

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

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 highspeed spectroscopy, as used, for example, by Norrish. Another is flash photolysis of the following type. Let us assume that a reactant has a (dimensionless)

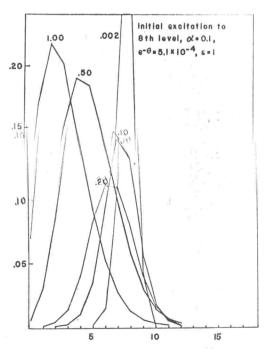


Fig. 4. The value of $e^{-\theta}$ used here and in Fig. 5 corresponds to that for oxygen at room temperature. As $t \to \infty$ only the zeroth level is populated. Note the change in vertical scale between Figs. 1, 2, and 3 and Figs. 4, 5, and 6.

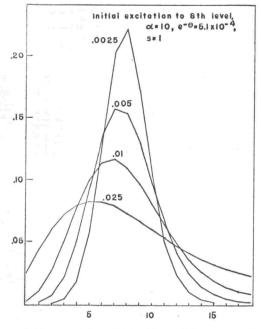


Fig. 5. The curve for which aMt=0.025 shows "piling up" at its right-hand end. This is also seen in some of the curves in Fig. 6.

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,

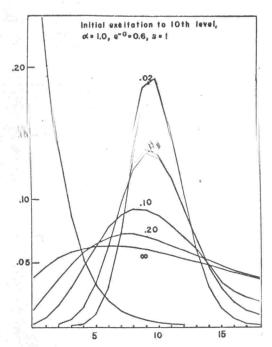


Fig. 6. Plots computed for a model identical to that shown in Fig. 5, except that the heat-bath temperature is much higher.