Molecular Relaxation

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Gas-phase molecular relaxation processes are reviewed with particular emphasis on recent results for the lower energy processes. New experiments have led to significant advances in understanding vibration-vibration ($V \rightarrow V$) and rotation-rotation ($R \rightarrow R$) energy transfer. Both of these processes are inaccessible to the conventional techniques of measuring heat capacities of an initially compressed or rarified gas. Spectroscopic techniques involving laser excitation and fluorescent observation are being applied to studies of $V \rightarrow V$ processes. Infrared–microwave and microwave–microwave double resonance techniques are being applied to studies of $R \rightarrow R$ relaxation processes. The recent results are discussed in terms of models of interaction for a binary collision.

I. Introduction

Thermal or Boltzmann equilibrium is defined for a large number of molecules by expressing the relative populations in various energy levels as a function of temperature. The number of molecules in level i, n_i, is given by

$$n_i = N g_i e^{-\epsilon_i/kT} \tag{1}$$

where N is the total number of molecules within a closed system, g_i is the degeneracy of the ith energy level with energy ϵ_i, and T is the temperature of the vessel containing the closed system of molecules. The energy of the ith level is normally written as a sum of internal energies corresponding to the electronic, ϵ_i^E, vibrational, ϵ_i^V, rotational, ϵ_i^R, and translational, ϵ_i^T, energies.

$$\epsilon_i = \epsilon_i^E + \epsilon_i^V + \epsilon_i^R + \epsilon_i^T \tag{2}$$

Substituting into eq 1 gives

$$n_i = N g_i e^{-\epsilon_i^E/kT} e^{-\epsilon_i^V/kT} e^{-\epsilon_i^R/kT} e^{-\epsilon_i^T/kT} \tag{3}$$

where g_i is now a product of the degeneracies for the four internal degrees of freedom. Thus, when the Hamiltonian for a molecule is separable into translational, T, rotational, R, vibrational, V, and electronic, E, degrees of freedom and when the separation of energies as in eq 2 is meaningful, we may define a temperature for each of the internal degrees of freedom. If the electronic thermal equilibrium is disturbed, the other degrees of freedom may still maintain thermal equilibrium.

Given this liberty, we can rewrite eq 1 for each set of levels.

Electronic: $n_i^E = N g_i^E e^{\epsilon_i^E/kT^E}$

Vibration: $n_i^V = N g_i^V e^{-\epsilon_i^V/kT^V}$

Rotation: $n_i^R = N g_i^R e^{-\epsilon_i^R/kT^R}$ $\tag{4}$

Translation: $n_i^T = N g_i^T e^{-\epsilon_i^T/kT^T}$

where T^E, T^V, T^R, and T^T define the internal temperatures and T is the vessel temperature. Of course, true thermal equilibrium is attained only when $T^E = T^V = T^R = T^T = T$ and eq 1 and 3 are satisfied. However, it is meaningful to discuss equilibrium and temperature within any of the internal degrees of freedom relative to the other degrees of freedom and relative to the vessel temperature.

In this paper we will discuss the relative thermal disturbance and the rate of return to thermal equilibrium in a system of molecules. We are interested specifically in (1) the rate of equilibration within each of the internal degrees of freedom (E $\rightarrow$ E, V $\rightarrow$ V, R $\rightarrow$ R, and T $\rightarrow$ T) and (2) equilibration between two or more degrees of freedom (V $\rightarrow$ R, V $\rightarrow$ T, R $\rightarrow$ T, and other combinations).

The rate of equilibration between the internal degrees of freedom and the ambient temperature of the containing vessel will not be considered here. We will also confine the discussion to the gas phase where the dominant process is caused by binary collisions.

Interest in molecular relaxation phenomena has arisen in studies of gas kinetics and transport properties,[2a] laser applications specifically in producing population inversions for amplifying electromagnetic energy,[2b] chemical kinetics where each binary molecular collision is an incipient chemical reaction,[3] and chemical kinetics involving highly excited (vibrational) reaction products.[4] In the latter case, it is important to know whether the molecule can relax vibrationally to produce a stable product before it crosses over to an unstable potential surface causing decomposition.

The classical kinetic theory of gases is the starting point of any discussion of collisional relaxation processes. The classical theory considers each molecule as a hard sphere with a radius equal to some combination of bond lengths. For instance, the benzene mole-

(1) Alfred P. Sloan Fellow.

(2) (a) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954; (b) B. A. Lengyl, "Introduction to Laser Physics," John Wiley and Sons, Inc., New York, N. Y., 1966.

(3) R. A. Marcus, *J. Chem. Phys.*, **45**, 4493, 4500 (1966); R. J. Suplinskas and J. Ross, *ibid.*, **47**, 321 (1967).

