

present know the nature of the positive and negative ions in the air around us. Their concentration,  $\sim 10^3 \text{ cm}^{-3}$ , is about the same as the ion concentration in the stratosphere, and for that matter, about the same as the D-region ion density. The ion density is not greatly different from 80 km to the surface of the earth. Measurements of the tropospheric ions should provide

us with a remarkably sensitive determination of at least two trace neutrals, one in the positive ions and one in the negative ions, and perhaps more. Possibly the ion composition will be variable as the critical species (as determined largely by energetics) vary with time, especially if anthropogenic pollutants turn out to be involved.

## Collision-Induced Energy Flow between Vibrational Modes of Small Polyatomic Molecules

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There is considerable fundamental and practical interest in determining the rates and mechanisms for collision-induced intermode energy flow in polyatomic molecules. Since the potential surfaces for the collisional interactions of polyatomic molecules are necessarily complex, such data serve as a guide and test for approximate theoretical models. In addition a knowledge of such rates and mechanisms can be used to influence the course of chemical reactions or to develop new laser systems.

The advent of monochromatic, intense, short-pulse infrared laser systems<sup>1</sup> provided an extremely convenient means for studying vibrational energy transfer via time-resolved infrared fluorescence techniques.<sup>2,3</sup> The application of these methods to the study of intermode energy transfer in small, rigid polyatomics has led to a considerable body of experimental data which provides a fairly detailed picture of collision-induced energy flow in at least a small number of molecular systems.<sup>4-6</sup> Some of the physical and chemical features which determine the rates and mechanisms for energy transfer in these molecules are now evident.

A detailed kinetic description of the energy-transfer processes which couple all vibrational states of energy less than (e.g.)  $3000 \text{ cm}^{-1}$  is enormously complex even for a triatomic. The number of kinetic rate constants required to describe fully such a system of  $n$  levels can be shown to scale like  $n(n-1)/2$ .<sup>7,8</sup> Thus even for a molecule with 10 levels of energy less than this arbitrarily chosen value of  $3000 \text{ cm}^{-1}$ , 45 independent rate constants and hence 45 independent pieces of data are required to completely characterize the energy-transfer kinetics! Fortunately, the situation is not as grim as it might seem. In fact, for a significant number of small, rigid polyatomics a few rate constants are of overwhelming importance in determining the energy flow mechanism while most of the remaining kinetic pa-

rameters are of minimal importance. When stated in the language of cross sections, this simply means that only a handful of kinetic collision events have "sizeable" cross sections. Because of this feature, a great deal of insight into polyatomic molecule energy flow mechanisms can be obtained from the rather simple models.

### A Minimum Model for Vibrational Relaxation of Small Molecules

Consider the block diagram of Figure 1. Here each vibrational mode for a triatomic has been represented by a single reservoir (box) which is in turn coupled to the other vibrational modes or reservoirs by a single channel. In addition only the lowest vibrational mode is coupled, again by a single channel, to the reservoir which represents the translational and rotational degrees of freedom. Though oversimplified, this model picture provides a great deal of physical insight into vibrational energy-transfer processes for small molecules. There are several reasons why this representation is a reasonable one, as will be demonstrated now with the molecule  $\text{CH}_3\text{F}$  as an example.

Why can all the states in a single mode be lumped into a single reservoir? This arises because the successive overtones of a given mode are rapidly coupled by kinetic events which are generally referred to as ladder-climbing processes. For example, if the vibrational mode  $\nu_3$  ( $1048 \text{ cm}^{-1}$ ) of  $\text{CH}_3\text{F}$  is pumped by a short pulse  $\text{CO}_2$  laser

laser pump



(1) M. A. Kovacs, G. W. Flynn, and A. Javan, *Appl. Phys. Lett.*, **8**, 62 (1966); G. W. Flynn, M. A. Kovacs, C. K. Rhodes, and A. Javan, *ibid.*, **8**, 63 (1966); J. V. V. Kasper and G. C. Pimental, *Phys. Rev. Lett.*, **14**, 352 (1965).

(2) L. O. Hocker, M. A. Kovacs, C. K. Rhodes, G. W. Flynn, and A. Javan, *Phys. Rev. Lett.*, **17**, 233 (1966).

(3) C. B. Moore, R. E. Wood, B. B. Hu, and J. T. Yardley, *J. Chem. Phys.*, **46**, 4222 (1967); J. T. Yardley and C. B. Moore, *ibid.*, **46**, 4491 (1967).

(4) C. B. Moore, *Annu. Rev. Phys. Chem.*, **22**, 387 (1971).

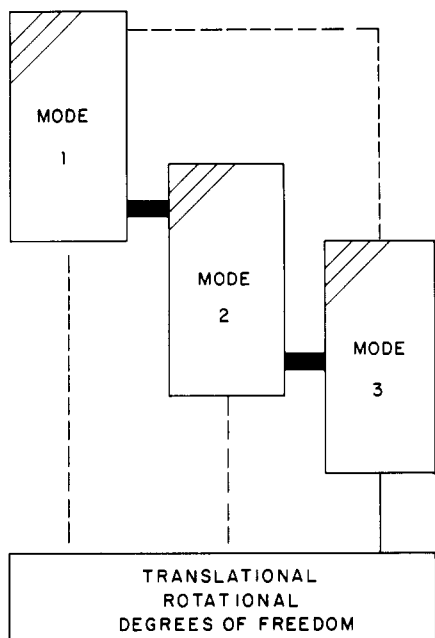
(5) E. Weitz and G. Flynn, *Annu. Rev. Phys. Chem.*, **25**, 275 (1974).

(6) E. Weitz and G. Flynn, *Adv. Chem. Phys.*, **47**, 185-235 (1981).

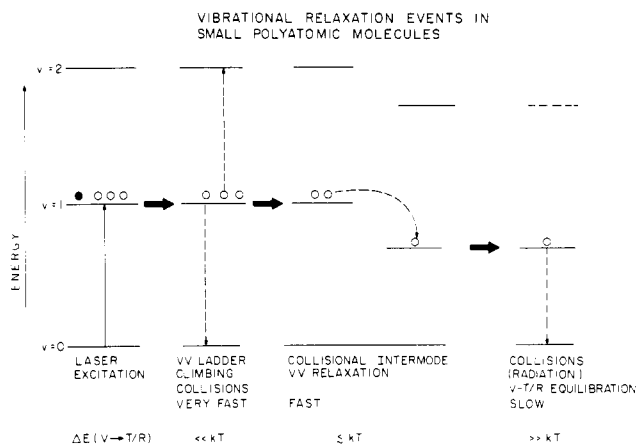
(7) See, for example, J. T. Yardley, "Introduction to Molecular Energy Transfer", Academic Press, New York, 1980.

