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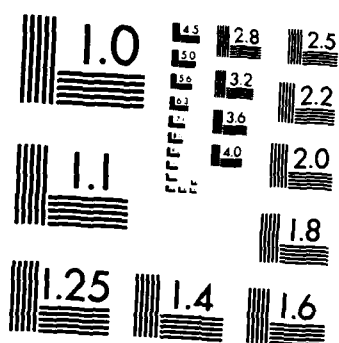
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Rotational Energy Transfer in HF

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El Segundo, Calif. 90245

16 May 1983

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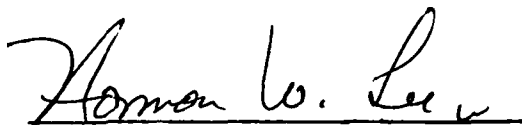
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HF chemical lasers	Rotational energy transfer									
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Power scaling law	Surprisal analysis									
Rate coefficients	Transfer rates									
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A rotational nonequilibrium model has been developed to simulate the infrared double-resonance experimental technique designed to study rotational relaxation of HF gas in the $v = 1$ and higher vibrational states. State-to-state rate coefficients for this rotation-to-translation relaxation model have been obtained from a surprisal analysis and are found to scale as an inverse power of the rotational energy transferred. Phenomenological rates for the rotational energy transfer in the $v = 1$ state for $J = 0$ to $J = 7$ with $\Delta J = +1, +2, +3$, and $+4$ are found to be in excellent agreement with the reported										

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phenomenological rates from available experiments for both the $v = 1$ and $v = 2$ states. It appears, therefore, that the state-to-state rate coefficients for rotational relaxation of HF are insensitive to v state. Angular momentum statistics corresponding to conservation of m_j are found to give better fits to the data than those with m_j assumed to be completely randomized. $\leftarrow$

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I. INTRODUCTION

State-to-state rate coefficients have not been measured directly for rotation-to-translation processes in self-relaxation of vibrationally excited HF gas. Peterson et al.¹ used a single HF-pulsed laser to excite a specific vibrational-rotational state of HF and the tail of the pulse was used as a probe. This pulse-probe technique is restricted to observation of the population in only the level pumped. Hinchin² used an infrared double-resonance technique that involved using two HF lasers. For example, in a gas cell, HF molecules in the $v = 0$, $J = 4$ state were excited to the $v = 1$, $J = 3$ state by absorbing radiation from a pulsed laser operating on a single $P_1(4)$ transition. A cw HF laser operating on a single $P_2(J)$ transition was used to probe the temporal behavior of the HF population in a specific J level of the $v = 1$ state after the pulse laser fires. Copeland et al.³ extended the Hinchin and Hobbs^{2,4,5} technique to a higher vibrational level by using the double-resonance technique on overtone transitions of HF. In this technique, a single rotational level in $v = 2$ of HF is excited by an intense laser pulse; a continuous laser monitors the collisional transfer of molecules to an upper J state of the $P_2(J)$ probe laser transition, since the lower level ($v = 1$, $J + 1$) initially is completely unpopulated. The temporal evolution of the gain provides the filling time of the probed rotational level.

A rate coefficient obtained in any of these three experiments is a phenomenological coefficient that is the cumulative behavior of all the pathways that can populate that given rotational state. On the time scales of these experiments, the collisional processes lead to the rapid simultaneous build-up of a number of neighboring states. The observed growth of a density in time is largely the result of the filling from a number of neighboring states by different classes of rotational processes. Thus, for these data to be useful in describing the rotational nonequilibrium processes that occur in chemical lasers, they must be related to state-to-state rate coefficients.

Hinchin and Hobbs^{4,5} employed a state-to-state rate equation model that assumes the rate to be proportional to the exponential of the energy defect in the collision. Rate coefficients for the Hinchin and Hobbs model for binary collisions of HF($v = 1$, J) with ground-state HF molecules are written as $R \rightarrow R$ transfer processes, but include $R \rightarrow T$ transfer when both the reactant and

product ground-state HF molecule are in the same J state. In their model, $R \rightarrow R$ rates are those that conserve rotational quanta. The Hinchey and Hobbs model predicts extremely slow rates for rotational relaxation from the high J levels of HF.

Recently Brunner et al.⁶ proposed a new scaling law that predicts that a state-to-state rate coefficient depends on the amount of energy transferred, to some exponent. The entire set of state-to-state rate coefficients for a given collision system can be represented with only two parameters. An important feature of this analysis is the use of an angular momentum statistical factor that assumes that the azimuthal angular momentum m_j is conserved. The usual statistical factor assumes that the rate coefficient does not depend on the initial or final value of m_j . For $\text{Na}_2^* - \text{Xe}$ collisions Brunner et al. found the reduced rate follows a simple law in ΔE_r , the increase in rotational energy, with an exponent close to -1. In addition, they found that all of the reduced rates at different initial values of the reactant initial j_0 state can be represented by a single power law function.

Wainger et al.⁷ applied the power law scaling to rotational energy transfer in collisions of Na_2^* ($A^1 \Sigma_u^+$) with He, H_2 , CH_4 , and N_2 . These results provided additional evidence for the wide applicability of the previous proposed power scaling law for rotational energy transfer. The significant aspect of their work is that rate data for rotational energy transfer in all of these systems scale with an angular momentum factor corresponding to the randomization of m_j .

Pritchard et al.⁸ applied the power scaling law to several other systems ($\text{N}_2 + \text{Ar}$, $\text{H}_2 + \text{Li}^+$, $\text{CO}_2 + \text{Ar}$, and $\text{LiH} + \text{Ar}$) to study rotational energy transfer. The data support a power law in preference to the exponential gap representation^{9,10} previously used to model rotational relaxation measurements. Other theoretical approximations that have been developed to handle a large number of channels in rotationally inelastic scattering include close coupling,¹¹ coupled states,¹² effective potential,¹³ statistical j_2 ,¹⁴ infinite-order sudden,¹⁵ and classical.¹⁶

In the present work, state-to-state rate coefficients are calculated for $R \rightarrow T$ rotational energy transfer in $\text{HF}(v = 1, J) + \text{HF}$ collisions. These rates

are obtained with the power scaling law and are incorporated into a nonequilibrium kinetic computer program that models the double-resonance technique.