(4) J. R. Airey, R. R. Getty, J. C. Polanyi, and D. R. Snelling, *ibid.*, **41**, 3255 (1964); F. J. Fletcher, B. S. Rabinovitch, R. W. Watkins, and D. J. Locker, *J. Phys. Chem.*, **70**, 2823 (1966).

cule has an approximate hard-sphere radius of 2×10^{-8} cm. The average speed of benzene at $T \simeq 300°K$ is $v \simeq 2.7 \times 10^4$ cm/sec. The mean free path or mean distance between collisions at standard conditions (1 atm pressure) is $\lambda \simeq 3 \times 10^{-5}$ cm. Therefore, the average period between collisions at standard conditions is $\tau = \lambda/v \simeq 10^{-9}$ sec. As the translational energy levels are a near continuum, each binary collision will lead to a change in translational energy which will maintain or drive the molecules toward translational equilibrium. Thus, T → T transfer will occur very fast, on the order of 10^{-9} sec for benzene at standard conditions.

The relaxation times mentioned in the following sections will be at standard conditions and it is convenient to think of rates relative to the classical kinetic collisions. Relaxations other than T → T will occur at different rates due to the different mechanisms of transferring energy. For instance, V → T transfer in most molecules will not occur for every kinetic collision but may occur within the broad range of once every $10-10^{10}$ collisions. The number of collisions necessary to produce the desired relaxation is normally given by the product of the relaxation time times the number of hard-sphere kinetic collisions per second.

II. Electronic Excitation and E → E Transfer of Energy

Molecules can be produced in their excited electronic states by thermal excitation, electromagnetic excitation, or as products of chemical reactions.

Relaxation from excited electronic states is primarily by spontaneous emission which is a pure intramolecular process. The decay of molecules in the excited state is given by the simple first-order rate law.

$$\frac{dn}{dt} = -nk$$

$$\frac{n_{initial}}{n_{final}} = e^{+kt}$$

(5)

The characteristic relaxation time, τ, for the system initially in the excited state is the value of $1/k$ where $n_i/n_f = e$. The probability per unit time (or rate constant) for spontaneous emission from an excited state to a ground state where the allowed electric dipole mechanism is operative is

$$P_{1\to0} = \frac{32\pi^3 D_{01}{}^2 \nu_{01}{}^3}{3c^3\hbar}$$

(6)

where D_{01} is the electric dipole moment matrix element between states 0 and 1. $\nu_{01} = (E_1 - E_0)/h$, c is the speed of light, and $\hbar$ is Planck's constant (h) divided by 2π. D_{01} is a product of the electronic transition dipole moment times the overlap between the vibrational functions (Franck–Condon factor) participating in the transition. In any event, D_{01} will be on the order of 1 D or less and typical electronic energy spacings are $E_1 - E_0 \simeq 5.0$ eV or $\nu_{01} \simeq 12 \times 10^{14}$ Hz. Substituting

into eq 6 gives

$$P_{1\to0} \simeq 5.2 \times 10^6 \text{ sec}^{-1}$$

or the relaxation time of

$$\frac{1}{P_{1\to0}} \simeq \tau_{10} \simeq 1.9 \times 10^{-7} \text{ sec}$$

(7)

At this short relaxation time, the molecule can emit the radiation and returns to the ground state before colliding with another molecule. Quenching or nonradiative deactivation of the excited state occurs when the collisional relaxation mechanism competes in time with the rate of spontaneous emission. The rate of spontaneous emission is decreased if D_{10} is small or zero.

The necessity for spin conversion can increase the radiative lifetime. The triplet → singlet $B^3\pi_{0}{}^+{}_{u} \to X^1\Sigma_{0}{}^+{}_{g}$ fluorescence in I_2 has been extensively studied under a variety of conditions.[5] The transition is electric dipole in origin and the energy separation is approximately 2 eV. Initial excitation of a single electronic–vibration–rotation level is effected by a monochromatic source such as from Hg or Na line emission. The transition matrix element in I_2 is reduced by the weakly allowed singlet–triplet transition[6] to yield a spontaneous emission lifetime of 7.2×10^{-7} sec.[7]

If D_{10} is zero, other mechanisms of spontaneous emission will be evident such as the magnetic dipole or electric quadrupole transitions. The radiative lifetimes will be quite long, however; $\tau = 1.7 \times 10^{-4}$ sec for the magnetic dipole $a^1\pi_g \to X^1\Sigma_g{}^+$ transition in N_2[8] or $\tau = 4 \times 10^4$ sec for the electric quadrupole $a^1\Delta_g \to b^1\Sigma_g{}^+$ transition in O_2.[9] Studies of quenching of the electronic emission (the E → E process) have been given wide attention due to the potential for controlling the path of a photochemical reaction by selecting the electronic states of the reactants.[10,11] For instance, the collision-induced E → E transfer or quenching of the $B^3\pi_{0+u}$ state in I_2 (in the gas phase) apparently proceeds by binary collisions with a mechanism which depends on the product of the I_2 polarizability times the square root of the reduced mass of the collision pair. The resultant electronic states after the quenching are the repulsive or nonbonding molecular states. The location of the repulsive states with respect to the bound states can be determined by a study of the quenching rate in the different vibrational states in I_2.[12] Similar

(5) J. I. Steinfeld and W. Klemperer, *J. Chem. Phys.*, **42**, 3475 (1965), and references cited therein.