(8) R. S. Sheorey and G. W. Flynn, *J. Chem. Phys.*, **72**, 1175 (1980).

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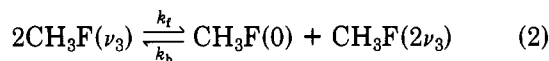
**Figure 1.** Simple block diagram of triatomic molecules. Vibrational energy increases going from the bottom to the top of the figure. Each of the vertical boxes represents one of the vibrational modes of the molecule while the horizontal box represents the translational/rotational energy bath.



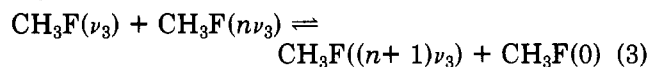
**Figure 2.** Energy flow in a polyatomic molecule can be approximated by a series of sequential steps beginning with excitation on the left. Although all of these events are actually taking place simultaneously, the differential time scales on which they occur allow these processes to be viewed as sequential.

higher levels equilibrate with  $\nu_3$  as shown schematically in Figure 2 via<sup>9</sup>

V-V ladder climbing



Equation 2 is called a vibration-vibration (V-V) ladder-climbing energy-transfer event since it “hikes” energy up the vibrational ladder of the  $\nu_3$  mode. Provided the mode is not too anharmonic, further coupling to higher levels also proceeds rapidly via



Processes such as (2) have been found to reach steady

(9) R. S. Sheorey, R. C. Slater, and G. W. Flynn, *J. Chem. Phys.*, **68**, 1058 (1978).

state in typically 4–30 gas kinetic collisions.<sup>10</sup> These events are so efficient largely because they are nearly “resonant”, requiring almost no exchange of energy between vibrational and translational/rotational degrees of freedom. As a result of these efficient ladder climbing coupling processes, which are ubiquitous for molecules, each mode can be treated as a single reservoir of tightly interacting levels on a time scale greater than  $\sim 4$ –30 gas-phase collisions.

As a consequence of processes 2, 3, . . . the collection of states  $\nu_3, 2\nu_3, \dots, n\nu_3$ , . . ., etc., can be shown to reach a steady-state vibrational distribution characterized by a single nonequilibrium temperature, if the mode is assumed to be harmonic.<sup>11</sup> For a single mode, purely harmonic oscillator of frequency  $\nu_3$  with no initial energy before laser pumping, this “vibrational” temperature  $T_v$  will satisfy the usual relationship

$$m h \nu_3 = \frac{h \nu_3 \exp[-h \nu_3 / k_B T_v]}{1 - \exp[-h \nu_3 / k_B T_v]} \quad (4)$$

where  $m$  is the number of laser photons per molecule of energy  $h \nu_3$  deposited initially in the  $\nu_3$  level and  $h$  and  $k_B$  are the Planck and Boltzmann constants, respectively. Rearranging (4) yields

$$T_v = (h \nu_3 / k_B) / \ln [(m + 1) / m] \quad (5)$$

For  $m = 0.1$ ,  $\nu_3 = 1048 \text{ cm}^{-1}$  and  $T_v \simeq 630 \text{ K}$ , while for  $m = 1.0$ ,  $\nu_3 = 1048 \text{ cm}^{-1}$  and  $T_v \simeq 2175 \text{ K}$ . The population  $N_j$  of successive levels in a given mode thus falls off like

$$N_j / N_{j-1} = \exp[-h \nu_3 / k_B T_v] \quad (6)$$

For relatively low temperature ( $T_v \lesssim (1/3)h \nu_3 / k_B$ ), the population of the lowest level ( $j = 1$ ) will be much larger than that of any higher levels.

Once a particular laser-pumped mode in a molecule reaches steady state, its energy or population will begin to spill over into the other modes as the molecule tries to return to equilibrium. The laser-pumped mode acts as a reservoir from which the other modes are filled by collision processes. Frequently, at least for small rigid molecules, energy transfer from one mode to another (intermode V-V relaxation) is much more efficient than the vibration to translation/rotation (V-T/R) energy-transfer processes which ultimately lead to the complete thermalization among all degrees of freedom. Thus a nonequilibrium steady state can often be established in which the vibrational modes are in equilibrium with each other, but much hotter than the translational/rotational energy reservoir. For polyatomic molecules the vibrational modes cannot be described by a single vibrational temperature even after they equilibrate with each other.<sup>12–15</sup>

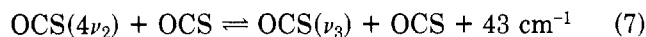
(10) Although the forward step in (2) is nonlinear in the number density  $N_{\nu_3}$  of level  $\nu_3$ , in the limit where  $N_{\nu_3} \ll N_0$  the back step dominates in the observed energy-transfer rate and level  $2\nu_3$  rises exponentially to its steady-state value with a rate  $\gamma \sim N_0 k_b$ . Obviously, in the nonlinear limit  $2\nu_3$  will grow even more rapidly. See, for example, K. R. Casleton and G. W. Flynn, *J. Chem. Phys.*, **67**, 3133 (1977).

(11) J. D. Teare, Seventh AGARD Colloquium, Oslo, 1966; J. D. Teare, R. L. Taylor, and R. L. Von Rosenberg, *Nature (London)*, **255**, 240 (1970); C. E. Treanor, J. W. Rich, and R. G. Rehm, *J. Chem. Phys.*, **48**, 1798 (1968).

(12) W. D. Breshears and L. S. Blair, *J. Chem. Phys.*, **59**, 5824 (1973); W. D. Breshears, *Chem. Phys. Lett.*, **20**, 429 (1973).

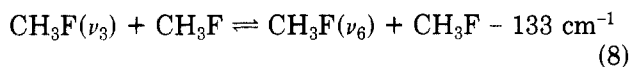
(13) I. Shamah and G. Flynn, *J. Am. Chem. Soc.*, **99**, 3191 (1977); *J. Chem. Phys.*, **69**, 2474 (1978).