The purpose of this study is to determine one set of state-to-state rate coefficients for $R \rightarrow T$ energy transfer in $\text{HF}(v = 1, J) + \text{HF}$ collisions. The goal is a nonequilibrium model that can reproduce accurately the phenomenological rate coefficients and other experimental observations of several laboratories. This effort is a continuation of past studies^{17,18} in which we have reported on the accurate simulations of $\text{HF}(v, J) + \text{M}$ collision processes. The details of these processes as they apply to HF lasers are important toward an understanding of the spectral power distributions observed in HF chemical lasers.

II. THE POWER SCALING LAW

The power law expression of the state-to-state rate coefficient for rotational energy transfer (RET) can be derived from surprisal analysis¹⁹:

$$k_{j_o j_f}(T) = aT^{1/2} N(j_o, j_f) |\Delta| \exp(\Delta) K_1(\Delta) |\Delta|^{-\gamma} \quad (1)$$

where $N(j_o, j_f)$ is the angular momentum degeneracy factor, $\Delta = [E_{\text{rot}}(j_o) - E_{\text{rot}}(j_f)]/(2kT)$, $K_1(\Delta)$ is the first-order modified Bessel function of the second kind, and j_o and j_f are the initial and final rotational quantum numbers, respectively. The state-to-state rate coefficient is usually assumed not to depend on the change in the azimuthal quantum number m during the collision. Therefore

$$N_{\Delta}(j_o, j_f) = 2j_f + 1 \quad (2)$$

is the most commonly used angular momentum degeneracy factor in surprisal analysis. If m_j does not change drastically in rotational energy transfer ($\Delta m_j = 0$), then Brunner et al.⁶ have shown

$$N_o(j_o, j_f) = (2j_{<} + 1)/(2j_o + 1) \quad (3)$$

where $j_{<}$ is the smaller of j_o and j_f . For collisions in which $j_f > j_o$, $N_o(j_o, j_f) = 1$, while for $j_f < j_o$, $N_o(j_o, j_f) = (2j_f + 1)/(2j_o + 1)$. Both N_{Δ} and N_o satisfy microscopic reversibility. The constant γ should be greater than 3/2 for N_{Δ} and 1/2 for N_o , since k_{j_o, j_o-L} is a decreasing function of j_o for $j_o > 1$ and $L = 1$. It can be shown that k_{j_o, j_o-L} is proportional to $j_o^{3/2-\gamma}$ for N_{Δ} and $j_o^{1/2-\gamma}$ for N_o . This scaling law has two independent components. One varies as a power of the rotational energy transferred; the other, the angular momentum statistical factor, reflects either randomization or conservation of the azimuthal quantum number.

III. THE MODEL

In the current work, the two parameters a and γ in Eq. (1) are established with a minimum of experimental data. Guess values of the parameters are used to generate state-to-state kinetic rate coefficients, which in turn are placed into the kinetic model. The model computes HF number densities as a function of time after pulse-laser excitation. Anchoring the parameters requires some experimental data, and the published oscilloscope traces⁵ reported by Hinch and Hobbs have been used. In an iterative series of code runs, it has been found that unique values of a and γ can be identified, given the form of Eq. (1). Initially, both $v \rightarrow v$ and $v \rightarrow R$ processes were considered in the modeling but were subsequently found to make a negligible contribution to the simulated phenomenological rate coefficients. The $v - v$ rate coefficients were generated by means of an analysis similar to Eq. (1) and other experimental data. The $v \rightarrow R$ rate coefficients were taken from trajectory calculations.²⁰ The $v \rightarrow R$ modeling results will be reported in a separate paper.

In an infrared double-resonance experiment,²⁻⁵ a HF pulsed laser operating on a single $P(J)$ transition is used to excite a specific $(v, J' = J - 1)$ state. An HF cw probe laser operating on a single $P_2(J'')$ transition is used to monitor the arrival of rotational population in J levels other than the pumped level. The absorption (or gain) of the probe laser measures the difference in rotational population between the affected J levels in the $v = 1$ and $v = 2$ states. In the Hinch experiments,^{2,4,5} densities in the $v = 2$ states are very low and consequently the absorption essentially measures rotational population in the $v = 1$ state. The total density is constant in a gas cell that contains only HF. Before the pumping pulse, all HF species in the v manifold have a rotational Boltzmann distribution. After the pumping pulse, rotational Boltzmann distributions are maintained in the v manifold with only two exceptions. There is a density spike at the J' level in $v = 1$, which is excited by the pumping pulse in the $v = 0$ state. There is a hole at the J -state density pumped from the $v = 0$ state. The subsequent transfer of rotational populations in the $v = 1$ state results from rotational relaxation caused by collisions. The cross sections for rotation-changing collisions are much larger than those for vibration-changing collisions. This allows one to

study rotational inelastic collisions that do not substantially change the vibrational quantum state. The populations in these J levels are assumed to be affected by collisions only, not by radiative flux.

The details of the nonequilibrium calculations have been described previously¹⁷ and will not be repeated here. In our model of the Hinch and Hobbs experiment, only state-to-state rate coefficients for $R \rightarrow T$ processes are used for the $v = 1$ state. To model the Copeland, Pearson, and Crim work,³ state-to-state $R \rightarrow T$ rate coefficients are assumed to be independent of the v state. The assumption is justifiable since Barnes et al.²¹ found in their studies of rotational relaxation of $HF(v = 1, 2; J)$ by Ar that relative probabilities of $R \rightarrow T$ energy transfer were independent of vibrational quantum number. The change in anisotropy of the $HF + Ar$ potential resulting from the increase in the HF -bond length is insufficient to produce a significant change in the relative cross sections for $R \rightarrow T$ energy transfer.

