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Pressure Dependence of Fluorescence Spectra. IV. Effects of Vibrational Energy Transfer between Fluorescing Molecules*

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Vibrational relaxation of a system of s-dimensional degenerate harmonic oscillators is investigated. The oscillators are impulsively excited and are then allowed to relax to thermal equilibrium by collisions with a heat bath and by transfer of vibrational quanta among themselves. The model is applicable to analysis of experimental data in which excited molecules are produced in concentrations not negligible in comparison to the concentration of heat-bath molecules.

INTRODUCTION

MOST of the work which has been done to date on vibrational energy transfer of molecules in the gas phase has been concerned with oscillators present in trace amounts and transferring energy only by colli-

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sions with heat-bath molecules.[1] Two notable exceptions are recent papers by Shuler and by Osipov,[2] in which it is shown that the equations describing the relaxation of a system of one-dimensional harmonic oscillators in collisional contact with each other and with nothing else may be exactly linearized; this linearization results in equations formally identical to equations solved earlier by Montroll, Rubin, Shuler, and their co-workers. Shuler's method, as we shall see shortly, works equally well in reducing the corresponding equations for s-dimensional degenerate harmonic oscillators ($[s]$ oscillators) to linear equations identical in form to a set we treated earlier.[1k] These relaxation equations, however, ignore interactions with the heat-bath and consider only the collisional permutation of vibrational quanta among the oscillators. They are therefore suitable only for the analysis of systems in which intermolecular vibrational energy transfer is quite efficient compared to transfer of energy from the vibrational degrees of freedom to the heat bath, and then only for times short compared to the natural time scale involved in the latter process.

A number of experimental papers have appeared the last few years in which relatively large concentrations of vibrationally excited species have been prepared by impulsive means, such as flash photolysis.[3] In these systems it appears questionable whether the neglect of collisional permutation of vibrational energy among the molecules of interest is warranted; this was noted by Norrish and his co-workers.[3]

We therefore investigate the relaxation of a system of $[s]$ oscillators exchanging energy with each other and with a heat bath. The remainder of this paper presents the model studied, the relaxation equations pertaining to the model, and the results of numerical integration of these equations.

We are indebted to Dr. Patricia Eberlein for the Heun–Euler subroutine we used in the computation, and to Suresh Thakore for his most helpful assistance in debugging. The computations were done on the IBM 7070 of the University of Rochester Computing Center.

MODEL

The following mechanism is appropriate for collisional transfer of vibrational energy in the dilute gas phase, where binary collisions only need be considered:

$$
\begin{aligned}
&A_i+M\rightarrow A_j+M && a_{ji}\\
&A_i+A_j\rightarrow A_k+A_l && \alpha(i,j;k,l). \qquad (1)
\end{aligned}
$$

Here A_p represents a molecule in its pth quantum state, p symbolizes the set of quantum numbers necessary to describe the state, and a_{ji} and $\alpha(i,j;k,l)$ are rate constants for the processes with which they are associated. The first process, interaction with the heat-bath molecules M (assumed at thermal equilibrium), has been analyzed in detail previously.[1] The second process was analyzed by Shuler and Osipov[2] for the case of $[1]$ oscillators. Note that in the second process energy must be conserved. The $\alpha(i,j;k,l)$ are related by the principle of microscopic reversibility; however, the requirement of conservation of energy implies that no temperature dependence is introduced by the requirement of microscopic reversibility.

One could then readily write out the relaxation equations pertaining to this set of processes; we shall not do so, however, until the model has been further specialized. We restrict ourselves to a representation of the molecules of interest as $[s]$ oscillators, as has been done by Kassel[4] and others. The transition rate factors a_{ji} are then just those used by us earlier[1k,5]; they are

$$
\begin{aligned}
a_{i+1,i}&=ae^{-\theta}(i+s),\\
a_{i,i+1}&=a(i+1),\\
a_{i,j}&=0,\ j\neq i\pm 1. \qquad (2)
\end{aligned}
$$

$\theta=h\nu/kT$, where ν is the frequency of the oscillators. A simple generalization of the joint transition probabilities used by Shuler[2a] yields the $\alpha(i,j;k,l)$; they are

$$
\begin{aligned}
\alpha(i+1,j;i,j+1)&=\alpha(i+1)(j+s),\\
\alpha(i-1,j;i,j-1)&=\alpha(i+s-1)j, \qquad (3)
\end{aligned}
$$

etc.;

$$\alpha(i,j;k,l)=0,$$

if $k\neq i\pm 1$, $l\neq j\mp 1$. a and α are constants.

