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.
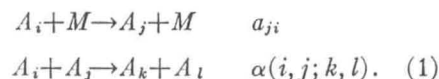
MODEL

The following mechanism is appropriate for collisional transfer of vibrational energy in the dilute gas

phase, where binary collisions only need be considered:

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

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

$$a_{i+1,i} = a e^{-\theta}(i+s),$$
$$a_{i,i+1} = a(i+1),$$
$$a_{i,j} = 0, j \neq i \pm 1. \quad (2)$$

$\theta = h\nu/kT$, 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

$$\alpha(i+1, j; i, j+1) = \alpha(i+1)(j+s),$$
$$\alpha(i-1, j; i, j-1) = \alpha(i+s-1)j, \quad (3)$$

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

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

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

[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).