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AEROSPACE REPORT NO.
ATR-77(8127)-3

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Modeling Study of Rotational Relaxation and Absorption

Prepared by W. C. HWANG and R. F. KAMADA
Chemistry and Physics Laboratory

20 January 1977

Prepared for
VICE PRESIDENT AND GENERAL MANAGER
THE IVAN A. GETTING LABORATORIES

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THE AEROSPACE CORPORATION
El Segundo, California

Aerospace Report No.
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MODELING STUDY OF ROTATIONAL
RELAXATION AND ABSORPTION

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ACKNOWLEDGMENT

The assistance of Cyrus Kamada in evaluation of solutions to differential equations is gratefully acknowledged. This work was supported by The Aerospace Corporation on Company funds and by the Energy Research and Development Administration under Contract No. E(04-3)-1017.

ABSTRACT

The rate of rotational relaxation can influence the amount of single-line absorption for a transition that involves discrete rotational states. The extent of selected-state laser chemistry can thus be affected by the rotational bottleneck effect. Models of rotational relaxation and pulsed single-line absorption have been constructed to determine the main factors governing the bottleneck effect, to determine the relaxation rate constants necessary to maintain equilibrium for a wide range of conditions, and to investigate the effects of rotational relaxation in a two-step photodissociative isotope enrichment scheme. Coupling the models with laboratory experiments could also yield a new method for determining rotational relaxation rates.

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CONTENTS

ACKNOWLEDGMENT	iv
ABSTRACT	v
I. INTRODUCTION	1
II. CONSTRUCTION OF MODELS	3
A. General	3
B. Rotational-Translational States and Interconnecting Processes	3
C. Analytical Models	7
D. Numerical Models	10
E. Enrichment Models	10
III. RESULTS	13
A. Analytical Models	13
B. Numerical Models	20
C. Enrichment Models	20
D. Coupling of Models and Experiments	23
IV. SUMMARY	29
APPENDIXES	
A. CALCULATION OF ALPHA AND GAMMA	31
B. COUPLING OF TRANSLATIONAL AND ROTATIONAL RELAXATION	33
C. CALCULATION OF A_{RT} , ROTATIONAL- TRANSLATIONAL RELAXATION CASE	35
D. CALCULATION OF A_R AND A_E	37
E. INPUTS FOR BASE CONDITIONS OF ENRICHMENT MODELS	39
REFERENCES	41

TABLES

1.	Variation of Degeneracy Ratio and Delta	22
2.	Results of Enrichment Models	24
3.	HBr Absorption for Mixtures of HBr and NO	25
4.	HBr Absorption for Mixtures of HBr, I ₂ , and Ar	26
5.	Sensitivity of Absorption to Rotational Relaxation Rate	28

FIGURES

1.	Rotational-Translational Model	5
2.	Variation of Rotational Relaxation Rate	14
3.	Variation of Laser Pulsewidth	15
4.	Variation of Rotational Partition Coefficients	17
5.	Variation of Translational Relaxation Rate	18
6.	Rotational Model and Translational Model	19
7.	Variation of Pulse Shape	21

I. INTRODUCTION

The extent of state-selected laser chemistry depends on the number of selectively excited species produced by laser absorption. For absorption of intense laser radiation involving discrete rotational states (without nonlinear effects), the amount of absorption is governed by the rate and duration of the absorption process and the rotational relaxation rate. When rotational relaxation rates are very fast compared with absorption rates, and equilibrium is maintained, the population of the whole rotational manifold is accessible to the absorption process. At the other extreme, when no relaxation occurs, only the populations of the individual rotational states that interact directly with the radiation are accessible. For conditions between these extremes, finite rotational relaxation rates can determine the amount of absorption.

The importance of rotational relaxation to selected-state chemistry was discussed by Letokhov¹ and demonstrated in the isotope separation studies of Ambartzumian and co-workers² and Lyman and Rockwood,^{3,4} in which evidence is given for limitation of excitation by the rotational bottleneck effect. Previous models of selected-state chemistry, however, assumed rotational equilibrium during absorption.^{5,6} Thus, a model that includes the effects of rotational relaxation on absorption is needed.

In this study, models of single-line absorption and rotational relaxation were constructed to: (1) determine the amount of absorption for various relaxation conditions; (2) determine the rotational relaxation rate constants necessary to maintain equilibrium for a wide range of experimental conditions; and (3) investigate the effects of rotational relaxation in a two-step isotope enrichment scheme. A simple model for translational or velocity relaxation is used to determine the conditions under which translational relaxation must be considered as well.

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II. CONSTRUCTION OF MODELS

A. GENERAL

The significance of rotational and velocity relaxation under any conditions is determined by comparing the total absorption in a model with finite relaxation rates to that of an equilibrium model (with infinite rates). Three sets of models are used; each set contains an equilibrium model and at least one finite relaxation model. The analytical models are used to determine the amount of absorption under finite relaxation conditions and the relaxation rate needed to approximate equilibrium. The numerical models are used to investigate limits of the analytical models. The enrichment models show the effect of rotational relaxation when the models are applied to a particular laser isotope enrichment experiment.