On inserting these expressions into the relaxation equations we obtain

$$
\begin{aligned}
dA_i/dt={}&a(i+s-1)e^{-\theta}MA_{i-1}+a(i+1)MA_{i+1}\\
&-a[(i+s)e^{-\theta}+i]MA_i+\sum_{j=1}\alpha(i+1)(j+s-1)A_{i+1}A_{j-1}\\
&+\sum_{j=0}\alpha(i+s-1)(j+1)A_{i-1}A_{j+1}\\
&-\sum_{j=1}\alpha i\cdot(j+s-1)A_{j-1}A_i-\sum_{j=0}\alpha(i+s)(j+1)A_{j+1}A_i. \qquad (4)
\end{aligned}
$$

A_i and M here represent the concentrations of the corresponding species.

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[1] Recent references are: (a) T. Carrington, J. Chem. Phys. **35**, 807 (1961); (b) T. Carrington, Discussion Faraday Soc. **1962** No. 33; (c) K. E. Shuler, G. H. Weiss, and K. Andersen, J. Math. Phys. (to be published); (d) E. W. Schlag, J. Chem. Phys. **35**, 2117 (1961); (e) B. S. Neporent and S. O. Mirumyants, Optics and Spectroscopy **8**, 336 (1960); (f) E. E. Nikitin, Doklady Akad. Nauk S.S.S.R. **135**, 1442 (1960); (g) D. J. Wilson, B. Noble, and B. Lee, J. Chem. Phys. **34**, 1392 (1961); (h) N. Chow and D. J. Wilson, J. Phys. Chem. **66**, 342 (1962); (i) J. Brauner and D. J. Wilson, J. Chem. Phys. **36**, 2547, (1962). References to numerous earlier papers are given in (j) E. W. Montroll and K. E. Shuler, Advances in Chem. Phys. **1**, 361 (1958); (k) D. J. Wilson, J. Chem. Phys. **36**, 1293 (1962).

[2] (a) K. E. Shuler, J. Chem. Phys. **32**, 1692 (1960); (b) A. I. Osipov, Doklady Akad. Nauk S.S.S.R. **130**, 523 (1960).

[3] See, for example, N. Basco, A. B. Callear, and R. G. W. Norrish, Proc. Roy. Soc. (London) **A260**, 459 (1961).

[4] L. S. Kassel, *Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Company, New York, 1932).

[5] F. P. Buff and D. J. Wilson, J. Chem. Phys. **32**, 677 (1960).

If we now calculate the rate of change of the mean energy of the oscillators [by multiplying the ith equation in (4) by i and summing], we find that the terms involving transfer of vibrational energy from one oscillator to another contribute nothing, and we obtain a simple linear differential equation for the relaxation of the mean energy;

$$d\langle\epsilon\rangle/d\tau=se^{-\theta}-(1-e^{-\theta})\langle\epsilon\rangle, \tag{5}$$

where $\tau=aMt$ and $\langle\epsilon\rangle=\sum_{i=0}iA_i$. The solution to this equation is

$$\langle\epsilon\rangle=[se^{-\theta}/(1-e^{-\theta})]\{1-\exp[-(1-e^{-\theta})\tau]\}\\ +\langle\epsilon_0\rangle\exp[-(1-e^{-\theta})\tau], \tag{6}$$

where $\langle\epsilon_0\rangle$ is the initial mean energy. This result is a simple extension of Montroll and Shuler's[6] Eq. (1.18), and is a special case of a problem discussed in reference 1(c).