Hinch and Hobbs⁵ published oscilloscope traces of cw laser intensity for probing rotational levels $J = 4, 5, 6$, and 7 after pumping $J = 3$ at $P = 0.04$ Torr. A comparison is made of the model $HF(v, J)$ densities with these oscilloscope traces. In their experiments,⁵ the presence of excited HF density is indicated by a drop in the intensity of the cw probe laser as a result of resonance absorption. According to Beer's Law, in the optical thin limit this change in intensity ΔI is directly proportional to the $HF(v, J)$ number density. With this relationship, model curves are constructed (see Fig. 2) to provide a comparison of experimental curve shapes in the densities with time. Since the experimental data on the absolute maximum intensity I_0 of the cw probe laser are lacking, the maximum calculated model density has simply been normalized to the maximum observed ΔI reported by Hinch and Hobbs.⁵ The computer model employed here simulates those scope traces by selecting the best values in the sense of least squares for the two parameters a and γ in Eq. (1). γ was varied from 0.75 to 2.1 and parameter a from 10^{12} to 10^{13} . A value of a is chosen and then γ is varied from 0.75 to 2.1 . For each value of a and γ , the power law expression is used to generate a set of state-to-state rate coefficients for rotational relaxation of HF . The state-to-state rate coefficients are used in the rotational nonequilibrium computer program to simulate the Hinch and Hobbs⁵ experiment. The best values of γ and a were 0.80 and 5.0×10^{12} , respectively. The degeneracy factors N_0

or N_{Δ} were tried for each value of a and γ in order to find which factor provided the best fit to the scope traces.

The relaxation is modeled by following the population changes of $HF(v = 1, J)$ for J greater than the pumped level J . An exponential growth of the absorption is assumed and the τ for relaxation from a specified, probed J state is obtained at the $(1 - 1/e) \approx 0.63$ point of maximum signal decrease. This approach is intentionally identical to that used by the experimenters themselves. The results from the best fit are shown in Fig. 1. The maximum number density or peak intensity occurs for times between two and four microseconds. Figures 2a through 2d show a comparison of the model simulation with the values obtained from the oscilloscope traces. The comparison is very good for rotational transitions $\Delta J = +1$ and $+2$, good for $\Delta J = +3$, and poor for $\Delta J = +4$. However, the lack of apparent agreement at $\Delta J = +4$ may be due in part to the poor signal-to-noise ratio of this trace. The state-to-state rate coefficients used to model the Hinchey and Hobbs experiments are shown in Figs. 3 and 4, which give plots for the up-rates $J \rightarrow J + \Delta J$ and down-rates $J \rightarrow J - \Delta J$, respectively.