Why is the energy transfer between two modes frequently dominated by a single channel? In small "stiff" molecules where the characteristic mode frequencies are typically  $\geq 500 \text{ cm}^{-1}$ , the kinetics of population transfer tend to be dominated by the lowest levels in a given mode at low to moderate temperatures. This is due to the relatively large population in these levels which is guaranteed by the single vibrational temperature Boltzmann "like" distribution arising from the ladder climbing events 2,3. A good rule of thumb is that energy or population cross over between two modes will occur through the levels having the most population, provided only that there are no other constraints preventing transfer between these two levels. Other constraints can exist, however, and will alter the preferred relaxation pathways. Most of the other constraints are "dynamic" ones which limit the efficiency of a given collisional transfer event. These "dynamic" constraints usually favor energy-transfer pathways which minimize both the change in the number of vibrational quanta and the amount of energy which must be released to or taken up from the translational/rotational degrees of freedom.<sup>16-18</sup> As an example, intermode energy transfer between the  $\nu_2(520 \text{ cm}^{-1})$  bending mode and the  $\nu_3(2062 \text{ cm}^{-1})$  C-O stretching mode of OCS appears to be dominated by the channel<sup>19-23</sup>



where  $43 \text{ cm}^{-1}$  is the amount of vibrational energy which must be transferred into translational/rotational degrees of freedom to effect (7). Although the levels  $3\nu_2$ ,  $2\nu_2$ ,  $\nu_2$  have much greater population than  $4\nu_2$  in laser-pumped OCS, (7) dominates because transfer from  $3\nu_2$ ,  $2\nu_2$ ,  $\nu_2$  would require "borrowing" approximately 500, 1000, or  $1500 \text{ cm}^{-1}$  from the translational/rotational energy bath. Typically, transfers which require much more than  $k_B T$  of energy from this bath (where  $T$  is the translational/rotational temperature) are very inefficient. Although (7) requires the formal exchange of 5 quanta, which is also a relatively forbidden event, mechanical anharmonic mixing of the OCS modes plus strong electrical anharmonicity in the  $\nu_2$  bending mode appear to mediate the effect of this constraint for OCS.<sup>18,21,23</sup>

In contrast, consider energy transfer from the laser-pumped  $\nu_3$  mode of  $\text{CH}_3\text{F}$  to the  $\nu_6$  mode ( $\nu_6 = 1182 \text{ cm}^{-1}$ ) which proceeds efficiently via

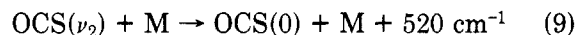


This step requires  $\sim 30$  gas kinetic collisions to reach

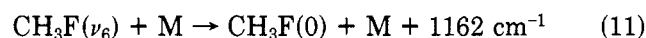
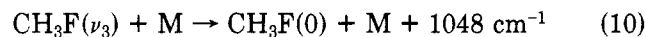
steady state<sup>8</sup> and withdraws  $133 \text{ cm}^{-1}$  of energy from the translational/rotational energy bath. At room temperature,  $k_B T \simeq 200 \text{ cm}^{-1}$ , and the channel represented by (8) has virtually no dynamic constraints since the energy gap is small and the number of quanta exchanged is the minimum for a V-V process. Transfer between  $2\nu_3$  and  $\nu_6$ , on the other hand, would require an exchange of 3 quanta and the release of almost  $900 \text{ cm}^{-1}$  of energy into the translational/rotational bath. In addition, the population of  $2\nu_3$  is much less than that of  $\nu_3$  and transfer from  $\nu_3$  to  $\nu_6$  is overwhelmingly favored on kinetic grounds as well as dynamic ones.

The above examples illustrate the interplay between kinetic and dynamic energy-transfer forces which, for small rigid molecules, frequently lead to the dominance by a single channel of the intermode V-V energy-transfer mechanism coupling two modes.

To complete our simple model, we need only ask why overall vibration-translational/rotation (V-T/R) relaxation usually proceeds via the lowest frequency mode? In fact the *lowest level* of this mode usually dominates V-T/R relaxation for both kinetic and dynamic reasons. It is usually the level with the largest steady-state population and the one which requires for relaxation the release of a minimum amount of vibrational energy into the translational/rotational energy bath in a single step. For example, in OCS V-T/R relaxation proceeds via



and requires an average of 3400 gas kinetic collisions.<sup>23</sup> In  $\text{CH}_3\text{F}$ , competition between the two lowest modes may exist<sup>17</sup>



but has not yet been experimentally documented. While *partial* V-T/R relaxation can and does occur during many V-V processes (see, e.g., eqn 7 and 8), complete V-T/R equilibration ordinarily cannot occur during such events. An exception to this arises for certain cyclic V-V relaxation mechanisms which have been dubbed "catastrophic cyclic paths".<sup>13,15,23</sup> The importance of such paths is unclear at present. Only indirect experimental evidence has been obtained for their existence in OCS<sup>23</sup> and possibly  $\text{COF}_2$ .<sup>24</sup> Figure 2 summarizes schematically the dominant energy-transfer processes which lead to the simple model represented by Figure 1.

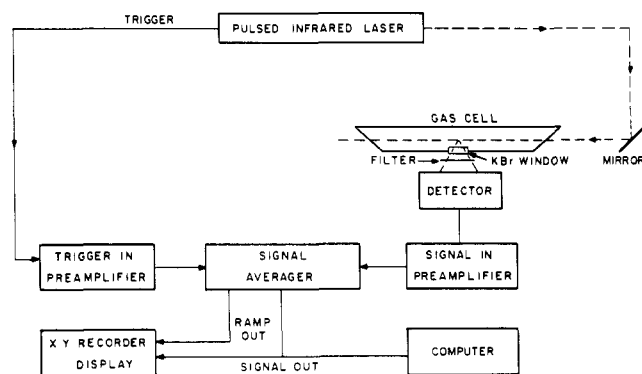
The above model is extremely useful for describing energy-transfer processes in small molecules at low to moderate temperatures. As the temperature rises, many of the relaxation processes which were ignored in formulating this model can become important and must be considered.