(6) J. T. Hougen, *Can. J. Phys.*, **42**, 433 (1964).

(7) L. Brewer, R. A. Berg, and G. M. Rosenblatt, *J. Chem. Phys.*, **38**, 1381 (1963). The emission is observed from the 26th vibrational state of the excited electronic state.

(8) W. Litchen, *ibid.*, **26**, 306 (1957).

(9) J. F. Noxon, *Can. J. Phys.*, **39**, 1110 (1961).

(10) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965.

(11) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966.

(12) J. I. Steinfeld, *J. Chem. Phys.*, **44**, 2740 (1966).

detailed steady-state experiments involving monochromatic electromagnetic excitation and fluorescent observations have been reported for NO[13,14] (the $A_2\Sigma^+$ state has a lifetime of 0.2×10^{-6} sec[15]), OH,[16] and other molecules. Similar results have been reported by pulse electronic excitation.[17,18] Extensive literature in the field of $E \rightarrow E$ energy transfer is available which includes work on larger organic molecules,[10,11,19] primarily in the liquid state.

A considerable amount of work is now available giving information on $E \rightarrow V$ exchange of energy as demonstrated in the quenching of the mercury 6^3P state.[20,21]

$$Hg(6^3P_1) + A_2 \longrightarrow Hg(6^3P_0) + A_2^* \qquad (8)$$
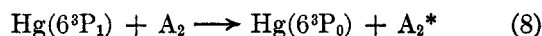
A_2^* is a vibrationally and translationally excited diatomic molecule. No empirical systematics were found in studying the relaxation caused by a large number of diatomic molecules. N_2 and CO produced efficient spin-orbit transfer but other diatomics caused energy transfer to the ground atomic electronic state.

III. Vibrational Excitation and $V \rightarrow T$, $V \rightarrow R$, and $V \rightarrow V$ Relaxation

The first experimental method of obtaining information on $V \rightarrow V$ and $V \rightarrow T$ energy transfer was to measure the heat capacity or transport properties of a liquid or gas. Transport properties depend on the classical kinetic theory of gases.[2a] Experimental deviations from the simple theories first indicated that a molecular system would absorb some of the kinetic energy necessary for the transport property being considered (thermal conductivity, viscosity) by converting the kinetic energy into intramolecular potential energy. It was soon found that the translational and rotational heat capacity responded much more rapidly to thermal activation than did the vibrational heat capacity. The largest number of studies of $V \rightarrow V$, $V \rightarrow R$, $V \rightarrow T$, and $R \rightarrow T$ energy exchanges have involved the measurement of the molecule's heat capacity as a function of time. $R \rightarrow R$ exchange rates have not been measured by these experiments. The measurement of sound propagation (absorption and dispersion) in gases has led to most of the results.[22,23] Studies of gas compression in shock waves[23] or adiabatic gas

expansion in a supersonic nozzle beam[24,25] are similar to the ultrasonic measurements. The method in these experiments is to compress or rarify the gas in a time shorter than the vibrational relaxation time. The translational and rotational systems reach equilibrium first and at a later time the vibrational temperature increases (shock wave) or decreases (supersonic nozzle) accordingly. Both processes are evident and periodically repeated in an ultrasonic experiment. These experiments have led to a large amount of information but they necessarily weight the lower vibrational states which have the largest heat capacity. In fact, in most cases only a single relaxation time is observed corresponding to the lowest vibrational $V \rightarrow T$ transition. If the lowest vibrational state is relatively isolated from the other modes as the torsion mode in CH_3CH_3,[26] two relaxations may be observable.