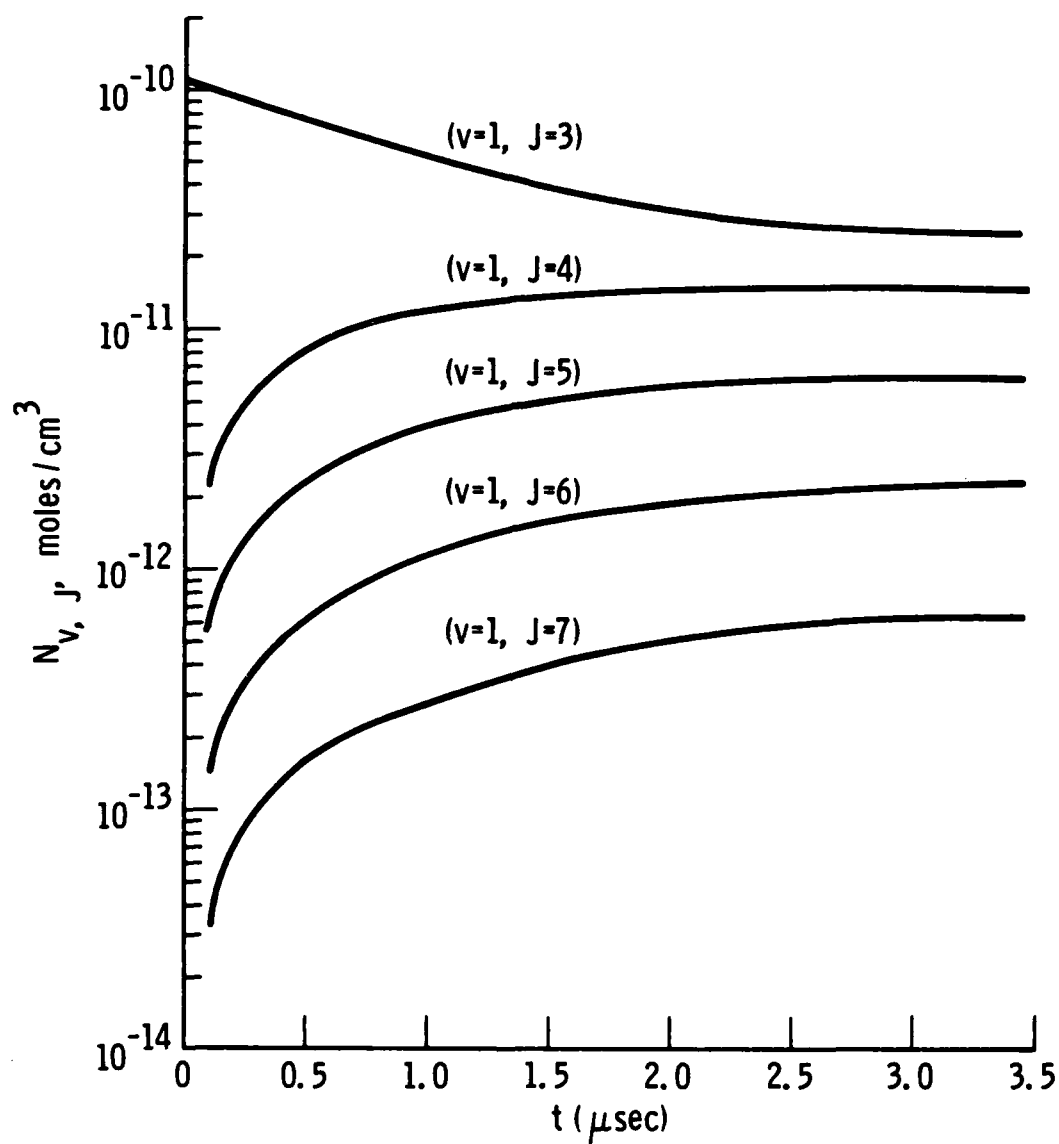


Fig. 1. Kinetic model results using generated R + T state-to-state coefficients. The curves show the number density $N_{v=1,J}$ of HF versus $t(\mu\text{sec})$ for $v = 1$, $J = 3, 4, 5, 6$, and 7 .

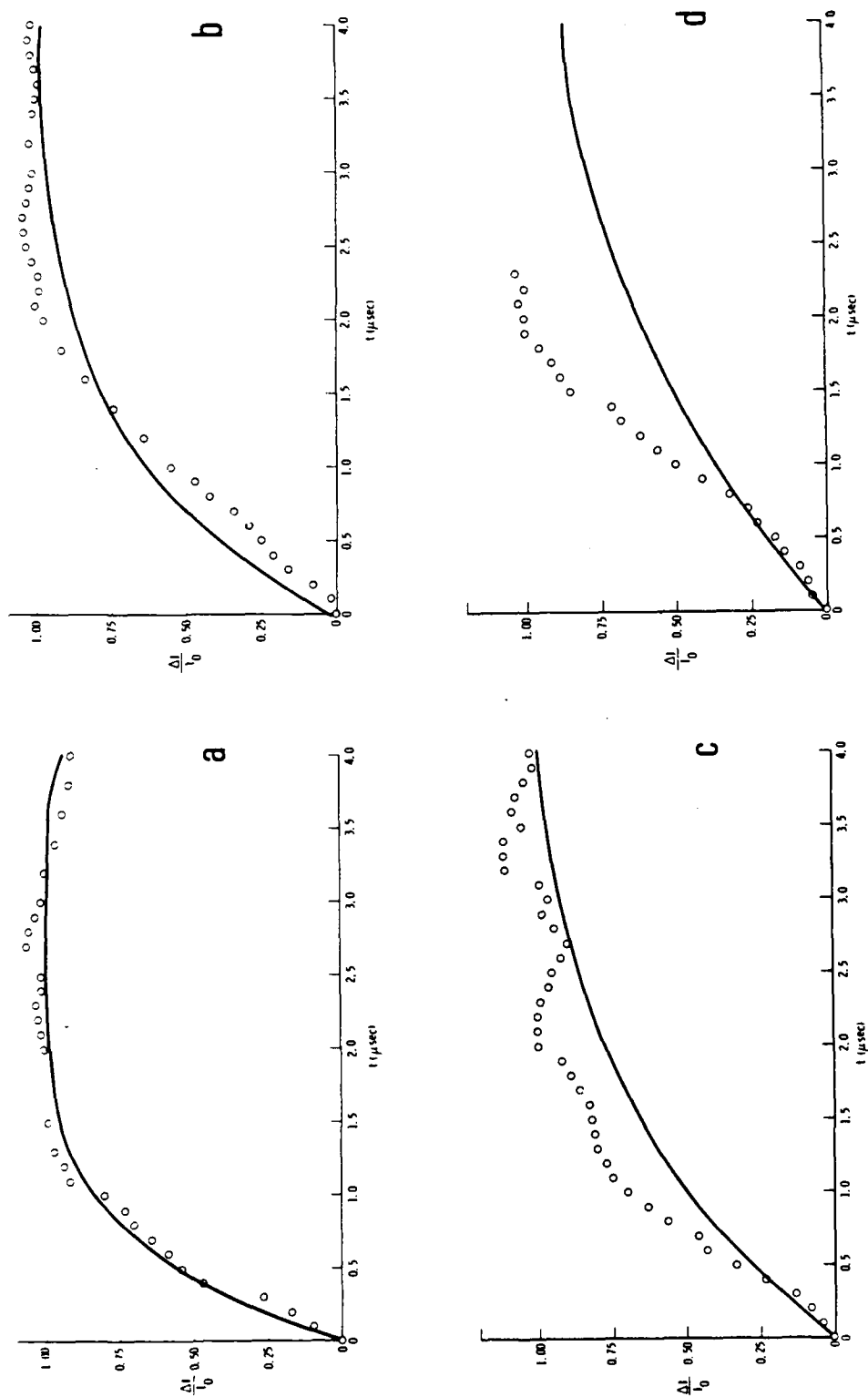


Fig. 2. Excitation of HF($v=1, J=3$) by HF pulsed laser radiation. Relative intensities (a) HF($v=1, J=4$); (b) HF($v=1, J=5$); (c) HF($v=1, J=6$); and (d) HF($v=1, J=7$) are shown as a function of time. The open circles represent experimental values obtained from scope traces of the Hinchey and Hobbs experiment.⁴ The solid curves give the model values developed from power law scaling for the state-to-state rate coefficients for rotational relaxation. $T=300$ K and $P=0.04$ Torr.