We may readily investigate the case in which interaction with the heat-bath molecules M can be ignored, so that $\langle\epsilon\rangle(t)=\langle\epsilon_0\rangle$. Noting that $\sum_{j=0}jA_j=\langle\epsilon\rangle$ and that $\sum_{j=0}A_j=1$ (assuming unit total concentration of A), we obtain from Eq. (4) the following result:

$$dA_i/dt=\alpha(\langle\epsilon_0\rangle+s)\left\{(i+1)A_{i+1}+(i+s-1)\right.\\ \left.\times\frac{\langle\epsilon_0\rangle}{\langle\epsilon_0\rangle+s}A_{i-1}-\left[i+(i+s)\frac{\langle\epsilon_0\rangle}{\langle\epsilon_0\rangle+s}\right]A_i\right\}. \tag{7}$$

This is identical in form to the equation obtained[1k] describing the relaxation of $[s]$ oscillators in contact with a heat bath at a temperature defined by $e^{-\theta}=\langle\epsilon_0\rangle/(\langle\epsilon_0\rangle+s)$. The equations can be solved in exactly the same way as was used in reference 1(k), a method used earlier by Montroll and Shuler.[6]

One may then take expression (6) for $\langle\epsilon\rangle$, substitute it for $\langle\epsilon_0\rangle$ in Eq. (7), and then substitute the right-hand side of this result in Eqs. (4) in place of the four summations. This converts (4) into a system of first-order, homogeneous, linear differential equations. Unfortunately, the coefficients depend on the time in a moderately complex way, so that this linearization of the nonlinear problem does not lead to simpler machine computation than would result from using Eqs. (4) as is.

Equations (4) were therefore programmed for numerical integration by the Heun–Euler method,[7] and the various examples were computed. As checks on rounding off and truncation errors, we computed $\sum_iA_i$, which should be unity, and $\sum_iiA_i$, which was then compared with the value of the energy computed by Eq. (6). These results enabled us to determine how small we needed to make the time intervals Δt in the numerical integration, and how many levels we needed to include to avoid having molecules "piling up" at the top level during the relaxation; inspection of the A_i also was used to avoid this last source of error.

One other point must be made before discussing our results. One can readily verify that substitution of

$$(1-e^{-\Theta})^{s-1}g_s(i)e^{-i\Theta},\qquad g_s(i)=(i+s-1)!/(s-1)!i!,$$

for A_i (with similar expressions for A_j, etc.) causes the four summations in Eqs. (4) to cancel out identically, no matter what value of Θ is used. Therefore, after the distribution A_i has once become of Boltzmann type, the system will continue to relax to equilibrium through a series of Boltzmann distributions in exactly the same way as does a similar system in which the only mode of energy transfer is to and from the heat bath. This latter problem has been studied in detail.[1k,6] It was therefore necessary for us to carry out our integrations only until a Boltzmann distribution (at a temperature generally quite different from that of the heat bath) was reached; the remainder of the relaxation could yield nothing not already understood.

The calculation above of the mean energy of the system showed that the transfer of quanta among the molecules of interest had no effect on the relaxation of the mean energy. As one would expect, however, the mean-square energy $\langle\epsilon^2\rangle=\sum_ii^2A_i$ does depend on the efficiency of this mode of energy transfer. If one multiplies Eqs. (4) by i^2, sums, uses the definitions of $\langle\epsilon\rangle$ and $\langle\epsilon^2\rangle$, and inserts the expression (6) for $\langle\epsilon\rangle$, one

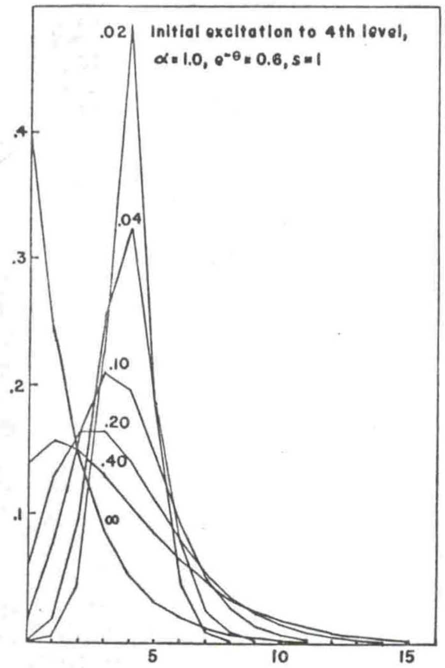

FIG. 1. Plots of A_n/Σ_iA_i vs n. The dimensionless time (aMt) elapsed since initial excitation is indicated by each plot.

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[6] E. W. Montroll and K. E. Shuler, J. Chem. Phys. **26**, 454 (1957).