In all cases, pulsed, single-line laser absorption is modeled. The rate of net absorption dA/dt is given by

$$dA/dt = k I (C_1 - gC_u) \quad (1)$$

where I is the laser intensity in photons/cm³, C_1 and C_u are the concentrations in molecules/cm³ of the lower and upper stages of the transition, respectively, k is the absorption rate constant in cm³/molecules-sec, and g is the degeneracy ratio of the lower to upper states. The usually small effects of spontaneous emission are ignored.

Cell dimensions in the model are sufficiently small that the laser intensity is not significantly perturbed by absorption; thus, the systems have spatial uniformity. This assumption should not be very limiting because most laser sources have great spectral brightness.

B. ROTATIONAL-TRANSLATIONAL STATES AND INTERCONNECTING PROCESSES

The absorption of single-line radiation connecting discrete rotational states results in nonequilibrium rotational distributions in both the upper

and lower manifolds of the transition. A strong perturbation of the upper manifold caused by absorption coupled with saturation effects (when net absorption is reduced significantly by stimulated emission) can reduce the amount of absorption relative to the equilibrium case. In all finite rotational relaxation models, both the upper and lower manifolds are divided into two states, R_i and R_j . The rotational state that can directly interact with laser radiation is r_i ; all other states are lumped into R_j .

A second relaxation process that can influence absorption is translational or velocity relaxation, particularly for the narrow laser linewidth and low pressure conditions found in many laser state-selected studies. For inhomogeneous broadening conditions (low pressures) and a laser line that is narrower than the Doppler absorption line, radiation can interact only with molecules that have proper velocity components. Whenever the absorption rate is too fast for translational or velocity relaxation processes to maintain an equilibrium velocity distribution, hole burning of the absorption line occurs, and the amount of absorption is reduced relative to the homogeneous case.

In the rotational-translational model, each R_i state (or level) is subdivided into two translational states, $R_i T_i$ and $R_i T_j$, as shown in Fig. 1, where superscript u denotes the upper level of the transition and l the lower level. The molecules in the $R_i T_i$ state are the only ones that can interact with the radiation in the low-pressure or inhomogeneous Doppler-shaped limit. As pressure increases, line broadening from collisions becomes more prominent, and the absorption line takes on more homogeneous character. Molecules in the $R_i T_j$ state can then interact with the radiation but with a lower rate constant. The absorption (processes 1 and 2) can be a vibrational-rotational transition involving one electronic level or a vibro-rotonic transition involving two electronic levels. For process 1, the forward rate constant K_{1F} equals kI , whereas $K_{1B} = gkI$ for the backward process. The rate constant for absorption K_L used in the calculations is considered to be equal to $K_{1F} + K_{1B}$. Similarly, $K_{2F} = aK_{1F} = akI$ and $K_{2B} = agkI$, where the value of a varies from zero (low-pressure limit, strictly

Figure 1. Rotational-Translational Model

Gaussian inhomogeneously broadened line) to one (high-pressure limit, strictly Lorentzian homogeneously broadened line). Its value is a function of the Doppler width (HWHM) of the absorption line $\Delta\nu_D$, the laser linewidth (HWHM) $\Delta\nu_L$, and the rate of line broadening collisions. The method of calculating a is given in Appendix I. The translational relaxation rate constant K_T is defined to be equal to $K_{iF} + K_{iB}$ for $i = 3, 4$.

Translational relaxation and rotational relaxation are represented by processes 3 through 4 and 5 through 8, respectively. The net rate of relaxation for the i^{th} relaxation processes is

$$K_{iF} C_{iF} - K_{iB} C_{iB}$$

where C is the reactant concentration, and subscripts F and B represent the forward and backward processes, respectively. In all model runs, the K 's are assumed to be constant with respect to reactant concentration. This pseudo first-order assumption is valid except for conditions where self-relaxation is dominant. The dependence on concentration can be included in the numerical and enrichment models. K_{iF} and K_{iB} are given by

$$K_{iF} = (1 - \alpha) \sum_k K_k^i C_k \quad i = 3, 4 \quad (2)$$

$$K_{iB} = (\alpha) \sum_k K_k^i C_k \quad i = 3, 4 \quad (3)$$

where K_k^i is the gas kinetic rate constant for a collision between the reactant of the i^{th} process and the k^{th} species in the system, α is the fraction of R_i molecules in the $R_i T_i$ state, and the summation is over all species. The method of calculating the translational fraction α is also given in Appendix A.

Rotational relaxation is assumed to involve translational relaxation as well. This assumption appears reasonable for narrow laser sources

since only a relatively small change in velocity is necessary to shift a molecule into or out of the resonance laser linewidth region of the Gaussian (low-pressure limit) absorption curve. An example of the energy changes and frequency shift for HBr is given in Appendix B. If 3% of the minimum rotational energy change is transmitted into HBr translation along the direction of light propagation, a shift in frequency equal to the estimated laser linewidth of 3 MGz will result.

