

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  $\epsilon^*$ , 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  $\delta t \gg 1$

$$\lim_{\delta t \gg 1} (\langle \epsilon^2 \rangle - \langle \epsilon \rangle^2) / \langle \epsilon \rangle^2 = (1/s e^{-\theta}) \{ 1 - [(\langle \epsilon_0 \rangle - \langle \epsilon_\infty \rangle) / \langle \epsilon_\infty \rangle] (1 - e^{-\theta}) \exp(-\delta t) \}. \quad (11)$$

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  $\alpha/aM$  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,  $\alpha$  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  $\alpha$  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.