[7] See, for example, H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1956), 2nd ed., Sec. 13.17.

obtains the following differential equation for $\langle\epsilon^2\rangle$:

$$(d\langle\epsilon^2\rangle/dl)+2(\delta+\alpha s)\langle\epsilon^2\rangle=2\gamma^2\alpha(s+1)\exp(-2\delta l)$$
$$+[4\beta\gamma\alpha(s+1)+2\alpha s+\gamma aM(2s\rho+1+\rho)]\exp(-\delta l)$$
$$+[2\beta^2\alpha(s+1)+\beta aM(2s\rho+1+\rho)+2\beta\alpha s+sa\rho M], \quad (8)$$

where

$$\delta=(1-\rho)aM,$$
$$\beta=s\rho/(1-\rho),$$
$$\gamma=\epsilon_0-s\rho/(1-\rho),$$
$$\rho=e^{-\theta}.$$

Solution of (8) yields, after simplification, the following expression for $\langle\epsilon^2\rangle$:

$$\langle\epsilon^2\rangle=\exp[-2(\delta+\alpha s)l]\left(\langle\epsilon_0{}^2\rangle-\langle\epsilon_0\rangle^2\frac{s+1}{s}-\langle\epsilon_0\rangle\right)$$
$$+\exp[-2\delta l](\langle\epsilon_0\rangle-\langle\epsilon_\infty\rangle)^2\frac{s+1}{s}$$
$$+\exp[-\delta l](\langle\epsilon_0\rangle-\langle\epsilon_\infty\rangle)\left(2\langle\epsilon_\infty\rangle+\frac{1+e^{-\theta}}{1-e^{-\theta}}\right)$$
$$+\langle\epsilon_\infty\rangle\left(\frac{1}{1-e^{-\theta}}+\langle\epsilon\rangle_\infty\right), \quad (9)$$
$$\langle\epsilon_0\rangle=\langle\epsilon\rangle(0),$$
$$\langle\epsilon_\infty\rangle=\langle\epsilon\rangle(\infty),$$
$$\langle\epsilon_0{}^2\rangle=\langle\epsilon^2\rangle(0).$$

The argument of the first exponential depends on the efficiency of energy transfer among the molecules of interest.

Boudart and Dubois proposed[8] that the nonequilibrium distributions arising in photochemical reactions, etc., be characterized by their vibrational temperature, which is, aside from a scale factor, our $\langle\epsilon\rangle$. Surely it would be helpful if one could simply express the information about such distributions which is most pertinent to their chemical behavior. Boudart and Dubois' T_{vib}, or our $\langle\epsilon\rangle$, is certainly one of the basic parameters needed. However, one can construct reasonable model distributions of $[s]$ oscillators having the same $\langle\epsilon\rangle$ and drastically different rates of decomposition. (We assumed a Kassel-type formula for the microscopic decomposition rates of activated molecules.[4]) Evidently, a more detailed description is needed than is supplied by the single parameter proposed. A logical second parameter to include in a simple description is the mean-square energy, or some quantity readily derived from it. $\langle\epsilon^2\rangle$ can often be fairly easily obtained on analysis of theoretical models,[1(e),9] and one should be able to obtain this quantity even for the rather general model considered by Gans.[10] We are indebted to Dr. Dubois for discussing with one of us the problem of simply characterizing nonequilibrium distributions, and to our referee for some useful suggestions on this point.

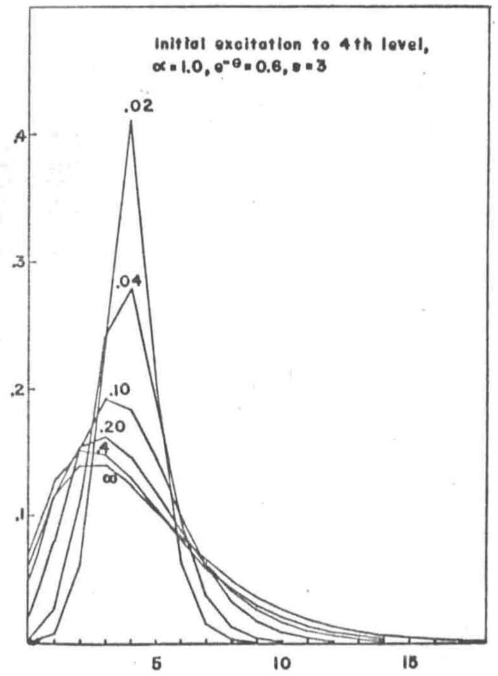

FIG. 2. Plots of $A_n/\Sigma_i A_i$ vs n. Figures 1, 2, and 3 show the effects of increasing molecular complexity