The R_j states are not divided into translational states because of the assumption of coupling of translational with rotational relaxation. The rate constants for rotational relaxation can then be given by

$$K_{iF} = \delta_i \sum_k K_k^i C_k \quad i = 5-8 \quad (4)$$

$$K_{iB} = \begin{cases} (1 - \delta_i) (\alpha) \sum_k K_k^i C_k & i = 5, 7 \\ (1 - \delta_i) (1 - \alpha) \sum_k K_k^i C_k & i = 6, 8 \end{cases} \quad (5)$$

$$(6)$$

where δ_i is the equilibrium fraction of molecules in the rotational manifold associated with the i^{th} processes that are in the R_i level (rotational partition coefficient), and K_k^i is now the rotational relaxation rate constant. The K_k^i 's are defined to be independent of δ_i . The rotational relaxation rate constant K_R is equal to $K_{iF} + K_{iB} + K_{(i+1)B}$ and $K_{iF} = K_{(i+1)F}$ for $i = 5, 7$.

C. ANALYTICAL MODELS

The analytical models are used to determine the amount of absorption for finite relaxation rates and the conditions under which equilibrium is approached. The two finite relaxation systems modeled are coupled rotational-translational relaxation and rotational relaxation. For simplification, the following three constraints are imposed on the systems:

1. Laser pulse with rectangular temporal profile
2. Equal rate constants for absorption and stimulated emission ($g = 1$)

3. Identical partition coefficients in the upper and lower levels of the transition (all δ_i are equal).

These constraints are later removed in the numerical models.

The states and processes in the coupled relaxation model are those shown in Fig. 1. The system can be described by using six coupled first-order differential equations with constant coefficients

$$\frac{dC_k}{dt} = \sum_{n=1}^6 K_{kn} C_n \quad k = 1 - 6 \quad (7)$$

where C_n is the concentration in the n^{th} state, and K_{kn} 's are given by Eqs. (1-6). If the initial concentrations (before the laser pulse) of the states are in equilibrium,

$$C(R_i T_i) = \left[\frac{\alpha}{1 - \alpha} \right] C(R_i T_j) \quad \text{and} \quad C(R_i T_i) = \left[\frac{\alpha \delta}{1 - \delta} \right] C(R_j)$$

for both rotational manifolds. Then, during the laser pulse

$$\frac{dC(R_i^l T_i)}{dt} = - \frac{dC(R_i^u T_i)}{dt}, \quad \frac{dC(R_i^l T_j)}{dt} = - \frac{dC(R_i^u T_j)}{dt}$$

and

$$\frac{dC(R_j^l)}{dt} = - \frac{dC(R_j^u)}{dt}$$

The six equations can thus be reduced to three that involve concentrations of only one rotational manifold. Since these three equations are still of the form given in Eq. (7), the solutions are given by

$$C_K = C_K^0 + \sum_{n=1}^3 B_{Kn} e^{D_n t} \quad K = 1 - 3 \quad (8)$$

where C_K^0 , B_{Kn} , and D_n are constants. The evaluation of the constants is given in Appendix C. The amount of absorption is then

$$A_{RT}(t) = \frac{1}{A_s} \sum_{K=1}^3 |C_K(t) - C_K(0)| \quad (9)$$

where A_s is the absorption when the transition is completely saturated.

In the rotational relaxation model, translational equilibrium is assumed, and the $R_i^m T_i$ and $R_i^m T_j$ states are combined into a single R_i^m state, $m = u, l$. Processes 2 through 4, 6, and 8 are removed; only one absorption and two rotational relaxation processes remain. A system that is initially at equilibrium can then be described by two equations

$$\frac{dC'_k}{dt} = K_{k1} C'_1 + K_{k2} C'_2 \quad k = 1, 2 \quad (10)$$

The solutions are of the form

$$C'_K = C'_K{}^0 + K'_{K1} e^{D'_1 t} + B'_{K2} e^{D'_2 t} \quad K = 1, 2 \quad (11)$$

where the constants are evaluated in Appendix IV.

The amount absorbed is

$$A_R(t) = \frac{1}{A_s} \left[|C'_1(t) - C'_1(0)| + |C'_2(t) - C'_2(0)| \right] \quad (12)$$

In the equilibrium model, both rotational and translational equilibrium are assumed. This model has only two states (one representing each manifold) and one process (absorption process 1). The amount of absorption is given by

$$A_E = B^0 [1 - \exp(-D^0)]$$

where B^0 includes normalization by A_s . Evaluation of B^0 and D^0 is also given in Appendix D.

D. NUMERICAL MODELS

The numerical models are used to determine the effects of removing the three constraints imposed on the analytical models. The system can be described by six simultaneous differential equations in the form of Eq. (7) with the additional complication of time varying coefficients. Since a general analytical solution could not be found, the equations were solved numerically by using a modification of the NEST computer program.^{7,8} The amount of absorption from the finite relaxation models is then compared with that from the equilibrium model.

E. ENRICHMENT MODELS

The enrichment models incorporate coupled rotational-translational relaxation into a model of the two-step photodissociation method of isotope enrichment. This method includes isotopically selective first-step infrared excitation, second-step ultraviolet photodissociation, vibrational energy transfer processes, and chemical reactions. The particular system modeled is HBr-NO, where $H^{79}Br$ is vibrationally excited to the $v = 1$ vibrational level by a single-line resonance laser, and an intense ultraviolet source dissociates vibrationally excited HBr. The bromine atoms are then scavenged with NO to form the isotopically enriched stable product BrNO. Construction of the equilibrium model is described by Hwang, Kamada, and Badcock⁹ in a separate paper.