### Experimental Methods: "Vibrational Temperature Jump Technique"

Though several techniques are available for studying vibrational-energy transfer in small molecules, the overwhelming majority of data comes from the infrared laser induced fluorescence technique.<sup>1-4</sup> This method has many features in common with the study of fast

(14) S. Mukamel and J. Ross, *J. Chem. Phys.*, **66**, 5235 (1977).  
 (15) A. Ben-Shaul and K. Kompa, *Chem. Phys. Lett.*, **55**, 560 (1978).  
 (16) R. N. Schwartz, Z. I. Slawsky, and K. F. Herzfeld, *J. Chem. Phys.*, **20**, 1591 (1952).  
 (17) J. L. Stretton, *Trans. Faraday Soc.*, **61**, 1053 (1965); F. I. Tanczos, *J. Chem. Phys.*, **25**, 439 (1956).  
 (18) G. W. Flynn, *J. Mol. Struct.*, **59**, 197 (1980); *ACS Symp. Ser.*, **No. 56**, 145 (1977).  
 (19) B. M. Hopkins, A. Baronavski, and H. -L. Chen, *J. Chem. Phys.*, **59**, 836 (1973).  
 (20) J. K. Hancock, D. F. Starr, and W. H. Green, *J. Chem. Phys.*, **61**, 3017 (1974).  
 (21) D. R. Siebert and G. W. Flynn, *J. Chem. Phys.*, **64**, 4973 (1976).  
 (22) K. Hui and T. Cook, *J. Chem. Phys.*, **65**, 3536 (1976).  
 (23) M. Mandich and G. W. Flynn, *J. Chem. Phys.*, **73**, 1265, 3679 (1980).

(24) R. Bohn, K. Casleton, Y. V. C. Rao, and G. W. Flynn, unpublished results.



**Figure 3.** Typical laser-induced infrared fluorescence apparatus. Laser pulse energies are in the 0.1–5-mJ range with repetition rates of 100–200 Hz and typical pulse widths of  $10^{-6}$  s.

chemical reaction processes in solution using the temperature-jump technique.<sup>25,26</sup> In essence a system at equilibrium is subject to a sudden, but relatively weak, perturbation. The return to equilibrium is then followed by a probe which does not disturb the system. In the study of vibrational relaxation via the laser fluorescence method, a short pulse of infrared laser radiation acts as the perturbation by pumping molecules from one vibrational state to another, thus upsetting the equilibrium population distribution. The return of this distribution to its equilibrium value is then followed by observing changes in the intensity of spontaneous infrared emission from the sample following the laser pulse. The intensity of infrared emission,  $I_{i0}$ , from a given vibrational state  $i$  to (for example) the ground state is directly related to the population density (concentration)  $N_i$  of that level

$$I_{i0} \sim A_{i0}N_i$$

where  $A_{i0}$  is the Einstein  $A$  coefficient (spontaneous emission rate) between level  $i$  and the ground state. Thus time-dependent changes in  $I_{i0}$  reflect accurately changes in the concentrations  $N_i$ . Provided the initial perturbation is weak enough, the return of the population distribution to equilibrium can be described by a set of *linear* coupled differential equations. In principle the kinetic rate constants can then be extracted from an analysis of the fluorescence growth and decay curves.

One of the key differences between ordinary T-jump and laser-induced fluorescence methods is that the laser excitation initially provides a (vibrational) temperature jump for only a *single pair of vibrational states* of a molecule while the ordinary T-jump produces a uniform temperature change for all degrees of freedom in a chemically reacting system. This difference allows us to study intermode energy transfer from an initially hot to an initially cold vibrational state.

A typical infrared fluorescence apparatus is shown in Figure 3. The laser is frequently of the  $\text{CO}_2$  Q-switched variety which provides output pulses of  $\sim 1$  mJ energy in a  $10^{-6}$  s time interval over the wavelength range 9.2–10.6  $\mu\text{m}$  (discretely tunable in  $\sim 2\text{-cm}^{-1}$  steps). The repetition rate of the laser is about 200 pulses/s, which provides for good signal averaging characteristics. The gas sample cell is usually stainless steel or brass,

with entrance and exit windows that transmit the laser. Typical sample pressures range from 0.1 to 100 torr. A fluorescence window is mounted on the side of the cell to observe spontaneous emission at  $90^\circ$  to the direction of laser propagation. Wavelength selection of the emission light is accomplished with a large-area IR interference filter having a bandwidth ranging from 0.2 to 2  $\mu\text{m}$ . Monochromators are ordinarily not used due to the weakness of the emission.

Because of the relatively low resolution of the interference filters, single vibration-rotation states cannot be monitored. Generally, fluorescence emission emanating from an entire vibrational band associated with one mode is collected at the same time. Because rotational relaxation within a given vibrational state is very fast, only rotationally averaged energy-transfer processes are monitored. An infrared detector, commonly cooled to 77 K, having a risetime of  $\sim 10^{-6}$  s is used to detect the fluorescence which passes through the interference filter. Detector signals are preamplified and fed to a high-speed signal averaging device which is triggered by a pulse derived from the laser. Typically the fluorescence obtained from 15 000–100 000 laser shots is averaged to obtain good signal/noise characteristics. Averaged data can be transferred to a chart recorder or directly to a computer where the fluorescence growth and decay curves are usually analyzed as a sum of exponentials.

The change in spontaneous emission observed from a given state or mode of a molecule following laser excitation in such an apparatus is directly proportional to the change in the number of molecules in that state viewed by the detector. Thus the rate of change of this fluorescence is sensitive to the energy-transfer processes which cause population to flow from one mode to another. A typical fluorescence curve might have the form

$$I \sim (e^{-\gamma_1 t} - e^{-\gamma_2 t}) \quad (12)$$

where  $I$  is the fluorescence intensity,  $t$  is the time since laser excitation,  $\gamma_2$  is a characteristic rate constant describing the growth of fluorescence (and hence population), and  $\gamma_1$  is a characteristic rate constant describing fluorescence decay. For collisional energy-transfer processes,  $\gamma_1$  and  $\gamma_2$  will depend linearly on pressure so that a plot of  $\gamma_i$  vs. pressure yields an overall energy-transfer rate which can be compared to the hard-sphere gas kinetic rate (typically  $10^7 \text{ s}^{-1} \text{ torr}^{-1}$  near 300 K). The interpretation of the  $\gamma$ 's and their relationship to microscopic energy-transfer processes require the solution of a detailed set of rate equations.