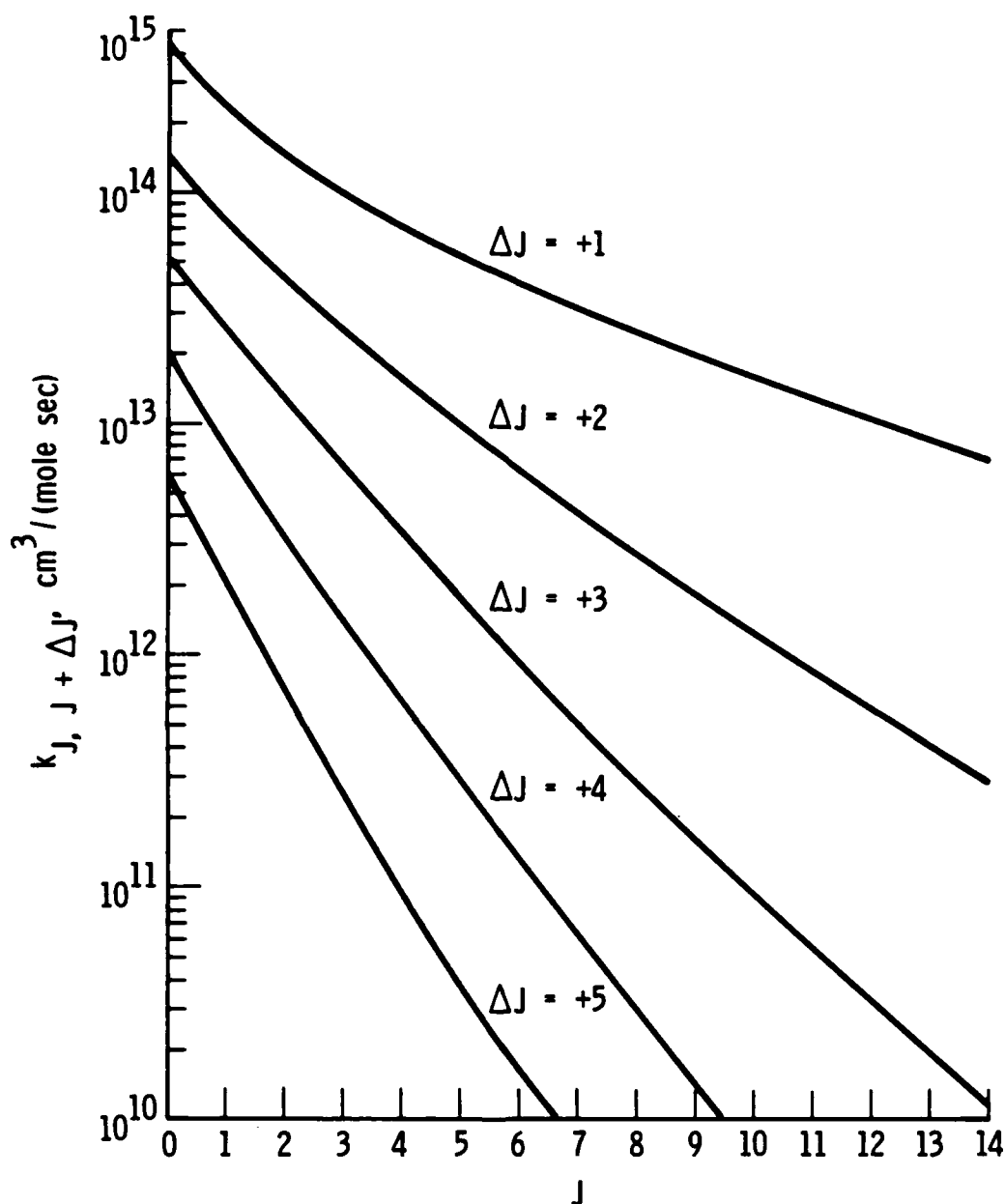


Fig. 3. State-to-state rate coefficients for R $\rightarrow$ T rotational relaxation for upward transitions with $\Delta J = +1, +2, +3, +4$, and $+5$ versus J levels. N_0 , the angular momentum factor, provided the best fit to the experimental data. The best a and γ values were found to be 5×10^{12} and 0.8, respectively.