In the finite relaxation model, the $H^{79}Br$ ($v = 0$) and $H^{79}Br$ ($v = 1$) levels are each divided into the sublevels shown in Fig. 1. The rotational relaxation rates constants are calculated from line-broadening data^{10,11} under the assumption that only rotational and translational relaxation collisions are responsible for line broadening. The K_L values are calculated with the same line-broadening data. The rate constants for ultraviolet photodissociation are independent of the rotational-translational state.

For kinetic processes (other than rotational relaxation) that involve H^{79}Br ($v = 0$) or H^{79}Br ($v = 1$) as a product in the equilibrium model, the rate constant at rotational equilibrium K_E is parcelled as follows:

1. $\alpha \delta K_E$ for $R_i T_i$ as product
2. $\delta(1 - \alpha) K_E$ for $R_i T_j$ as product
3. $(1 - \delta) K_E$ for R_j as product.

For reactions with two rotational-translational states as products, the same parcelling process was used for the nine different combination of products.

A set of base conditions is used to facilitate comparison of results upon variation of conditions. The base absorption and kinetic parameters used are given in Appendix E. Unless specified, base conditions were used.

The enrichment is measured by two criteria: enrichment ratio and isotopic product difference. The enrichment ratio β is defined by $(E \times R^0) / (E^0 \times R)$, where E and R are the number of atoms in the products per unit volume of the enriched isotope and all other isotopes, respectively. E^0 and R^0 are the initial abundances of the enriched isotope and all other isotopes, respectively. The enrichment ratio is a measure of increase in isotope ratio of products, and its values range from one (no enrichment) to infinity (complete enrichment). The isotopic product difference γ is defined by $(E/E^0) - (R/R^0)$. It is a measure of quantity of enriched products and has units of concentration.

III. RESULTS

A. ANALYTICAL MODELS

The effects of rotational relaxation on single-line laser absorption are governed by the rotational relaxation rate constant; rotational partition coefficient; laser pulsewidth; absorption rate constant; and, to some extent, the translational relaxation rate constant. The effects of varying the rotational relaxation and absorption rate constants are shown in Fig. 2. For a constant K_R value, A_{RT} increases linearly with K_L for low K_L values and approaches an asymptote for high K_L values. For $A_{RT} \ll 1$, the asymptotic behavior is caused by the rotational bottleneck, whereas saturation of the transition (optical bleaching) causes the asymptotic approach for A_{RT} near unity. For low K_r values ($< 5 \times 10^4$), A_{RT} is not a large function of K_R because the amount of absorption is too small to either strongly perturb the distribution of the lower manifold or significantly populate the upper manifold. For larger K_r (and hence A_{RT}), the dependence of A_{RT} on K_R increases until saturation effects are significant. The A_{RT} values for other conditions can be calculated from the equations given in Appendix C.

The minimum rotational relaxation rate constant needed to maintain equilibrium K_R^* was also calculated, where equilibrium was assumed whenever $A_{RT}/A_E \geq 0.9$. The K_R^* value, which is a function of total pressure, is an indication of the optimum total pressure for state-selected chemistry. A lower pressure and K_R value would produce the bottleneck effect and limit absorption. A higher pressure and K_R value would increase the rate of energy transfer collisions that destroy state selectivity without increasing absorption.

The K_R^* value as a function of laser pulsewidth t and K_L is shown in Fig. 3. For a particular t , as K_L is increased, K_R^* increases rapidly at first, peaks, decreases slightly, and then reaches an asymptote. The original rapid increase is caused by the rapid increase in the amount of

Figure 2. Variation of Rotational Relaxation Rate

Figure 3. Variation of Laser Pulsewidth

absorption. The peaking and decrease are caused by larger saturation effects in the equilibrium model. This decreasing region is the saturation region, and the asymptotic value is approached as complete saturation is approached in both the finite relaxation and equilibrium models.

When pulse duration is increased by a factor of 10, both the asymptotic K_R^* value and the K_L value at the K_R^* peak decrease by approximately a factor of 10. Thus, the asymptotic $K_R^* t$ value is 230, and K_R peaks at $K_L t = 180$ for all t . For K_L values below saturation, the slope of the curves becomes greater as t is decreased. For very low K_L values, no relaxation is required because the amount of absorption is too small. This K_L region, marked by the absence of curves, occurs at increasing K_L values with shorter pulse durations.

Variation of the rotation partition coefficient δ yields results similar to those obtained with variation of t (Fig. 4). Thus, K_R^* peaks at $\delta K_L t = 1.8$, and the asymptotic $\delta K_R t$ value is 2.3 for all t and δ . Before the saturation region, the slope of the curves for lower δ 's is larger because the K_R^* values are independent of K_L for $K_L < 10^6 \text{ sec}^{-1}$.

Variation of the translational relaxation rate K_T makes no difference in the saturation region (Fig. 5). Before that region, translational relaxation does lower the necessary rotational rate, and the lowering is greater as K_L decreases.