### Kinetic Rate Matrices and Kinetic Modeling

Provided weak laser excitation is employed, the rate of change of the population deviations  $n_i$  of each molecular vibrational state will be linearly related to the deviations  $n_i$  themselves according to the relationship

$$\dot{\mathbf{n}} = \mathbf{A} \cdot \mathbf{n} \quad (13)$$

where  $\mathbf{n} = (n_1, n_2, \dots)$  is a vector formed of the individual population deviations  $n_i$ ,  $\dot{\mathbf{n}}$  is the corresponding vector formed from the time derivatives of the  $n_i$ , and  $\mathbf{A}$  is a matrix of *constant* coefficients. It is precisely the entries in the matrix  $\mathbf{A}$  which are the microscopic kinetic energy transfer rate constants of interest. In the absence of degenerate eigenvalues,  $\gamma_j$ , for  $\mathbf{A}$ , the solution to the set of differential equations (eq 13) is of the form

(25) M. Eigen and L. De Maeyer, *Tech. Org. Chem.*, 8 (2), 895 (1961).

(26) G. Flynn and N. Sutin in "Chemical Applications of Lasers", C. B. Moore, Ed., Academic Press, New York, 1974, p 310.

$$n_i = \sum_j (c_{ji} \exp[-\gamma_j t]) \quad (14)$$

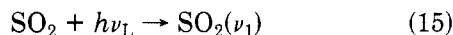
where  $t$  is the time since the laser pulse. The constants  $c_{ji}$  and  $\gamma_j$ , which depend linearly on pressure in the weak laser excitation limit, are in general complex combinations of the kinetic rate constants which enter **A**. Each population deviation is thus a sum of exponential terms. As noted in the introduction, for a system of  $n$  levels,  $n(n-1)/2$  independent  $\gamma$ 's are required to fully describe each population deviation. Fortunately, for many molecules only two or three of the amplitudes  $c_{ji}$  are large enough to observe for a given state, and the analysis of a given  $n_i$  becomes experimentally tractable. Nevertheless, a major difficulty in present studies of vibrational energy transfer via the laser fluorescence technique is obtaining the rate constants from the experimental values of  $c_{ji}$  and  $\gamma_j$ .

Ordinarily, the rate constants for the microscopic energy-transfer processes which enter the differential equation 13 are obtained by choosing trial values for the constants and then computing from these the observed rates  $\gamma_j$  and amplitudes  $c_{ji}$  until the best fit is obtained. In the past few years several experimental "tricks" have been developed<sup>6,27-29</sup> which are capable in some cases of providing enormous simplification in this modeling or inversion process. These techniques are all sensitive to the dominant energy-transfer pathways in the molecule and essentially tell us which entries in the matrix **A** are most important and which can be ignored.

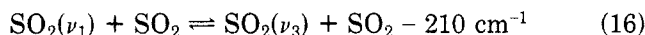
### Results for Some Simple Molecules

Sulfur dioxide is one of the simplest polyatomic molecules in which vibrational energy transfer has been studied, yet it is unique. Even before the advent of laser fluorescence techniques, SO<sub>2</sub> was known to have a slow intermode vibrational-energy exchange rate from ultrasound studies.<sup>30</sup> The combination of laser fluorescence<sup>31</sup> and ultrasound work has established the dominant energy-transfer processes for SO<sub>2</sub>. These can be represented by

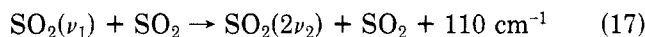
excitation



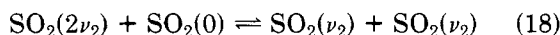
V-V relax



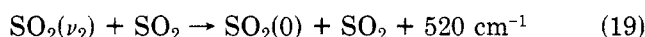
V-V relax



inverse ladder climbing



V-T/R relax



In pure SO<sub>2</sub> at room temperature, step 16, which is

(27) J. M. Preses, E. Weitz, and G. W. Flynn, *J. Chem. Phys.*, **69**, 2782 (1978).

(28) R. E. McNair, S. F. Fulghum, G. W. Flynn, M. S. Feld, and B. J. Feldman, *Chem. Phys. Lett.*, **48**, 241 (1977).

(29) V. A. Apkarian and E. Weitz, *J. Chem. Phys.*, **71**, 4349 (1975).

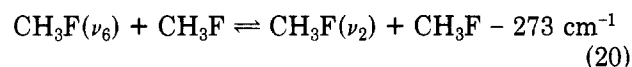
(30) J. D. Lambert, D. G. Parks-Smith, and J. L. Stretton, *Trans. Faraday Soc.*, **66**, 2720 (1970).

(31) D. R. Siebert and G. W. Flynn, *J. Chem. Phys.*, **62**, 1212 (1975).

translationally/rotationally endothermic, requires  $\sim 135$  collisions to reach steady state while step 17 requires  $\sim 2600$  collisions. The rate for (18) has not been measured but is presumed to be very fast (5-50 collisions). The overall V-T/R relaxation (step 19) requires 250 collisions. Thus in SO<sub>2</sub> the  $\nu_1$ ,  $\nu_3$  stretching modes equilibrate rapidly with each other but only slowly with the bending mode  $\nu_2$ , and V-T/R relaxation is actually faster than this last intermode V-V process (a rare occurrence). The slow rate for  $\nu_1 \rightarrow 2\nu_2$  transfer, which requires the exchange of only  $110 \text{ cm}^{-1}$  of energy with the translational/rotational degrees of freedom, is presumed to be slow due to the exchange of 3 vibrational quanta during the collision and the weak anharmonic mixing of  $2\nu_2$  with  $\nu_1$  or  $\nu_2$ .<sup>18</sup>

The energy-transfer processes coupling the four lowest vibrational states ( $\nu_3$ ,  $2\nu_3$ ,  $\nu_6$ , and  $\nu_2$ ) of CH<sub>3</sub>F are now well established.<sup>5-9</sup> They are represented by eqn 1, 2, 8, 10, and

endothermic intermode V-V



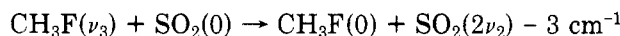
While in principle 10 kinetic rate constants are necessary to describe fully the coupling of the levels  $\nu_3$ ,  $2\nu_3$ ,  $\nu_6$ ,  $\nu_2$ , and the ground state, the energy-transfer mechanism is in fact dominated by just the 4 processes 2, 8, 10, 20 which illustrate extremely well the simple picture of Figure 1. In pure CH<sub>3</sub>F equilibration of  $2\nu_3$  and  $\nu_3$  requires approximately 4 collisions while the intermode spillover steps require 30 ( $\nu_3 \rightarrow \nu_6$ ) and 120 ( $\nu_6 \rightarrow \nu_2$ ) collisions, respectively, to reach steady state. Overall equilibration of the vibrational and translational/rotational degrees of freedom (eq 10) requires nearly 15 000 collisions.