Recent work by Cottrell and coworkers has perfected the measurement of vibrational relaxation times by the use of the spectrophone.[27,28] The spectrophone is potentially a very powerful apparatus because each vibrational mode (or combination or overtone) can be selectively excited. The spectrophone employs the optical-acoustical transfer of energy and measures the time lag in the increase of translational temperature after the vibrational temperature has been increased by electromagnetic excitation. Unfortunately, the measurement is limited to the relaxation of the rate-determining step in the $V \rightarrow T$ transfer which is normally from the lowest energy vibrational level. However, by measuring the relaxation for different vibrational excitations, an upper limit on the $V \rightarrow V$ relaxation time between modes can be obtained. In methane a relaxation time of 1.6×10^{-6} sec was obtained by exciting either the asymmetric bend at 1306 cm^{-1} or the asymmetric stretch at 3020 cm^{-1}.[27] Thus, the $V \rightarrow V$ rate of exchange between the above modes must be considerably faster than 10^{-6} sec (see discussion on vibrational fluorescence below). The value of $\tau = 1.6 \times 10^{-6}$ sec obtained by the spectrophone also agrees well with the ultrasonic work.[23]

Direct observation of the relaxation from the excited vibrational states would allow a better measurement of the $V \rightarrow V$ and $V \rightarrow T$ processes. We have been working in our laboratory on using microwave spectroscopy as a tool for observing vibrational relaxation in the excited vibrational states. The experiment is to measure the time lag in $V \rightarrow T$ or $V \rightarrow V$ transfer after vibrational excitation. The desirable features of phase sensitive detection are available.[29]

(13) H. P. Broida and T. Carrington, *J. Chem. Phys.*, **38**, 136 (1963).

(14) A. B. Callear and I. W. M. Smith, *Trans. Faraday Soc.*, **59**, 1735 (1963).

(15) M. Jeunehomme, *J. Chem. Phys.*, **45**, 4433 (1966).

(16) T. Carrington, *ibid.*, **31**, 1418 (1959).

(17) A. B. Callear, *Discussions Faraday Soc.*, **33**, 28 (1962).

(18) A. B. Callear and G. J. Williams, *Trans. Faraday Soc.*, **62**, 2030 (1966).

(19) S. L. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966).

(20) A. B. Callear and G. J. Williams, *Trans. Faraday Soc.*, **60**, 2158 (1964).

(21) P. G. Dickens, J. W. Linnett, and O. Sovers, *Discussions Faraday Soc.*, **33**, 52 (1962).

(22) K. F. Herzfeld and T. A. Litovitz, "Absorption and Dispersion of Ultrasonic Waves," Academic Press, Inc., New York, N. Y., 1959.

(23) T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworths, London, 1961.

(24) J. B. Anderson, R. D. Andres, and J. B. Fenn, "Molecular Beams," J. Ross, Ed., Interscience Publishers, New York, N. Y., 1966, p 275.

(25) I. R. Hurle, A. L. Russo, and J. G. Hall, *J. Chem. Phys.*, **40**, 2076 (1964); I. R. Hurle in "Molecular Relaxation Processes," Academic Press, New York, N. Y., 1966, p 277; R. Campargue, *ibid.*, p 287.

(26) R. Holmes, G. R. Jones, and N. Pusat, *J. Chem. Phys.*, **41**, 2512 (1964).

(27) T. L. Cottrell, I. M. Macfarlane, A. W. Read, and A. H. Young, *Trans. Faraday Soc.*, **62**, 2655 (1966).

(28) T. L. Cottrell, I. M. Macfarlane, and A. W. Read, *ibid.*, **63**, 2093 (1967).

The quenching of vibrational fluorescence can also be used to measure vibrational relaxation times. Spontaneous emission between vibrational states is very slow relative to electronic transitions as shown from eq 6. For $D_{01} = 1$ D, and $E_1 - E_0 = 1000$ cm^{-1} or $\nu_{10} = 3 \times 10^{13}$ sec^{-1}, the spontaneous emission relaxation time is

$$\tau = \frac{1}{P_0} \simeq 0.3 \text{ sec}$$

Even with this slow relaxation time, vibrational spontaneous emission has been observed in CO with a relaxation time of 0.033 sec.[30] The observation of vibrational fluorescence allows a direct measurement of the competing relaxing mechanisms induced by binary collisions.[31]

A related but more powerful technique in V → V studies is the observation of vibrational fluorescence after laser excitation.[32] Yardley and Moore have used a He–Ne laser to monochromatically excite a specific vibration-rotational transition in the asymmetric stretch of methane.[33] By observing vibrational fluorescence in both the stretching and bending mode, they were able to measure the V → V transfer between the vibrational modes. The V → V relaxation time was indeed much faster ($\tau \simeq 6 \times 10^{-9}$ sec corresponding to about 60 kinetic collisions) than the V → T transfer from the lower frequency bend which was 1.6×10^{-6} sec. The latter value is in agreement with the spectrophone[27] and ultrasonic results mentioned above.[23]

Extensive relaxation studies have been reported for CO_2. It is interesting to compare the vibrational fluorescence studies of V → V transfer with the V → T studies by ultrasonic and shock methods.[23] The latter methods give the V → T relaxation time of 6.8×10^{-6} in CO_2.[23] This time is apparently the (0,1,0) → (0,0,0) rate. (0,0,0) is the ground vibrational state, (1,0,0) represents the first excited state of the symmetric stretch, (0,1,0) is the bend, and (0,0,1) is the asymmetric stretch.