For our model, the mean-square deviation of the (dimensionless) energy is given by

$$\langle\epsilon^2\rangle-\langle\epsilon\rangle^2=\exp(-2\delta l)\{[\langle\epsilon_0{}^2\rangle-\langle\epsilon_0\rangle^2-(\langle\epsilon_0\rangle^2/s)$$
$$-\langle\epsilon_0\rangle]\exp(-2\alpha sl)+(1/s)(\langle\epsilon_0\rangle-\langle\epsilon_\infty\rangle)^2\}$$
$$+(\langle\epsilon_0\rangle-\langle\epsilon_\infty\rangle)[(1+e^{-\theta})/(1-e^{-\theta})]\exp(-\delta l)$$
$$+[\langle\epsilon_\infty\rangle/(1-\rho)]. \quad (10)$$

If one excites to an initial Boltzmann distribution, the coefficient of $\exp(-2\alpha sl)$ vanishes, as one would expect. If one excites to an initial delta-function distribution $\langle\epsilon_0{}^2\rangle=\langle\epsilon_0\rangle^2$, then the absolute value of the ratio of the coefficient of $\exp(-2\alpha sl)$ to the constant term in the square brackets is greater than $1+s/\langle\epsilon_0\rangle$. Since these coefficients are of the order of $\langle\epsilon_0\rangle^2$ and the other terms in (10) are of the order of $\langle\epsilon_0\rangle$, one would use a large value of $\langle\epsilon_0\rangle$ in order to obtain an estimate of α. For the initial distribution function $P_m=\frac{1}{2}(\delta_{m0}+\delta_{mn})$, this ratio is $[1-(1/s)-(2/\langle\epsilon_0\rangle)]\cdot s$.

From the above two examples, we can see that there exist initial distributions for which the behavior of the mean-square deviation of the energy may be rather strongly influenced by the vibration–vibration transfer mechanism.

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[8] M. Boudart and J. T. Dubois, J. Chem. Phys. **23**, 223 (1955).

[9] P. M. Mathews, I. I. Shapiro, and D. L. Falkoff, Phys. Rev. **120**, 1 (1960).

[10] P. J. Gans, J. Chem. Phys. **33**, 691 (1960).

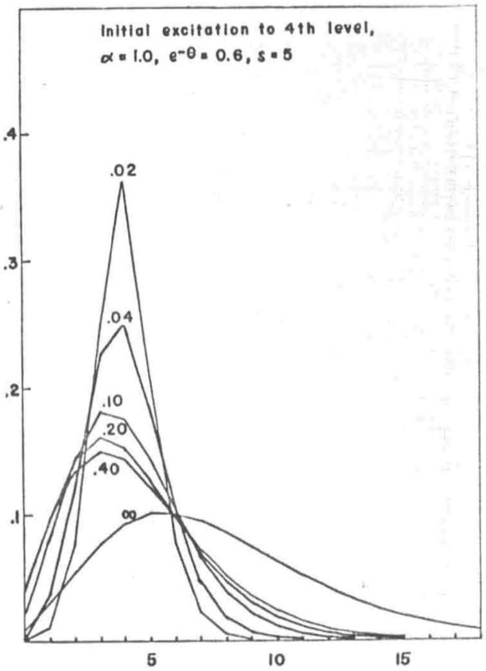

FIG. 3. Plots of $A_n/\Sigma_i A_i$ vs n.

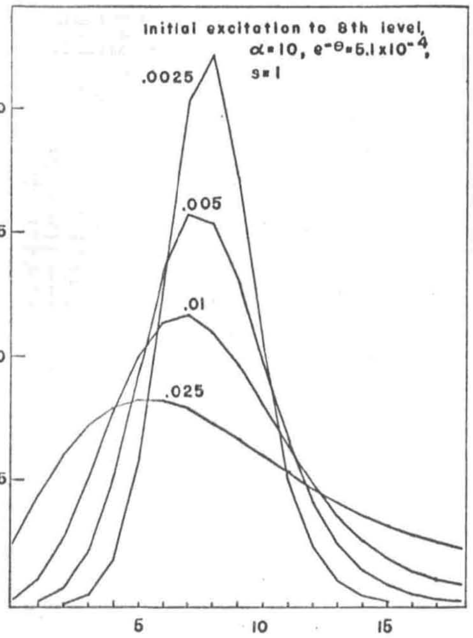

FIG. 5. The curve for which $aMt=0.025$ shows "piling up" at its right-hand end. This is also seen in some of the curves in Fig. 6.