In order to determine when translational equilibrium is a valid assumption, the absorption from the rotational-translational model A_{RT} is compared with that from the rotational model A_R . An example is given in Fig. 6, where the A_{RT}/A_R ratio is plotted as a function of K_L . The ratio is close to unity for low K_L values because the absorption level is low. At moderate K_L values, the ratio decreases rapidly because neither K_R nor K_T is high enough to maintain equilibrium. At high K_L values, saturation effects for process 1 increase the ratio.

In general, translational equilibrium can be assumed ($A_{RT}/A_R \geq 0.9$) whenever K_T or $K_R \geq 10^8 \text{ sec}^{-1}$, $K_L t < 2 \times 10^{-3}$, or $K_L t > 3 \times 10^4$. A

Figure 4. Variation of Rotational Partition Coefficients

Figure 5. Variation of Translational Relaxation Rate

Figure 6. Rotational Model and Translational Model

relaxation rate constant of 10^8 sec^{-1} is sufficient to produce essentially a Lorentz-broadened line. Since a Lorentzian, pressure-broadened line is considered homogeneous, hole burning can not occur. For $K_L t < 2 \times 10^{-3}$, absorption is so small that equilibrium is not significantly perturbed. For $K_L t > 3 \times 10^4$, saturation effects promote translational equilibrium. For other conditions, the equations in Appendixes C and D must be used for determination of A_{RT}/A_R .

B. NUMERICAL MODELS

The numerical models were used to study the effects of removing the three constraints imposed on the analytical models. The results obtained upon variation of pulse shapes with constant pulse energies are shown in Fig. 7. The absorption as a function of K_R behaves similarly for Gaussian,¹² triangular, and rectangular pulses. For maintenance of rotational equilibrium, a Gaussian pulse requires the lowest K_R , whereas the rectangular pulse requires the highest. For equal halfwidths, the Gaussian pulse has the longest base and the rectangular pulse has the shortest. Thus, the K_R^* values calculated in the analytic models are upper bounds. The differences, however, are not expected to be large inasmuch as the K_R range at a particular absorption in Fig. 7 is always less than a factor of 2.5.

The effects of varying g and the ratio of upper- to lower-level partition coefficients are shown in Table I. The worst case was taken for $\Delta J = \pm 1, 0$ transitions by setting $g = 1/3$ and the δ^u/δ^l ratio = 3. Most transitions would have values closer to unity, the conditions of the analytical models. The results are within 2% of the analytical results except at the highest K_L value used (which is in the asymptotic region), where there is 17.5% deviation. Thus, the analytical results should be valid for most values of b or the δ_u/δ_l ratio.

C. ENRICHMENT MODELS

The enrichment models were used to study the effects of rotational relaxation on the enrichment produced by the two-step photodissociative system of HBr and NO. Results for various pressures, laser intensities, and

Figure 7. Variation of Pulse Shape

Table I. Variation of Degeneracy Ratio and Delta^a

K_L	A/A_{eq} ($g = 1/3, \delta_u^{eq} = 0.03$)	A/A_{eq} ($g = 1, \delta_u^{eq} = 0.01$)
10^4	0.986	0.986
10^5	0.985	0.985
10^6	0.978	0.976
10^7	0.910	0.897
10^8	0.609	0.611
10^9	0.490	0.594

^aConditions: $\delta^l = 0.01$; $K_R = 10^8 \text{ sec}^{-1}$; $K_T = 10^8 \text{ sec}^{-1}$;
 $t = 10^{-6} \text{ sec}$; $\gamma_D = 90 \text{ MHz}$; $\Delta\nu_L = 9 \text{ MHz}$.

rotational relaxation rate constants are shown in Table II. The enrichment of the finite relaxation model is compared with that of the equilibrium model (with subscript eq). Differences of less than 1% are not significant because of the estimated uncertainties in β and γ .

For base conditions, inclusion of rotational relaxation does not alter enrichment. For lower initial pressures and relaxation rate constants, the ratio γ/γ_{eq} is about the same as the A/A_{eq} ratio, whereas the changes in β/β_{eq} are smaller. The results are somewhat different for the strongly saturating condition when the pulse energy is increased to 7.5 mJ. The β/β_{eq} and γ/γ_{eq} ratios are smaller than the A/A_{eq} ratio. In this case, greater absorption in the first part of the laser pulse in the equilibrium model produces higher enrichment of $H^{79}Br$ since there is less isotopic energy transfer.

Thus, although inclusion of rotational-relaxation processes does not alter enrichment for base conditions, it can promote significant differences for lower pressures, slower relaxation rate constants, or higher laser energies. In addition, rotational relaxation can have a greater effect on enrichment than on absorption for strongly saturating conditions.

D. COUPLING OF MODELS AND EXPERIMENTS

The models can be used to determine the range of proper experimental conditions and the optimization of conditions. As an example, the absorption calculated in the analytical models as a function of laser pulse duration for constant energy pulses is given in Table III. The inputs are for the HBr-NO two-step photodissociation enrichment system with 50 Torr NO and 4 Torr HBr at 300 K and a 1.5 mJ pulse. The results indicate that a rotational bottleneck will not result for pulse durations greater than 30 μ sec.