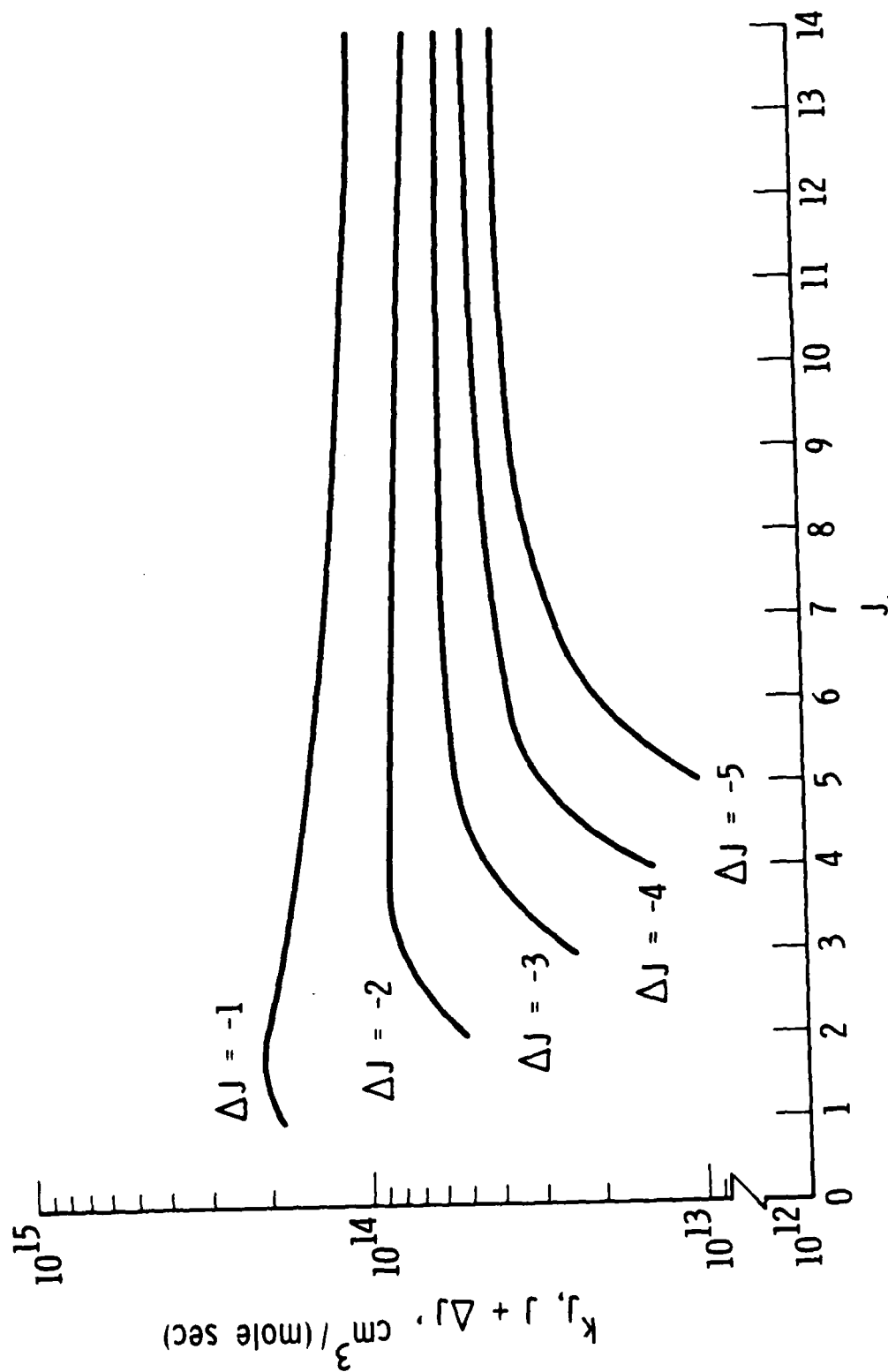


Fig. 4. State-to-state rate coefficients for $R \rightarrow T$ rotational relaxation versus J levels. Rates are for the downward transitions. Rates were obtained from upward rates by means of the microscopic reversibility relation.

IV. RESULTS AND DISCUSSION

The best fit to the Hinch and Hobbs data is obtained by using N_0 for the angular momentum degeneracy factor. The rate coefficients for these upward transitions have degeneracy factors consistent with conservation of initial m_J states. Systems with potential energy surfaces having their lowest minima in nonperpendicular orientations are known to conserve m_J during rotationally inelastic collisions. Preliminary trajectory studies of this system by Wilkins²² seem to confirm this idea. In Fig. 4 it can be seen that power law scaling indicates that decreasing rate coefficients result from multiquantum transitions. However, for a given ΔJ these rate coefficients at high J levels do not decrease as rapidly as would be predicted from an exponential gap law, which underestimates these rates for large transfers of energy in HF + Ar collisions. The state-to-state rate coefficients generated by this simple power law are in agreement with the pattern of rotational relaxation observed by Polanyi and Woodall.⁹

Hinch and Hobbs⁵ have shown that rotational lasing has a more serious effect on the populations below the pulse-laser-pumped J level than upon the J levels above the pumped level. The pure rotational lasing that occurs makes interpretation difficult. Since the double-resonance method of probing for densities requires long paths, the prospects for stimulated emission effects on rotational transitions are enhanced. In this study only J levels above the pumped level are reported, although phenomenological rates can obviously be computed by using this model in the exoergic as well as the endoergic directions.

Table 1 shows that there is good agreement between the measured and model-determined phenomenological rotational relaxation rates. The data for $v = 1$, $J = 3$, a state radiatively pumped by the pulse laser, are used to determine the two state-to-state rate coefficient parameters. The rest of the numbers are essentially predictions from the current model for $v = 1$ or $v = 2$, since it has been assumed that the rate manifold is independent of v . The agreement with the experimental numbers of Hinch and Hobbs⁴ is quite good except for the $J = 2$ pumped state, where the numbers differ by a factor of two. More interestingly, the results are in very good agreement with the recently published values of Copeland et al.³ for $v = 2$. The predicted model

Table 1. Phenomenological Bimolecular Rotational Relaxation Coefficients $(P\tau_c)^{-1}$ for HF^(a)

Pumped J v = 1	Observed J v = 1	Ref(4) v = 1	Ref(3) v = 2	Model v = 1
0	1			114.
0	2		45.5	45.5
0	3		27.5	24.
0	4		17.4	14.
1	2		65.5	65.8
1	3		30.5	29.1
1	4		17.2	16.3
1	5		16.1	10.5
2	3	104.	48.0	39.
2	4	50.	23.9	26.
2	5	27.	17.6	13.
2	6	19.		11.
3	4	48.	34.4	42.(b)
3	5	24.	23.4	25.(b)
3	6	19.		18.(b)
3	7	17.		13.(b)
4	5	58.	48.2	48.
4	6	34.		31.
4	7	30.		24.
4	8	10.		19.
5	6	68.		66.
5	7	33.		43.
5	8			35.
5	9			17.
6	7			69.
6	8			46.
6	9			35.
6	10			18.
7	8			66.
7	9			45.
7	10			35.
7	11			17.

(a). The units of $(P\tau_c)^{-1}$ are $(\mu\text{sec})^{-1} \text{ Torr}^{-1}$, $T = 300 \text{ K}$.

(b). State-to-state rate coefficients for R + T transfer used in the model were obtained by simulating the Hinchey and Hobbs experiment, in which they pumped $J = 3$ and probed $J' = 4, 5, 6$, and 7.

rates had been generated before the Copeland work became available. It appears, therefore, that the state-to-state rate coefficients for rotational relaxation of HF are insensitive to the v state, and that the original assumption to that effect is reasonable. The power law expression for $R \rightarrow T$ rate coefficients would also seem to be generally successful.