Shock tube studies at high temperatures[34] indicate that CO_2 V → V relaxation between the bending and asymmetric stretching mode is on the order of ten times faster than the V → T transfer. This V → V enhancement is still much slower than the corresponding V → V bend-stretch transfer of 6×10^{-9} sec in methane as mentioned above. Indeed, the slower V → V transfer from the (0,0,1) state of CO_2 enables laser oscillation with the (1,0,0) state due to the build-up in population of the upper state and a rapid relaxation in the lower state. Vibrational fluorescence after laser excitation

of the (0,0,1) level in CO_2 (at 300°K) gives a V → V relaxation time of $\tau = 3.7 \times 10^{-6}$ sec[32] which is somewhat longer than the higher temperature shock tube indication. More detailed studies of the various V → V transfer processes in CO_2 have been reported[35] where various mechanisms of V → V transfer are discussed. It is generally found that the V → V relaxation time is proportional to the excess kinetic energy that must be absorbed by the system.

Callear's[36] earlier suggestion, that the logarithm of the number of collisions necessary for V → V energy exchange is proportional to the excess kinetic energy in the process, has been confirmed[37] on the basis of more data on V → V energy exchange in NO + CO,[38] NO + N_2,[38] and CO + O_2.[39]

A similar plot is presented by Lambert[39] concerning V → T transfer. Lambert finds that the logarithm of the number of collisions necessary for V → T energy exchange is proportional to the energy of the lowest molecular vibration (see eq 9 below).

Finally, it is interesting to note that Yardley and Moore[40] report (0,0,1) V → V rates for CO_2 mixed with the rare gases from He to Xe. The mixed-gas rates range from 11×10^{-6} to 40×10^{-6} sec throughout the series. Cottrell and Day[41] have recently reported complete measurements on the (0,1,0) V → T rates for the CO_2–rare gas mixtures. The V → V and V → T rates are nearly identical except for He where the V → T rate is 30 times the V → V rate. This observation clearly indicates that by adding He gas to a CO_2 laser system the laser power can be increased considerably as has been observed.[32,35]

A physical picture of vibrational V → T relaxation can be obtained by considering the collision of an atom with an oscillator. The period of the collision must be of the same order of magnitude as the period of oscillation in order to have a nonadiabatic collision. Molecular velocities at 300°K are about $v = 3 \times 10^4$ cm/sec. Vibrational periods for $(E_1 - E_0) \simeq 1000$ cm^{-1} are $\tau_v \simeq 3.3 \times 10^{-14}$ sec. Thus, in order for the period of the collision, τ_c, to be 3.3×10^{-14} sec, the interaction length, l, must be very short. $l/v = \tau_c = 3.3 \times 10^{-14}$ sec; $l = 10^{-9}$ cm $= 0.1$ Å. This short length is suggestive of an extremely steep repulsive potential between the atom and molecule. Exponential repulsion due to overlap between closed shell orbitals normally leads to softer potentials with $l \cong 0.5$–0.8 Å.[42]

(29) R. G. Gordon, J. Chem. Phys., **46**, 4399 (1967).

(30) R. C. Millikan, ibid., **38**, 2855 (1963).

(31) R. C. Millikan, ibid., **43**, 1439 (1965).

(32) G. W. Flynn, M. A. Kovacs, C. K. Rhodes, and A. Javan, Phys. Rev. Letters, **17**, 233 (1966); M. A. Kovacs, G. W. Flynn, and A. Javan, Appl. Phys. Letters, **8**, 62 (1966); G. W. Flynn, M. A. Kovacs, C. K. Rhodes, and A. Javan, Phys. Letters, **8**, 63 (1966).

(33) J. T. Yardley and C. B. Moore, J. Chem. Phys., **45**, 1066 (1966).

(34) W. J. Witteman, ibid., **37**, 655 (1962).

(35) C. B. Moore, R. E. Wood, B. L. Hu, and J. T. Yardley, ibid., **46**, 4222 (1967).

(36) A. B. Callear, Discussions Faraday Soc., **33**, 28 (1962).

(37) A. B. Callear, Appl. Opt., Suppl. No. 2, 145 (1965).

(38) N. Basco, A. B. Callear, and R. G. W. Norrish, Proc. Roy. Soc. (London), **A269**, 180 (1963); A. B. Callear and I. W. M. Smith, Trans. Faraday Soc., **59**, 1735 (1963).

(39) J. D. Lambert, "Atomic and Molecular Processes," D. R. Bates, Ed., Academic Press, New York, N. Y., 1962, p 783.

(40) J. T. Yardley and C. B. Moore, J. Chem. Phys., **46**, 4491 (1967).