Another example is given in Table IV, where the analytical model absorptions are calculated as a function of pressure and laser energy. The inputs are for the HBr + I vibrational photochemistry system with initial concentrations of 0.25 Torr HBr, 0.3 Torr I_2 , and a variable amount of inert buffer Ar. The K_L value of $3.4 \times 10^5 \text{ sec}^{-1}$ corresponds to a 1.5 mJ $P_1(5)$ HBr single-line laser pulse. The results indicate that 20 Torr Ar is sufficient to produce an A/A_{eq} ratio ≥ 0.9 for laser pulse energies up to 9.5 mJ.

Table II. Results of Enrichment Models

Conditions	Relaxation Model				
	β	$\gamma \times 10^{-13}$ molecules/ cm^3	$\frac{\beta}{\beta_{\text{eq}}}$	$\frac{\gamma}{\gamma_{\text{eq}}}$	$\frac{A}{A_{\text{eq}}}$
Base conditions: 50 Torr NO; 4 Torr HBr; 1.5 mJ laser pulse; $K_R = 9.3 \times 10^{-10}$ and $3.7 \times 10^{-10} \text{ cm}^3/\text{molecule-sec}$ for HBr- HBr and HBr-NO collisions, respectively.	1.87	1.63	1.00	1.00	1.00
10 Torr NO, 0.5 Torr HBr	1.78	0.451	0.995	0.955	0.975
1.5 Torr NO, 1 Torr HBr	1.03	0.401	1.00	0.86	0.865
$K'_R = 1.85 \times 10^{-10}$ and 7.4×10^{-11} $\text{cm}^3/\text{molecule-sec}$ for HBr-HBr and HBr-NO collisions, respectively.	1.87	1.59	1.00	0.98	0.985
$K'_R = 4.65 \times 10^{-11}$ and 1.85×10^{-11} $\text{cm}^3/\text{molecule-sec}$ for HBr-HBr and HBr-NO collisions, respectively.	1.85	1.51	0.99	0.93	0.94
7.5 mJ laser pulse	2.07	5.87	0.985	0.90	0.995

Table III. HBr Absorption for Mixtures of HBr and NO^a

K_L, sec^{-1}	$t, \mu\text{sec}$	A/A_{eq}
2.15×10^5	1000	0.999
7.2×10^5	300	0.997
2.15×10^6	100	0.991
7.2×10^6	30	0.972
2.15×10^7	3	0.844
2.15×10^8	1	0.780

^aConditions: $\delta = 0.14$; $K_R = 7.2 \times 10^8 \text{ sec}^{-1}$; $K_T = 4.0 \times 10^7 \text{ sec}^{-1}$; $\gamma_D = 50.7 \text{ MHz}$; $\Delta\gamma_L = 5.07 \text{ MHz}$;
 $\beta = 0.818182$.

Table IV. HBr Absorption for Mixtures of HBr, I₂, and Ar^a

K_L, sec^{-1}	Ar, Torr	K_R, sec^{-1}	K_T, sec^{-1}	A/A_{eq}
3.4×10^5	20	5.2×10^7	1.1×10^8	0.954
3.4×10^5	10	3.0×10^7	5.5×10^7	0.923
3.4×10^5	5	1.9×10^7	2.8×10^7	0.875
3.4×10^5	2	1.25×10^7	1.25×10^7	0.815
3.4×10^5	0	8×10^6	1.7×10^6	0.739
8.55×10^5	20	5.2×10^7	1.1×10^8	0.945
2.15×10^6	20	3.0×10^7	1.1×10^8	0.915
5.4×10^6	20	1.9×10^7	1.1×10^8	0.862
1.35×10^7	20	1.25×10^7	1.1×10^8	0.807
3.4×10^7	20	8×10^6	1.1×10^8	0.812

^aConditions: $\delta = 0.14$; $t = 6 \times 10^{-7}$ sec; $\gamma_D = 50.7$ MHz; $\Delta\gamma_L = 5.07$ MHz; $\beta = 0.818182$.

The models can also be coupled with absorption experiments to determine rotational relaxation rate constants. The amount of absorption can be a sensitive measure of the rotational relaxation rate, as shown in Table V. A factor of 2 difference in K_R can result in 35 to 50% variation in the amount of absorption. For pressures (and thus K_R or K_T values) high enough to approximate homogeneous broadening, absorption is also independent of the laser linewidth and other translational relaxation parameters. Thus, single-line laser absorption experiments coupled with modeling should yield rotational relaxation rate constants and their J-dependence. Although this type of experiment yields results directly related to relaxation of rotational states, it requires neither transient detection of the rapid relaxation process nor a very high resolution spectrometer. The laser linewidth can also be determined with an adequate translational relaxation model by operating under inhomogeneous broadening conditions.

Table V. Sensitivity of Absorption to Rotational
Relaxation Rate^a

K_R, sec^{-1}	$\Delta\gamma, \text{MHz}$	A_{RT}
4×10^7	9.0	0.667
2×10^7	9.0	0.453
1×10^7	9.0	0.296
5×10^6	9.0	0.200
2.5×10^6	9.0	0.147
4×10^7	0.9	0.680
4×10^7	2.7	0.677
4×10^7	27.0	0.645

^a Conditions: $t = 3 \times 10^{-7} \text{ sec}$; $K_L = 10^4 \text{ sec}^{-1}$; $\delta = 0.1$;
 $K_T = 10^7 \text{ sec}^{-1}$; $\gamma_D = 90 \text{ MHz}$

IV. SUMMARY

Models of rotational and translational relaxation and single-line pulsed absorption were constructed. General analytical solutions that yield the amount of absorption were derived for simple models. The relaxation rates necessary to maintain rotational equilibrium and the conditions necessary to maintain translation equilibrium were calculated for a variety of cases.