Thus CH<sub>3</sub>F is a virtually perfect example of a molecule which shows very rapid ladder-climbing equilibration of a pumped mode, rapid spillover into adjacent modes, and very slow V-T/R relaxation. The vibrational modes reach a metastable ("hot") steady state in about 125 collisions which then lasts for 15 000 collisions before cooling off. The vibrational-energy distribution for this metastable state is quite fascinating. If we define the vibrational temperatures  $T_i$  for the modes  $\nu_3$ ,  $\nu_6$ ,  $\nu_2$  by

$$kT_i = -h\nu_i / \ln(N_i/N_0)$$

where  $N_i$  is the population density of the  $\nu = 1$  level of mode  $i$  with frequency  $\nu_i$  and  $N_0$  is the population density of the ground state, it is a simple matter to show  $T_3 > T_6 > T_2$  for the metastable state.<sup>13,28</sup> In fact, depending on the conditions,  $T_3$  can become very large compared to  $T_6$  and  $T_2$ . Thus the metastable steady state established by V-V energy transfer is a multi-temperature "object".

Energy transfer between the vibrational modes of SO<sub>2</sub> and CH<sub>3</sub>F is complex due to the large number of levels. However, one aspect of the energy exchange in this mixed system is unique and illustrates the propensity rules alluded to in the introduction.<sup>18</sup> The nearly resonant energy-transfer step



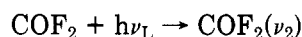
has been found to be undetectable experimentally while processes such as



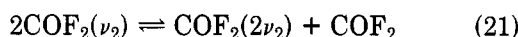
are very rapid ( $\sim 30$  collisions).<sup>32</sup> Again this illustrates the low probability of exchanging two bending quanta of  $\text{SO}_2$  energy for one quantum of any other mode even when essentially an exact resonance or energy match is provided. The situation here is analogous to the energy exchange between  $\nu_1$  and  $2\nu_2$  of pure  $\text{SO}_2$  represented by eqn 17. The  $\text{SO}_2$ ,  $2\nu_2$  state appears to be singular in this behavior, probably because of its weak anharmonic coupling to  $\nu_1$  and  $\nu_2$ . (The transition  $0 \rightarrow 2\nu_2$  is as yet spectroscopically unobserved). There is strong evidence in OCS,  $\text{COF}_2$ , and  $\text{CH}_3\text{F}$  that multiple vibrational quanta exchanges do occur readily when significant mechanical and/or electrical anharmonicities are present in a molecule.

Carbonyl fluoride is a molecule under active investigation at the present time.<sup>24</sup> Nevertheless, the coupling between the  $\nu_2$  (symmetric C-F stretch) and  $\nu_1$  (C=O stretch) has been established.<sup>33</sup> The excitation/relaxation mechanism is

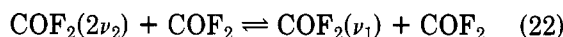
excitation



V-V ladder climbing



intermode V-V



The levels  $2\nu_2$  and  $\nu_1$  are strongly mixed by Fermi interactions and hence the two steps (21) and (22) cannot be distinguished. The overall time required for these processes to reach steady state is 30 gas kinetic collisions. While energy-transfer rates to the remaining modes have not yet been fully mapped, the  $\nu_1$ ,  $2\nu_2$ ,  $\nu_2$  levels do require about 500 gas kinetic collisions to relax into the rest of the vibrational manifold.<sup>33</sup> Thus the  $\nu_1$  and  $\nu_2$  modes form a vibrationally hot, coupled pair on a time scale corresponding to 30–500 collisions after laser excitation.

### A Vibrational Energy Transfer Map for OCS

Data for OCS are now sufficiently detailed that a nearly complete map describing the flow of vibrational energy in this molecule can be developed.<sup>19–22</sup> The excitation/relaxation processes are shown schematically in Figure 4. Because of large electrical anharmonicity in the  $\nu_2$  bending mode, optical excitation of the overtone occurs with about the same probability as for the fundamental for OCS. The rate for the  $\nu_2$  ladder climbing process has not been directly measured but is very fast (10–30 collisions). In pure OCS at room temperature, spillover into  $\nu_3$  from  $4\nu_2$  requires approximately 680 collisions while spillover from  $2\nu_2$  to  $\nu_1$  requires approximately 2400 collisions. Overall equilibration of the vibrational and translational/rotational degrees of freedom occurs through V-T/R relaxation from the lowest level ( $\nu_2$ ) and requires approximately 3400 collisions in pure OCS. Rates and cross sections for these energy-transfer steps in OCS/rare gas collisions have

(32) R. C. Slater and G. W. Flynn, *J. Chem. Phys.*, **65**, 425 (1976).

(33) K. R. Casleton and G. W. Flynn, *J. Chem. Phys.*, **67**, 3133 (1977).

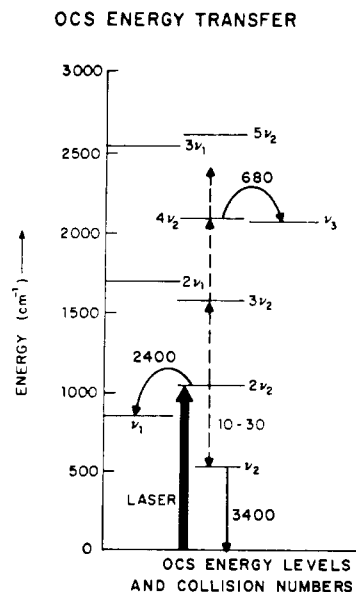


Figure 4. Energy flow map for the molecule OCS. The laser excites the overtone  $2\nu_2$  of the bending mode.

also been obtained. In general, except for helium, the energy-transfer rates for the rare gases are smaller than for pure OCS.