One can conceive of various experiments by which the presence of such a mechanism could be detected. One of them is obviously flash excitation and high-speed spectroscopy, as used, for example, by Norrish. Another is flash photolysis of the following type. Let us assume that a reactant has a (dimensionless) critical energy ϵ^*. If we flash excite a trace of reactant to energy levels a short distance below ϵ^*, energy exchange with the heat bath (assumed at room temperature) only will occur, and, as shown previously, this will result in only a negligible number of molecules being collisionally excited to energies $\geq \epsilon^*$, so that the primary quantum yield would be low. In this case,

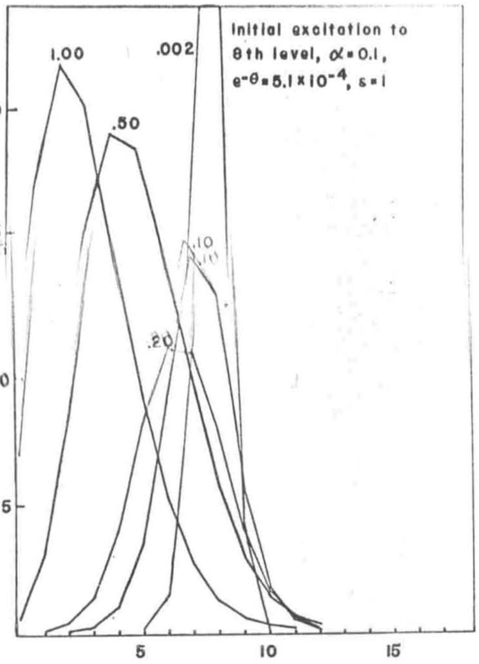

FIG. 4. The value of $e^{-\theta}$ used here and in Fig. 5 corresponds to that for oxygen at room temperature. As $t\rightarrow\infty$ only the zeroth level is populated. Note the change in vertical scale between Figs. 1, 2, and 3 and Figs. 4, 5, and 6.

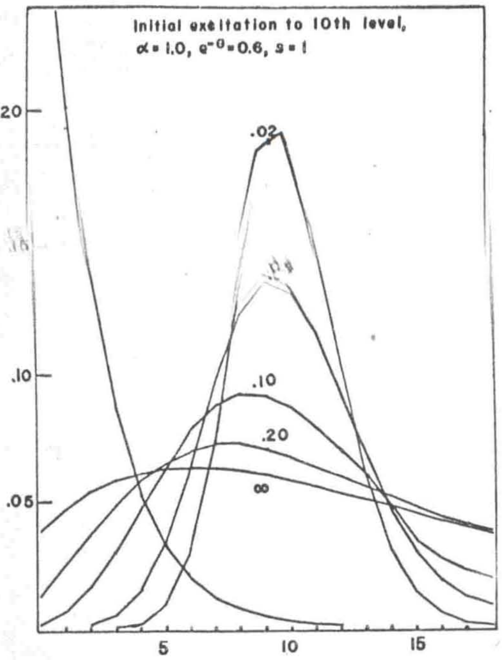

FIG. 6. Plots computed for a model identical to that shown in Fig. 5, except that the heat-bath temperature is much higher.

when $\langle\epsilon\rangle(t)$ is large, $\langle\epsilon^2\rangle-\langle\epsilon\rangle^2$ is small. If, on the other hand, we flash excite a rather high concentration of reactant molecules to energy levels a short distance below ϵ^*, an efficient vibration–vibration transfer mechanism would permit rapid "spreading" of the distribution before heat-bath interactions had cooled it down. In this case, the vibration–vibration transfer mechanism permits the distribution to simultaneously have large values of $\langle\epsilon\rangle(t)$ and $\langle\epsilon^2\rangle-\langle\epsilon\rangle^2$. Since we may now have many molecules having vibrational energy $\geq\epsilon^*$, we would expect, for this case, to find quite appreciable primary quantum yields. Further, it is readily seen that these quantum yields will increase with increasing flash intensity, in contrast to the previous case.