More complex models that require numerical solutions were constructed in order to test the validity of the simpler analytical models and to investigate the effects of rotational relaxation on a particular laser isotope enrichment system. The analytical models appear valid for most conditions where self-relaxation is not dominant. Rotational equilibration is essentially maintained for the optimum pressure and laser intensity conditions for the HBr-NO two-step dissociation enrichment system. For different conditions or a different system, a rotational bottleneck can definitely limit enrichment.

The results of the analytical models were applied in determining the range of experimental conditions and the optimum conditions to prevent rotational bottlenecks for two experimental systems. The models can also be coupled with absorption experiments to yield rotational relaxation rate constants and their J-dependence.

APPENDIX A. CALCULATION OF ALPHA AND GAMMA

A. CALCULATION OF TRANSLATIONAL FRACTION α

Alpha is the fraction of molecules that have the proper velocity component to interact with the radiation in the low pressure limit. For a Gaussian absorption curve and a narrow rectangular resonance laser radiation

$$\alpha = \text{Erf} \frac{\Delta v_L}{\gamma_D} \sqrt{\ln 2} \quad v_L < \gamma_D$$

where Erf is the error function, Δv_L is the laser linewidth (HWHM), and γ_D is the Gaussian linewidth (HWHM).

B. CALCULATION OF TRANSLATIONAL ABSORPTION COEFFICIENT γ

Gamma is the absorption coefficient for the T_j state relative to that for the T_i state.

$$\gamma = \frac{(1 - f) (\alpha)}{(1 - \alpha) (f)}$$

$$f = \frac{\int_0^{\Delta v_L} \left\{ \frac{\exp - \left[\ln 2 \frac{\Delta v}{\gamma_D} \right]^2}{\left(\left(\frac{2\pi \Delta v}{K_R + K_T} \right)^2 + 1 \right)} \right\} d\Delta v}{\int_0^{\infty} \left\{ \frac{\exp - \left[\ln 2 \frac{\Delta v}{\gamma_D} \right]^2}{\left(\left(\frac{2\pi \Delta v}{K_R + K_T} \right)^2 + 1 \right)} \right\} d\Delta v}$$

These integrals are solved numerically.

APPENDIX B. COUPLING OF TRANSLATIONAL AND ROTATIONAL RELAXATION

Translational relaxation will be coupled to rotational relaxation if the change in velocity due to a rotational relaxation collision is sufficient to move a molecule into or out of the linewidth of the laser. The case for the HBr system is considered here.

The linewidth of the HBr laser has not been measured. It is estimated to be 3 MHz (FWHM), the same as measured for the HB laser.¹³ The Doppler shift is given by

$$\nu = \nu_0 \left(1 \pm \frac{V}{C} \right)$$

where V is the molecular velocity, C is the speed of light, and ν_0 is the original frequency.

For the $\text{H}^{79}\text{Br } P_1(5)$ line, $\nu_0 = 2451.7 \text{ cm}^{-1}$

$$|\nu - \nu_0| = \nu_0 \left(\frac{V}{C} \right) = 3 \times 10^6 = (2451.7 \text{ c}) \left(\frac{V}{C} \right)$$

$$V = 1.224 \times 10^3 \text{ cm/sec}$$

$$\frac{1}{2} mV^2 = (5 \times 10^{-1}) (8 \times 10^1) (1.224 \times 10^3)^2 = 6 \times 10^7 \text{ erg/mole}$$

Thus, a shift of 3 MHz would require an energy change of 6×10^7 erg/mole along the direction of light propagation.

The minimum energy change associated with a rotational relaxation collision of HBr is $2B$, where $B = 23.584 \text{ cal/mole}$. The minimum change $2B$ is thus 2×10^9 erg/mole. Thus, if only 3% of the minimum energy change is transferred into translation of HBr in the direction of light propagation, a Doppler shift of 3 MHz will result.

APPENDIX C. CALCULATION OF A_{RT} FOR ROTATIONAL-
TRANSLATIONAL RELAXATION

$$A_{RT} = 1 - A_0 \left(A_1 e^{r_1 t} + A_2 e^{r_2 t} + A_3 e^{r_3 t} \right)$$

$$A_0 = \frac{1}{D} \left(\frac{1}{1 + \alpha} \right)$$

$$A_1 = \left(1 + \frac{r_1}{K_R} \right) \left\{ \alpha \left[C_1^2 (\delta - C_2^3) + C_1^3 (C_2^2 - \delta) \right] + C_2^2 (C_1^3 - \delta) + C_2^3 (\delta - C_1^2) \right\}$$

$$A_2 = \left(1 + \frac{r_2}{K_R} \right) \left\{ \alpha \left[C_1^3 (\delta - C_2^1) + C_1^2 (C_2^3 - \delta) \right] + C_2^3 (C_1^1 - \delta) + C_2^1 (\delta - C_1^3) \right\}$$

