 CONTINUE
DO 3 I=1,JM
  R(1,I)=R(1,I)/Z
DO 4 I=1,50
  R(2,I)=(2*I-1)*EXP(-(I-1)*I*(A(2,2)-A(2,3))*(M+0.5)))/TEM)
  Z=Z+R(2,I)
  Z1=B(2,I)/Z
  IF(Z1.GE.0.01) GO TO 4
  LM=I
GO TO 5
4 CONTINUE
DO 6 I=1,LM
  R(2,I)=R(2,I)/Z
RETURN
END
    
```