(41) T. L. Cottrell and M. A. Day in "Molecular Relaxation Processes," Academic Press, New York, N. Y., 1966, p 253.

(42) W. H. Flygare and D. W. Hafemeister, J. Chem. Phys., **43**, 789 (1965).

Thus, only the molecules and atoms in the upper wings of the Maxwell velocity distribution curve will have the velocity necessary to effect the V → T transfer of energy. The rate constant for V → T of energy can be written in exponential form as

$$k = \frac{1}{\tau_{01}} = A e^{-l\nu/v} \qquad (9)$$

Correlations of rate with ν_{01} have been attempted,[23,40] and it can be easily shown that the above relation is included in the well-known treatment of V → T transfer of Schwartz, Slawsky, and Herzfeld (SSH).[43] The SSH treatment deals with harmonic oscillators and yields $\Delta v = 0, \pm 1$ selection rules for V → T transfer of energy. $\Delta v = \pm 2$ transitions can easily be obtained with an anharmonic oscillator or with a softer repulsive potential.[44] Exact quantum mechanical calculations of V → T exchange are now available and show that the higher exchanges of vibrational energy ($\Delta \nu = \pm 2$, $\Delta \nu = \pm 3$) are more probable as the energy of the colliding species increases.[45]

There is evidence that V → T energy transfer in an excited electronic state is faster than in the ground state.[13] This may be due to the existence of a harder repulsive potential in the excited electronic state. Also, an attractive component in the potential of the excited state would initially attract the collision partners increasing the rate.

Enhancement of V → T relaxation times may be obtained in collision with molecules with small moments of inertia (normally hydrogen-containing molecules). A considerable increase in relative velocity is obtained by a light rotor leading to V → R exchange of energy.[46] Consider a methyl free rotor in a molecule with a moment of inertia about the C_3 axis of $I = 5.3 \times 10^{-40}$ g cm². The angular velocity, ω, is approximately related to the rotational angular momentum quantum number J by

$$Jh \simeq \omega I \qquad (10)$$

The component of linear velocity is $v = r\omega$ where r is an approximate radius of the rotor. Thus, $v = r\omega = Jhr/I \simeq 2J \times 10^4$ cm/sec for the free methyl rotor where $r \simeq 10^{-8}$ cm. Thus, according to our previous discussion and eq 9, the rotational contribution to the relative velocity ought to contribute substantially to the rate of vibrational relaxation. V → R conversion is the principal reason that H_2O is a more efficient quencher of vibrational energy than expected.[23]

IV. Rotational Excitation and R → R, T → T, and R → T Relaxation

Normally, T → T rates of relaxation are faster than all other energy-exchange processes. This is because of the near continuum of translational states available to a molecule. As mentioned earlier, rates measured in ultrasonics, shock waves, or in nozzle beams are all relative to the fastest process which is T → T. Thus, in a shock wave, the T → T rate in the shock front initiates the high translational temperature. As time advances, the translational temperature drops, first due to rotational heating (T → R), and at a later time the translational temperature drops again due to vibrational heating (T → V).

Due to the extremely rapid rates, there are very few measurements of R → T processes. Ultrasonic work on O_2 and N_2 indicates that approximately ten kinetic collisions are needed in order to produce a R → T transfer of energy.[23] This conclusion has been verified in shock-wave studies.[47,48] R → T transfer in HCl has also been found to require about ten kinetic collisions, which indicates that the dominant R → T transfer mechanism does not depend strongly on the molecular electric dipole moment.

The pressure dependence of line widths in microwave rotational transitions has been employed to determine the relaxation time of the upper rotational state. The validity of the line-width analysis has been emphasized by the recent observation of the rotational emission from the $J = 1$ to the $J = 0$ rotational states in OCS.[49] The lifetime in emission (of the excited state) was found to be identical with the lifetime as obtained from the line width. However, neither the line width nor the emission experiments can distinguish R → R from R → T relaxation. The rotational line width and emission relaxation times are about an order of magnitude faster than the values obtained by the macroscopic R → T measurements. In addition, line widths decrease when a gas with an electric dipole moment is buffered by a rare gas atom which will weight the R → T mechanism. Thus, it appears that R → R relaxation rates are much faster than R → T rates.