$$A_3 = \left(1 + \frac{r_3}{K_R} \right) \left\{ \alpha \left[C_1^1 (\delta - C_2^2) + C_1^2 (C_2^1 - \delta) \right] + C_2^1 (C_1^2 - \delta) + C_2^2 (\delta - C_1^1) \right\}$$

where

$$D = C_2^1 (C_1^2 - C_1^3) + C_2^2 (C_1^3 - C_1^1) + C_2^3 (C_1^1 - C_1^2)$$

$$C_1^i = \frac{K_R \left(\frac{\delta}{1 - \delta} \right) + K_T \left(\delta + \frac{(1 + \delta) r_i}{K_R} \right)}{\left(r_i + K_T + \gamma K_L + \frac{K_R}{1 + \delta} \right) (1 + \alpha)} \quad i = 1, 2, 3$$

$$C_2^i = \frac{\frac{r_i}{K_R} (1 + \delta) \left[\alpha K_T + (1 + \alpha) (K_R + \gamma K_L + r_i) \right] + \delta \left[\alpha K_T + \frac{K_R}{(1 + \delta)} + \gamma (1 + \alpha) K_L \right]}{(1 + \alpha) \left(\gamma K_L + K_T + \frac{K_R}{1 + \delta} + r_i \right)}$$

where

$$r_1 = 2(-p/3)^{1/2} \cos\left(\frac{a'}{3}\right) - \frac{a_2}{3}$$

$$r_2 = -2(-p/3)^{1/2} \cos\left(\frac{a' + \pi}{3}\right) - \frac{a_2}{3}$$

$$r_3 = -2(-p/3)^{1/2} \cos\left(\frac{a' - \pi}{3}\right) - \frac{a_2}{3}$$

where

$$a' = \cos^{-1} \left[\frac{-q}{2 \sqrt{-(p/3)^3}} \right]$$

where

$$p = -\frac{a_2^2}{3} + a_1$$

$$q = 2\left(\frac{a_2}{3}\right)^3 - \frac{a_1 a_2}{3} + a_0$$

where

$$a_2 = \left(\frac{2 + \delta}{1 + \delta}\right) K_R + K_T + (1 + \gamma) K_r$$

$$a_1 = K_R \left[K_T + \frac{K_R}{1 + \delta} \right] + K_L \left[\gamma K_L + \left(\frac{\alpha + \gamma}{1 - \alpha}\right) K_T + (1 + \delta) K_R \right]$$

$$a_0 = \left(\frac{\delta}{1 + \delta}\right) K_L K_R \left[\gamma K_L + \left(\frac{\alpha + \gamma}{1 + \alpha}\right) K_T + \left(\frac{\alpha + \gamma}{1 + \alpha}\right) \left(\frac{1}{1 + \delta}\right) K_R \right]$$

APPENDIX D. CALCULATION OF A_R AND A_E

A. ROTATIONAL RELAXATION CASE

$$A_R = 1 - \frac{1}{r_2 - r_1} \left[(r_2 - r_0) e^{r_1 t} - (r_1 - r_0) e^{r_2 t} \right]$$

where

$$r_0 = -\left(\frac{\delta}{1+\delta}\right) K'_L$$

$$r_1 = -\frac{K'_L}{2} - \frac{K_R}{2} + \left[(K'_L + K_R)^2 - \frac{4\delta}{(1+\delta)} K_R K'_L \right]^{1/2}$$

$$r_2 = -\frac{1}{2} \left\{ K'_L + K_R + \left[(K'_L + K_R)^2 - \frac{4\delta}{(1+\delta)} K_R K'_L \right]^{1/2} \right\}$$

B. EQUILIBRIUM CASE

$$A_E = 1 - e^{r_0 t}$$

$$r_0 = -\left(\frac{\delta}{1+\delta}\right) K'_L$$

where

$$K'_L = (\alpha + \gamma - \alpha\gamma) K_L$$

APPENDIX E. INPUTS FOR BASE CONDITIONS OF ENRICHMENT MODELS

For calculation of K_L , the following parameters were used:

1. A 1.5 mJ $H^{79}Br$ ($P_1(5)$) laser with a Gaussian pulsewidth of 3×10^{-7} sec FWHM
2. Line strength of $191.3 \text{ cm}^{-1} \text{ atm}^{-1(13)}$
3. HBr-HBr line-broadening parameter of $9.4 \times 10^{-6} (T)^{1/2} \text{ cm}^{-1} \text{ Torr}^{-1(10)}$
4. HBr-NO line-broadening parameter of $5.1 \times 10^{-6} (T)^{1/2} \text{ cm}^{-1} \text{ Torr}^{-1}$, estimated from HCl-CO line broadening¹¹

For calculation of K_R , the line-broadening parameters given above were used.

For calculation of K_T , a hard sphere diameter of $3.41 \times 10^{-8} \text{ cm}^{14}$ was used with NO pressure = 50 Torr, HBr pressure = 4 Torr, temperature = 300 K, $\gamma_D = 50.7 \text{ MHz}$, $\Delta\nu_L = 5.07 \text{ MHz}$, $\beta = 0.818182$, $\delta^u = 0.1489$, and $\delta^l = 0.1309$.

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