The energy-transfer map for OCS illustrates some remarkable features of vibrational relaxation in small molecules. First, it appears to violate the rule of thumb that multiple quantum exchanges are unfavorable<sup>18</sup> since 4 quanta of  $\nu_2$  are exchanged for one of  $\nu_3$  and 2 quanta of  $\nu_2$  are exchanged for one of  $\nu_1$ . However, there are well-known mechanical anharmonic mixing effects involving the  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  modes, as well as large electrical anharmonicity in the bending mode  $\nu_2$ , which mitigate the rule against the change of multiple quanta during a collision process.<sup>21,22</sup> In addition, these rates are in fact relatively slow for intermode energy-exchange processes, and this is surely related to the requirement that many quanta must change in these steps. Nevertheless, this map illustrates a major feature of our initial simple model (Figure 1): energy exchange between modes is frequently dominated by a single relaxation channel. Thus on the time scales required for intermode energy transfer, only a few microscopic kinetic rate constants are required to describe the time dependence of the population flow. Many of the entries in the collisional A matrix of eq 13 can be set to zero.

### Nonlinear Effects

As already noted, the equations describing relaxation of vibrational populations can be linearized in the limit of weak laser excitation, leading to eq 13 and 14. However, when laser intensity is increased, a regime can be reached where the population deviation of a given level ( $n_i$ ) can be large compared to its pre-laser value,  $N_i^0$ . Under these conditions certain types of energy-transfer processes become nonlinear in the population deviations. An example where such nonlinear effects become important is ladder climbing such as that described by eq 2 for  $\text{CH}_3\text{F}$ . When this process reaches steady state, the relationship among the populations  $N_{\nu_3}$ ,  $N_0$ , and  $N_{2\nu_3}$  for levels  $\nu_3$ , 0, and  $2\nu_3$  is

$$N_0 N_{2\nu_3} = (N_{\nu_3})^2 \quad (23)$$

where the excellent approximation  $k_f = k_b$  has been

made.  $N_i = N_i^0 + n_i$  is the instantaneous total population of level  $i$ . Generally, even when  $n_i > N_i^0$  for excited-state populations, the condition  $n_0 \ll N_0^0$  can be met. Remembering  $N_i = N_i^0 + n_i$  and  $N_0^0 N_{2\nu_3}^0 = (N_{\nu_3}^0)^2$  (equilibrium result) transforms (23) to

$$n_{2\nu_3} \simeq (1/N_0^0) [2N_{\nu_3}^0 n_{\nu_3} + (n_{\nu_3})^2] \quad (24)$$

assuming  $N_0 \simeq N_0^0$ . Equation 24 shows immediately that for  $n_{\nu_3} \ll N_{\nu_3}^0$ ,  $n_{2\nu_3}$  responds linearly to  $n_{\nu_3}$ ; however, when  $n_{\nu_3} \gg N_{\nu_3}^0$ , the population deviation  $n_{2\nu_3}$  is proportional to the *square* of  $n_{\nu_3}$ !

Suppose now that level  $\nu_3$  is undergoing *slow* V-T/R relaxation such as that described by eq 10. In such a case  $n_{\nu_3}$  will be decaying at a rate  $\gamma_{V-T/R}$ , and its time dependence will be to an excellent approximation

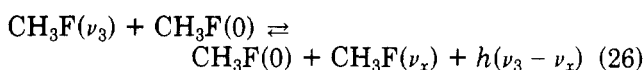
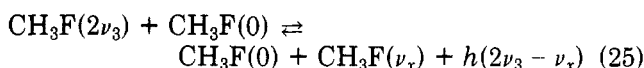
$$n_{\nu_3} \sim e^{-\gamma_{V-T/R} t}$$

Thus in the *linear* limit  $n_{2\nu_3}$  will appear to decay at the same rate as  $n_{\nu_3}$ ,  $\gamma_{V-T/R}$ , but in the *nonlinear* regime ( $n_{\nu_3} \gg N_{\nu_3}^0$ )

$$n_{2\nu_3} \sim (n_{\nu_3})^2 \sim e^{-2\gamma_{V-T/R} t}$$

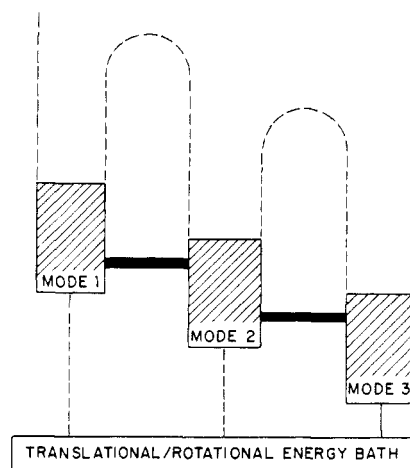
This result provides an extremely simple experimental technique for showing when ladder-climbing events are important in equilibrating two states. Slow decay rates are measured for the *overtone level* under low and high levels of excitation. A doubling of the rate under high excitation indicates the presence of a nonlinear ladder-climbing event in the coupling of two states. Indeed this method was used in studies of  $\text{COF}_2$  to show that the Fermi-mixed set  $\nu_1, 2\nu_2$  is coupled to  $\nu_2$  by just such a mechanism.<sup>10,33</sup>

The above observation is only the tip of an enormously powerful method for determining intermode energy-transfer pathways in small molecules. Suppose, for example, that one wishes to determine whether a second mode  $\nu_x$  couples to the  $\nu_3$  or to the  $2\nu_3$  level of  $\text{CH}_3\text{F}$ . Schematically, the mechanisms might be



Again, assume (25), (26), and the ladder climbing process 2 are all fast compared to overall decay of  $\nu_3$  at the slow rate  $\gamma_{V-T/R}$ . If the measured rate of decay of  $\nu_x$  is the same as that for  $\nu_3$  ( $\gamma_{V-T/R}$ ) under *both* weak and strong excitation, mechanism 26 (or some other *linear* coupling of  $\nu_x$  and  $\nu_3$ ) is indicated. On the other hand, if the decay rate doubles (to  $2\gamma_{V-T/R}$ ) under strong excitation, a nonlinear mechanism such as (25) is indicated. For small molecules the number of physically reasonable mechanisms is frequently small enough that a crisp delineation between two possibilities such as (25) and (26) can be made by using this "nonlinear collisional coupling phenomenon".