In Fig. 5 we show that a nonthermal rotational distribution of HF molecules peaked initially at some high J level relaxes to a thermal distribution without generating a single peak at intermediate J values. This double-peaked distribution was first observed by Polanyi and Woodall⁹ in their studies on HCl rotational relaxation. The state-to-state $R \rightarrow T$ rate coefficients used here for relaxation from high J states are not nearly as small as those generated in the Hinchin and Hobbs⁵ model. This shows that the double-peaked distribution results from slower relaxation of the high rotational states, but the rotational relaxation rates do not have to be as slow as those predicted by the Hinchin and Hobbs model.

Sentman²³ applied a rotational nonequilibrium model to Hinchin's³ HF rotational relaxation experiment, using species rate equations to determine the two constants in the exponential gap expression for rotational transition probability employed by Polanyi and Woodall.⁹ The predicted phenomenological rate coefficients obtained from the Sentman model do not reproduce Hinchin's results as well as this simple power law does. The $R \rightarrow T$ rates predicted by Sentman decrease too rapidly with increasing J because of the exponential gap law representation, which underestimates the J dependence at large values of J .

Belbruno et al.²⁴ obtained state-to-state rate coefficients by inverting self-broadened HF linewidth data by means of the energy-corrected sudden (ECS) scaling inversion procedure. They found that $R \rightarrow R$ processes are dominant for relaxation in pure HF and that such processes decrease with the increasing vibrational excitation of one of the collision partners. Their state-to-state rate coefficients for $R \rightarrow R$ transfer appear to be much too large to model the Hinchin and Hobbs experiment. Belbruno et al.²⁴ found their $R \rightarrow T$ rates were less than one-half their corresponding $R \rightarrow R$ rates; they obtained multiquantum $R \rightarrow T$ relaxation rates by assuming an exponential gap dependence of the fundamental rates, and they used the ECS scaling theory to calculate the remaining data. These $R \rightarrow T$ rates decrease too rapidly with increasing J

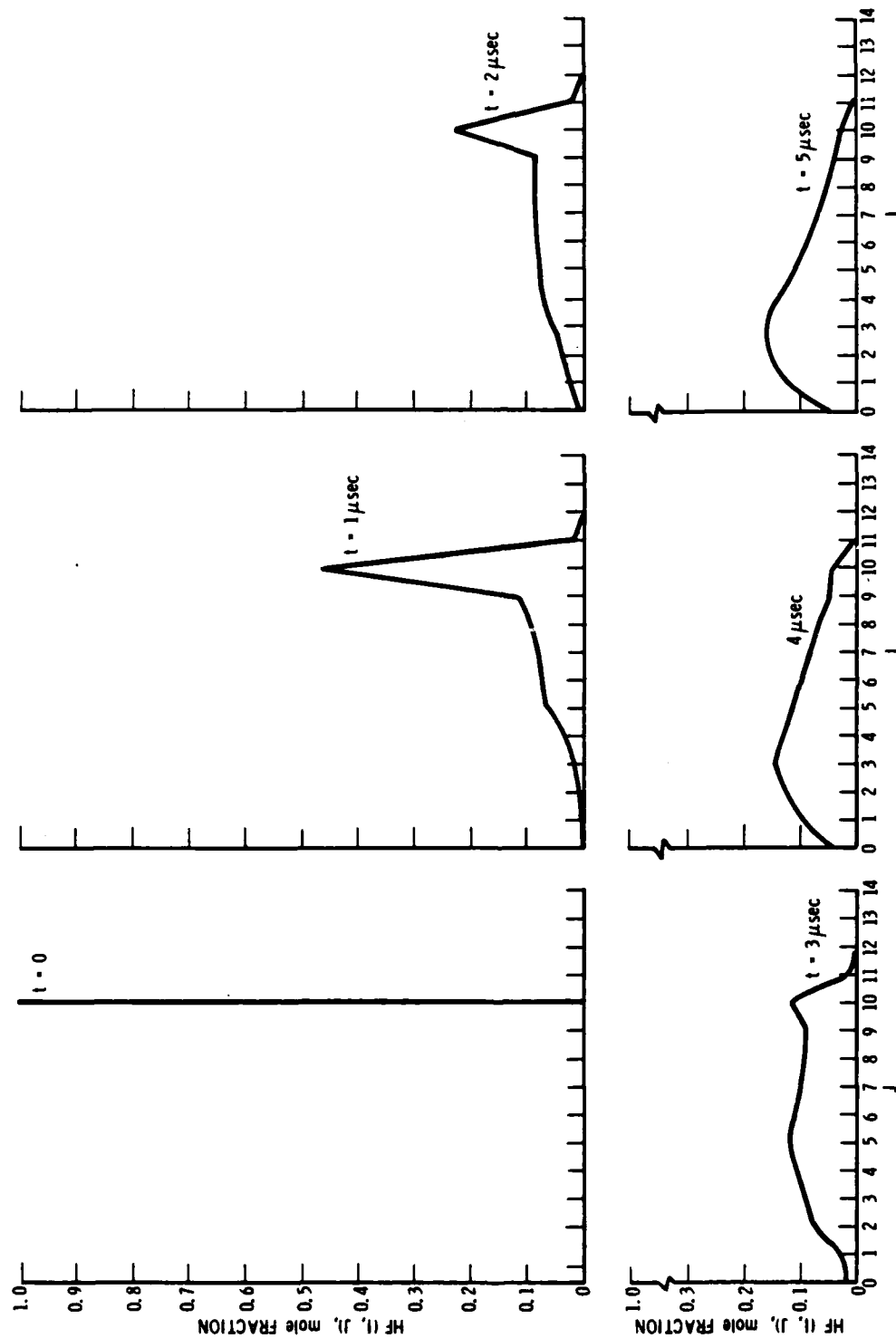


Fig. 5. Time evolution of HF(v = 1, J) densities from a delta function, using the R → T rate coefficients generated from a simple inverse power law with ΔJ up to ± 5 .

because of the exponential gap law tendency to underestimate the J dependence at large values of J.

