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(c),9] and one should be able to obtain this quantity even

[8] M. Boudart and J. T. Dubois, J. Chem. Phys. 23, 223 (1955).
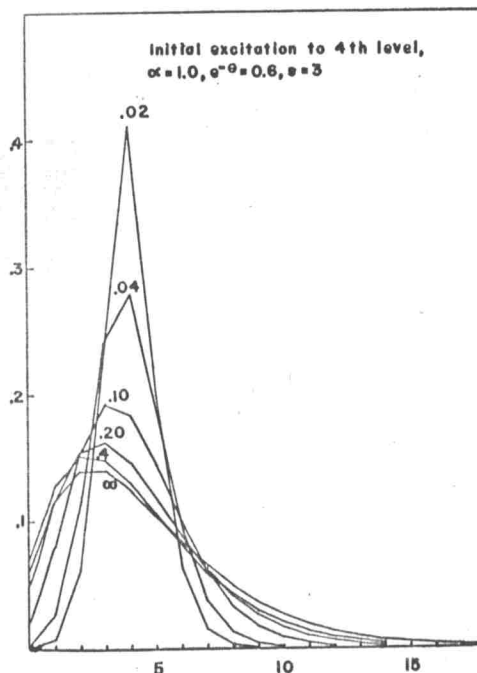[9] P. M. Mathews, I. I. Shapiro, and D. L. Falkoff, Phys. Rev. 120, 1 (1960).

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 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.

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

$$\langle \epsilon^2\rangle - \langle \epsilon\rangle^2 = \exp(-2\delta l)\{[\langle \epsilon_0{}^2\rangle - \langle \epsilon_0\rangle^2 - (\langle \epsilon_0\rangle^2/s)$$

$$- \langle \epsilon_0\rangle]\exp(-2\alpha s l) + (1/s)(\langle \epsilon_0\rangle - \langle \epsilon_\infty\rangle))^2\}$$

$$+ (\langle \epsilon_0\rangle - \langle \epsilon_\infty\rangle)[(1+e^{-\theta})/(1-e^{-\theta})]\exp(-\delta l)$$

$$+ [\langle \epsilon_\infty\rangle/(1-\rho)]. \quad (10)$$

If one excites to an initial Boltzmann distribution, the coefficient of $\exp(-2\alpha s l)$ 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 $\exp(-2\alpha s l)$ 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.

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