While there are pitfalls in this method ( $\gamma_{V-T/R}$  itself is a weak function of the level of excitation,  $N_0^0$  must be large compared to  $n_0$ , combination levels also exhibit nonlinearity effects, linear and nonlinear paths may exist simultaneously, etc.), it is an extremely promising technique for studying kinetic mechanisms in vibrationally relaxing systems. So far, however, the method has not been heavily exploited.<sup>33-35</sup>



**Figure 5.** Vibrational energy transfer model applicable to small molecules which have been highly excited or large molecules with moderate levels of excitation. Vibrational energy increases going from the bottom to the top of the figure. The blending of vibrational modes at higher energies (top of the figure) is brought about by mechanical anharmonicities which cause the usual normal mode picture to break down.

### A More Complex Model for Vibrational Energy Transfer

The model which we have used so far treats each of the vibrational modes of a polyatomic molecule as a distinct entity. For small molecules at low to moderate levels of excitation, this is a reasonable assumption except in special cases such as the  $\nu_1$  and  $2\nu_2$  Fermi mixed levels in  $\text{COF}_2$  which were described earlier. Nevertheless, for strongly excited small molecules or only moderately excited large molecules, vibrationally excited molecules begin to occupy energy levels where significant anharmonic coupling takes place, thus blurring the normal mode character of the levels. Figure 5 shows a simple model which can be used to describe vibrational energy transfer for such systems.

The molecule is thought of as a water bucket with fingers (modes) that protrude from its bottom. If water (energy or population) is placed in one of the fingers (modes) but kept at a level below the main (common) body of the bucket, it can only flow into one of the other fingers via the capillary coupling tubes (horizontal bars) which directly connect the fingers. These tubes (bars) represent the relatively slow *collisional* energy-transfer mechanisms which couple the distinct low energy quantum states of one mode to another. On the other hand, if sufficient water (energy) is placed in a finger (mode) to reach the upper common body of the bucket, the water (energy) immediately spills into the other fingers or modes without the necessity of proceeding through the capillary coupling tubes (collisional energy-transfer channels). Thus for highly excited molecules where strong anharmonic coupling is present, rapid *collision free* energy transfer is expected to occur and compete successfully with the collisional coupling which exists among the distinct low-lying levels.

Obviously, the degree to which the low-energy or high-energy channels will dominate the energy-transfer mechanism depends critically on the degree of mode mixing and the level of vibrational excitation in a given

(34) J. M. Preses, "Vibrational Energy Flow in  $\text{CH}_3\text{F}$ ", Ph.D. Thesis, Columbia University, Department of Chemistry, 1975.

(35) G. W. Flynn, unpublished notes.



molecule. Experiments employing UV/visible laser-induced fluorescence to probe the vibrational populations of molecules pumped by powerful CO<sub>2</sub> TEA lasers (megawatt power levels) have recently been reported.<sup>36-40</sup> The preliminary results suggest, as expected, that energy transfer in highly excited molecules is quite fast; nevertheless, the detailed competition between various energy-transfer pathways has not yet been mapped out. Future experiments are expected to unravel more completely many of the features of vibrational-energy transfer in complex, highly excited molecules. In principle this same technique, which has inherently much higher resolution than infrared laser fluorescence methods, can also be used to measure energy-transfer rates from a specific vibration-rotation level  $|v,J\rangle$  of one mode to a specific vibration-rotation level  $|v',J'\rangle$  of a second mode.

### Concluding Remarks

Sufficient vibrational energy transfer data have now been obtained to provide a relatively simple picture of intermode vibrational energy flow processes in small,

(36) D. M. Brenner and K. Brezinsky, *Chem. Phys. Lett.*, **67**, 36 (1979).

(37) D. M. Brenner, K. Brezinsky, and P. M. Curtis, *Chem. Phys. Lett.*, **72**, 202 (1980).

(38) D. M. Brenner, *J. Chem. Phys.*, to be published.

(39) D. M. Brenner, *J. Chem. Phys.*, to be published.

(40) D. M. Brenner, *J. Chem. Phys.*, to be published.

weakly excited molecules. Energy transfer within a given mode is very rapid due to collisional ladder climbing processes which bring the mode into a nonequilibrium steady state. Spillover of energy from one mode to another is usually dominated by a single energy-transfer channel between distinct low-lying vibrational states of the different modes. Channels which minimize the amount of vibrational energy released to or taken from the translational/rotational energy bath and which minimize the number of vibrational quanta exchanged in the energy-transfer process tend to be favored. Anharmonic mixing of levels increases significantly the probability of energy transfer between states which formally require the exchange of more than two vibrational quanta to proceed. Much experimental work remains to be done before the complex energy-transfer pathways of strongly excited small molecules or even weakly excited large molecules in their ground electronic state can be unravelled.

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## A Systematic Look at Weakly Bound Diatomics

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A little more than 100 years ago, Johannes van der Waals proposed his celebrated equation of state for a real gas.<sup>1</sup> This equation incorporated two parameters to represent the macroscopic effects of intermolecular repulsions (molecular size) and intermolecular attractions. Comparisons among these parameters constituted one of the first systematic attempts to organize, interpret, and understand variations in weak intermolecular bonding from molecule to molecule.

What should one expect to learn from weak bonding? By ordinary chemical standards, such bonds are ridiculously weak. As a consequence, most of chemical thought is organized around an understanding of strong chemical forces. Terms such as covalent bond, donor-acceptor bond, hydrogen bond, charge delocalization, and the like conjure specific models with a host of

well-understood consequences. Weakly bound molecules have historically not been thought of in these terms, but it is not at all obvious where one draws (or even if one should draw) the line separating molecules into categories based on bond energies.

Nevertheless, weakly bound molecules have a well-defined set of bound quantum levels which can be analyzed by methods familiar to the realm of stable chemical compounds. Can such analyses expose the origins of weak bonding in greater detail? Can weak bonding be described *without* recourse to the terminology of chemical bonding, or are there clear examples of molecules for which this language is *essential*, despite the weakness of the interaction? In this account we discuss recent attempts to answer these and related questions.

### Families of Weakly Bound Diatomics

A cursory glance through the periodic table leads one to predict most of the weakly bound homonuclear dia-

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(1) J. D. van der Waals, "Over de continuïteit van den gas- en vloeistooftoestand," Thesis, Leiden, 1873. An interesting account of van der Waals' early work is given by M. J. Klein, *Physica*, **73**, 28 (1974).