Figure 6 shows that the $R \rightarrow T$ model with power law scaling provides a better fit to the Hinch and Hobbs experiment than does the $R \rightarrow R$ model they used. It is indeed surprising and satisfying that state-to-state rate coefficients generated from simple power law scaling simulate the measured phenomenological rates so well, considering the wide range of increased rotational energies for high J levels. The fact that analyses reported in the experiments³⁻⁵ also produce sets of state-to-state coefficients deemed fairly acceptable indicates that, hitherto, the experiments have not been really sensitive to significant differences in the state-to-state rate set. These various rate sets can differ vastly in details as a function of J. A certain nonuniqueness remains in producing a detailed set of state-to-state rate coefficients from such phenomenological rates.

The new power scaling law results in improved agreement of experimental phenomenological rates over previous experiments. These rotational relaxation rates have been used to model eight other experiments on HF relaxation. The results of these model studies are in very good agreement with the available experimental data and will be reported in future papers. The state-to-state rate coefficients provided in this paper should be useful in providing an understanding of spectral power distributions observed in HF chemical lasers.

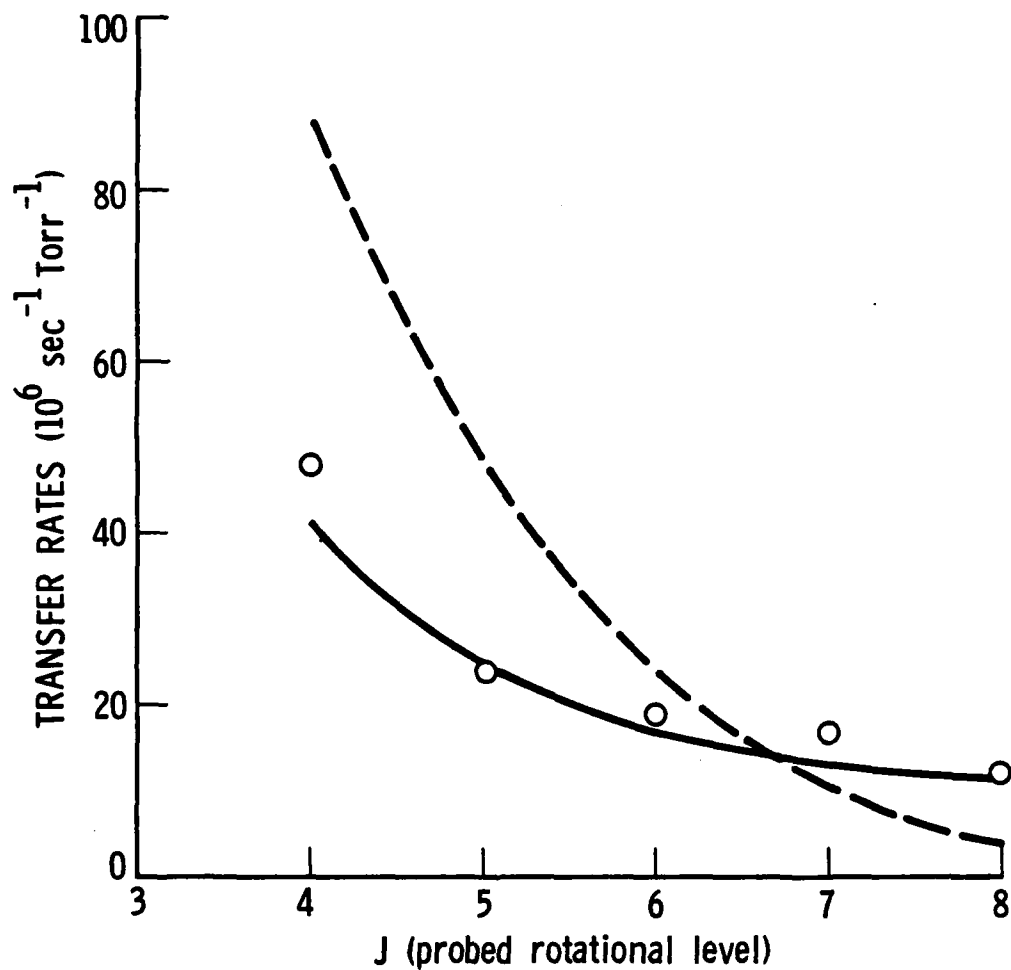


Fig. 6. Transfer rate or phenomenological rate coefficient for $J = 3$ pumped versus J level probed. The $R \rightarrow T$ model using a power scaling law is compared with the $R \rightarrow R$ model employed by Hinchen and Hobbs.⁴ The dashed lines represent the Hinchen and Hobbs model results. The open circles represent the published experimental results of Hinchen and Hobbs. The solid curve represents our results obtained from a $R \rightarrow T$ model using a power scaling law. $T = 300$ K, $P = 0.04$ Torr.

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LABORATORY OPERATIONS

The Laboratory Operations of The Aerospace Corporation is conducting experimental and theoretical investigations necessary for the evaluation and application of scientific advances to new military space systems. Versatility and flexibility have been developed to a high degree by the laboratory personnel in dealing with the many problems encountered in the nation's rapidly developing space systems. Expertise in the latest scientific developments is vital to the accomplishment of tasks related to these problems. The laboratories that contribute to this research are:

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Space Sciences Laboratory: Atmospheric and ionospheric physics, radiation from the atmosphere, density and composition of the upper atmosphere, aurorae and airglow; magnetospheric physics, cosmic rays, generation and propagation of plasma waves in the magnetosphere; solar physics, infrared astronomy; the effects of nuclear explosions, magnetic storms, and solar activity on the earth's atmosphere, ionosphere, and magnetosphere; the effects of optical, electromagnetic, and particulate radiations in space on space systems.

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