The behavior with time of the quantity $(\langle\epsilon^2\rangle-\langle\epsilon\rangle^2)/\langle\epsilon\rangle^2$ is of some interest. From Eqs. (6) and (10) we could write a rather complicated expression for this quantity; instead we choose to write down the limiting expression for $\delta t\gg1$

$$\lim_{\delta t\gg1}\left(\langle\epsilon^2\rangle-\langle\epsilon\rangle^2\right)/\langle\epsilon\rangle^2$$

$$=(1/se^{-\theta})\{1-[(\langle\epsilon_0\rangle-\langle\epsilon_\infty\rangle)/\langle\epsilon_\infty\rangle](1-e^{-\theta})\exp(-\delta t)\}. \tag{11}$$

It is interesting to note that the side from which equilibrium is finally approached is independent of everything except $\langle\epsilon_0\rangle-\langle\epsilon_\infty\rangle$.

RESULTS

Some of our numerical results are illustrated in Figs. 1–6, in which distribution functions are plotted as functions of vibrational quantum number at various times after initial impulsive excitation of the molecules to one vibrational level. It must be noted here that, in marked contrast to the linear problems treated previously, one cannot obtain the solution to the problem with an arbitrary initial distribution by choosing suitable linear combinations of solutions to problems having initial delta-function distributions.

Figures 1–3 show the effect of increasing molecular complexity while holding $e^{-\theta}$ and α/aM constant, and initially exciting impulsively in all cases to the level containing four quanta. For $s=1$, $\langle\epsilon\rangle(t)$ decreases with time; for $s=3$, it changes relatively little; for $s=5$, it increases quite markedly with time. Plots of distribution functions in which $\langle\epsilon_0\rangle$ is substantially larger than skT show somewhat less dependence on s during the initial relaxation, and the rate of the initial relaxation is considerably more rapid, due to the fact that all of the coefficients in the relaxation equations increase with increasing quantum number.

Figures 4 and 5 show the effects of varying the efficiency of the transfer of vibrational energy from one molecule of interest to another. Experimentally, this could be done by simply increasing the concentration of "interesting molecules," since this mode of energy transfer involves quadratic terms in the A_i's, while the heat-bath interactions lead to only linear terms in the A_i's. In Fig. 4, α is 0.1; in Fig. 5, it is 10—aside from this, the two models are identical. It is evident that an efficient vibration–vibration transfer process profoundly affects the time evolution of the distribution. This process, if efficient, causes a rapid decay to a Boltzmann distribution, which then relaxes to a Boltzmann distribution at the temperature of the heat bath in exactly the same way as does a similar system in which energy transfer from one molecule of interest to another does not occur.

Figure 6 is included for comparison with Fig. 5 and Fig. 1. The heat-bath temperatures of the models analyzed in Figs. 5 and 6 are quite different; nevertheless, the initial relaxations of the two distributions are very similar. The values of α differ by a factor of 10; the over-all result of this is to change the time scale of the initial relaxation. Figure 6 and Fig. 1 differ only in the level to which initial excitation occurs; the initial distribution having the higher energy "spreads out" substantially more rapidly than does the other one, as remarked above.

The right-hand ends of the curves shown in Fig. 6 indicate truncation error, due to the inclusion of only 19 energy levels in the model. One of the curves in Fig. 5 shows the same effect. Such error was also indicated by the fact that values of $\langle\epsilon\rangle(t)$ calculated by summing the defining series differed appreciably from values calculated from Eq. (6). Since the collision mechanism conserved molecules (no leakage of molecules from the 19th state to those above was permitted), this type of error does not affect the requirement that molecules be conserved. The error, appreciable though it is for the model depicted in Fig. 6, does not, we feel, invalidate the conclusions mentioned above.

The results of our calculations indicate that studies of vibrational relaxation in which vibrationally excited molecules of interest constitute an appreciable fraction of the species present should lead to considerable information about the nature of vibration–vibration transfer of energy between molecules, provided that the initial distributions of vibrational energy are not Boltzmann-like.