A direct measurement of the rate in R → R transfer in OCS has been made by Unland and Flygare by employing a microwave–microwave double resonance experiment.[50] The technique is to disturb the rotational equilibrium with monochromatic radiation, remove the disturbance, and then observe the return to rotational equilibrium by monitoring, spectroscopically, the differences in the rotational populations. The experiment is insensitive to R → T mechanisms unless the molecule relaxes by a R → T → R path, which is improbable. Unland and Flygare found a

(43) R. N. Schwartz, Z. I. Slawsky, and K. F. Herzfeld, *J. Chem. Phys.*, **20**, 1591 (1952).
(44) J. I. Steinfeld, *ibid.*, **46**, 4550 (1967).
(45) D. Secrest and R. B. Johnson, *ibid.*, **45**, 4556 (1966). See this work for references to earlier calculations and a comparison with exact classical calculations.
(46) T. L. Cottrell and A. J. Matheson, *Trans. Faraday Soc.*, **58**, 2336 (1962); **59**, 824 (1963); T. L. Cottrell, R. C. Dobbie, J. McLain, and A. W. Read, *ibid.*, **60**, 241 (1964); C. B. Moore, *J. Chem. Phys.*, **43**, 2979 (1965).

(47) A. B. Callear, *Ann. Rept.*, **61**, 48 (1964).
(48) B. Levitt and D. F. Hornig, *J. Chem. Phys.*, **36**, 219 (1962).
(49) R. M. Hill, D. E. Kaplan, G. F. Herrmann, and S. K. Ichiki, *Phys. Rev. Letters*, **18**, 105 (1967).
(50) M. L. Unland and W. H. Flygare, *J. Chem. Phys.*, **45**, 2421 (1966).

faster relaxation time (twice as fast as indicated for the upper level from line widths) for return to rotational equilibrium. A two-level system exchanging heat with a large manifold of states would return to equilibrium with an apparent rate twice as fast as the rate of decay from a single state as observed in emission quenching. Thus, the faster relaxation time of Unland and Flygare is indicative of R → R transfer of energy and indicates that the line width and emission times are also true R → R transfers. The R → R relaxation time in OCS at standard conditions (1 atm) is 2.3×10^{-11} sec. This corresponds to fewer than one kinetic collision for each R → R energy transfer. In other words the effective molecular diameter for R → R relaxation is considerably larger than the kinetic diameter.[50] In OCS the R → R molecular diameter is about 10 Å. Thus, it appears that R → R energy transfer is certainly faster than R → T transfer.[50] It also appears that R → R transfer is faster than T → T transfer for molecules which have permanent electric dipole moments.

Recently, a number of studies of rotational collisional R → R selection rules have been determined by using the techniques of microwave–microwave double resonance.[51–54] Rates have not been measured but progress has been made in identifying the R → R transfer map in a molecule. Cox, Flynn, and Wilson found that collisions did not mix the M states of OCS.[54] M is the projection of the rotational angular momentum on a space-fixed axis. Experiments by Oka[55] on the K doublets and λ doublets in several molecules has shown that ΔJ transitions larger than 0 and ±1 are readily obtained but the K and λ states retain their identity.

Similar R → R collisional selection rules have been obtained by Ronn and Lide by using infrared–microwave double resonance techniques.[56] Their experiments employ a CO_2 laser to excite a vibrational transition in methyl bromide. Microwave transitions in the ground vibration state, utilizing rotational states not connected with the infrared resonance, are monitored giving R → R selection rules. Oka has also demonstrated that electric dipole selection rules are dominant in collisional R → R transfer in ethylene oxide.[57]

Due to the extremely fast rates of R → R transfer, it is clear that the interaction mechanism is relatively long range (of the order of molecular dimensions or larger) and, therefore, probably electrostatic in origin. A model of interaction can be constructed according to Unland and Flygare.[50] In the case of the collision between two diatomics with electric dipole moments,

the dominant interaction will be the Stark effect. The electric field at some point in space due to an electric dipole is given approximately by a μ/r^3 law. Thus, the electric field at a point 10 Å from a point dipole of 1 D is 3×10^5 V/cm. This field is of sufficient magnitude to greatly alter the rotational states in another molecule at the 10 Å point and thus allow a transfer of energy during a collision. ±M degeneracies are not broken and cannot mix as the Stark effect does not couple different M states. Time-dependent magnetic fields will cause a time-dependent first-order perturbation in M which breaks the degeneracies and allows mixing and transfer of energy between the M states. However, the magnetic field at a point 10 Å from a magnetic moment of 1 BM is only 9.3 G which leads to an insignificant first-order Zeeman effect relative to the Stark effect. Only if the molecule has no electric moment and a large magnetic moment of 1 BM will the Zeeman effect be large enough to cause M mixing. However, even in the ideal case of O_2, the pure rotational transitions are extremely narrow[58] and the line width is probably caused by R → T relaxation. Most molecules have closed-shell electron distributions leading to rotational magnetic moments which are considerably smaller than 1 BM (for instance, the rotational magnetic moment of fluoroacetylene in the $J = 1$ state is only 3×10^{-7} BM[59]). Thus, the M, K, and λ mixing should be small for most molecular systems, which is in agreement with the experimental results. The $\Delta J \neq \pm 1$ transitions observed in R → R processes can arise from higher order electrostatic multipole interactions.

V. Summary

The methods of measuring molecular energy exchange are reviewed with emphasis on the newly developed methods of measuring V → V and R → R relaxation times and selection rules. We can summarize our knowledge of V, T, and R relaxation times by considering a fairly large polyatomic molecule with several modes of vibrational motion. The approximate relaxation times at standard conditions are shown in Scheme I. The number of collisions for each transfer process can be obtained relative to the single collision in the T → T process. It should be emphasized that any of the τ in Scheme I may overlap with any other τ. Thus, Scheme I gives only a typical representation of relaxation times. Many exceptions can be found to this simple scheme.

Simple physical arguments are given for a useful model in understanding the mechanisms of perturbations in a binary collision. V → V, V → T, and V → R mechanisms all require hard collisions. R → R mechanisms are electrostatic in origin and R → T mechanisms are similar to T → T classical collisions as the energy spacings are small relative to kT. R → T

(51) T. Yajima and K. Shimoda, *J. Phys. Soc. Japan*, **15**, 1668 (1960); T. Yajima, *ibid.*, **16**, 1594, 1709 (1961).

(52) A. Battaglia, A. Gozzini, and E. Polacco, *Nuovo Cimento*, **14**, 1079 (1959).

(53) M. L. Unland, V. W. Weiss, and W. H. Flygare, *J. Chem. Phys.*, **42**, 2138 (1965).

(54) A. P. Cox, G. W. Flynn, and F. B. Wilson, Jr., *ibid.*, **42**, 3094 (1965).

(55) T. Oka, *ibid.*, **47**, 13 (1965); see also A. M. Ronn and E. B. Wilson, Jr., *ibid.*, **46**, 3262 (1967).
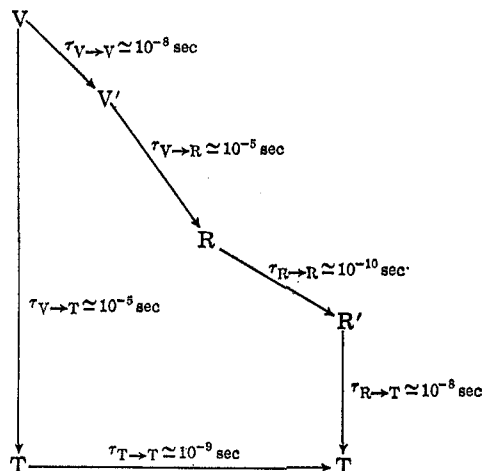
(56) A. M. Ronn and D. R. Lide, Jr., *ibid.*, **47**, 3669 (1967).

(57) T. Oka, *ibid.*, **45**, 754 (1966).

(58) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(59) V. W. Weiss, H. D. Todd, M. K. Lo, H. S. Gutowsky, and W. H. Flygare, *J. Chem. Phys.*, **47**, 4021 (1967).

Scheme I

relaxations take longer than T → T relaxations, probably because of a simple geometric factor. For instance, two diatomic molecules colliding with each other on an axis parallel to the rotational angular momentum vector will not lead to any R → T exchange. This collision will lead to T → T exchange.

Experimental activity in the field of energy transfer is enormous and is growing rapidly. New experiments should be attempted building on the previous work. One experiment would be to apply the conventional spectrophone to the measurement of R → T energy exchange. There are a large number of high-power microwave tubes that could be employed for the optical analog in the optical-acoustic effect. A larger sonic cavity would allow lower pressures in order to measure the R → T phase lag with a reasonable rate of switching

of the microwave power. Ferrite switches are now available to increase the switching rate.

Experimental work on relaxation processes in supersonic nozzle beams will certainly be continued as the methods of producing high-intensity beams are just now being realized. It would be most appropriate to add spectroscopic detection of populations (electronic, vibrational, and rotational) to the nozzle beam experiment. In addition, due to the low temperatures produced in a nozzle beam, it may be possible to select proton spin states in a methyl group to study nuclear spin conversion.

Experimental work on R → R collisional selection rules will certainly continue and should lead to a more satisfactory theory of rotational energy transfer.

Vibrational fluorescence of laser-stimulated systems will certainly be developed extensively to understand better the V → V energy-transfer mechanism.

A microwave detector of rotational, vibrational, or translational temperatures of excited vibrational states will probably be developed in conjunction with laser or black-body vibrational excitation. By observing the rotational transitions in excited vibrational states as a function of alternating vibrational excitation, one ought to be able to detect V → V relaxation dependent signals.[29,50]

The study on E → E processes is also receiving a large share of attention. The applications in laser technology have stirred this area of research and we will continue to see experiments where microwave or infrared detection and monitoring devices will be used as a probe of E → E, E → V, E → R, and E → T relaxation mechanisms.