Vibration–Vibration Energy Transfer in Gaseous Collisions

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1 Introduction

Most chemical reactions only occur when sufficient vibrational energy is acquired in a particular interatomic bond of the molecule concerned. The rate at which this energy is taken up or lost, and the ease with which it can flow between the different molecular vibrational modes, are thus of fundamental importance in chemical kinetics. In particular, the various theories of unimolecular gas reactions are based on detailed assumptions about rates of energy transfer.[1]

The conversion of *translational* into *vibrational* energy in molecular collisions has been extensively investigated by measurements on ultrasonic disperson and absorption. The velocity of propagation of an adiabatic sound wave in a perfect gas is given by

$$V^2 = (\mathbf{R}T/M)(1 + \mathbf{R}/C_v) \qquad (1)$$

and for a monatomic gas, where molecular translational energy is freely interchanged at every collision, is independent of the sound oscillation frequency. This is no longer so for polyatomic gases, where the quantised internal degrees of freedom do not freely interchange with translation. Supposing P_{10} is the probability per collision for a change in vibrational quantum number from $1 \rightarrow 0$ (and is less than unity), the average number of collisions required for a molecule to lose one quantum will be $Z_{10} = 1/P_{10}$. If Z is the total number of collisions one molecule suffers per second, a *vibrational relaxation time*, β, may be defined by the equation

$$Z_{10} = Z\beta \qquad (2)$$

Since Z_{10}, the *collision number*, is a constant, and Z is proportional to the gas pressure, β will be inversely proportional to pressure. For convenience, relaxation times, β, are always referred to a pressure of 1 atm. Equation (2) is an approximation, as the gas kinetic collision number Z requires modifying by a factor taking into account the Boltzmann distribution of molecules between quantum states. For a simple harmonic oscillator of fundamental frequency ν, the correct equation is;

$$Z_{10} = Z\beta\,[1 - \exp(-\,\mathbf{h}\nu/\mathbf{k}T)] \qquad (3)$$

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[1] H. M. Frey, *Ann. Reports*, 1960, **57**, 28.

which approximates closely to (2) for high values of ν. At sound frequencies where the period of the adiabatic oscillation becomes comparable with the vibrational relaxation time, the vibrational temperature of the gas lags behind the translational temperature throughout the compression–rarefaction cycle, and the effective values of C_v and V^2 in eqn. (1) become frequency-dependent. This phenomenon occurs at ultrasonic frequencies, and is known as *ultrasonic dispersion*; it is accompanied by a non-classical *absorption* of sound. Measurement of either may be used to obtain relaxation times.

The measurement of vibrational relaxation times by ultrasonic and other (*e.g.*, shock tube) methods has been fully discussed in an earlier Quarterly Review by McCoubrey and McGrath,[2] and in other subsequent articles and books.[3] Values of Z_{10} are observed varying from a few collisions to several hundred thousand, and showing an exponential dependence on the frequency of the relaxing vibrational mode. In addition, for heteromolecular collisions, the values are highly specific for the nature of the collision partner; for example CO_2–H_2O collisions are some 10^3 times more efficient than CO_2–CO_2 collisions. Such inefficient transfer, and such a high degree of specificity, are not in accord with observations on the kinetics of unimolecular gas reactions,[2] and it was pointed out thirty years ago by Patat and Bartholom´ that *vibration–vibration* energy transfer between molecules is likely to be at least as important from the point of view of chemical kinetics as *vibration–translation* transfer.[4] Conventional ultrasonic methods give no direct information about vibration–vibration transfer, since the energy transferred remains internal, and there is no effect on the adiabatic compressibility of the gas. But indirect information has recently been obtained from experiments on ultrasonic dispersion in polyatomic gases possessing several active vibrational modes, and in their mixtures. This work forms the main subject of the present Review, together with discussion of spectroscopic and theoretical sources of information about vibration–vibration transfer.

2 Intramolecular Transfer of Vibrational Energy. Ultrasonic Dispersion in Polyatomic Gases.

Intramolecular transfer of energy between different vibrational modes of a polyatomic molecule can only occur in collision. The energy in the different modes is quantised and, except in rare cases where there is exact resonance between harmonics, the energy discrepancy must be made up by translational energy. For a molecule with two active vibrational modes of frequency, ν_1 and ν_2, there are three possible vibrational transitions, which are illustrated on the energy level diagram in Figure 1: (*a*) Transfer of translational energy to $0 \rightarrow 1$ excitation of the mode ν_1, with relaxation time β_1. (*b*) Transfer of translational energy to $0 \rightarrow 1$ excitation of the mode ν_2, with relaxation time β_2. (*c*) The

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[2] J. C. McCoubrey and W. D. McGrath, *Quart. Rev.*, 1957, **11**, 87.

[3] K. F. Herzfeld and T. A. Litovitz, 'Absorption and Dispersion of Ultrasonic Waves', Academic Press, New York, 1959; T. L. Cottrell and J. C. McCoubrey, 'Molecular Energy Transfer in Gases', Butterworths, London, 1961; J. D. Lambert, 'Atomic and Molecular Processes', ed. Bates, Academic Press, New York, 1962, ch. 20.

[4] F. Patat and E. Bartholomé, *Z. phys. Chem.*, 1936, *B*,**32**, 396.

complex transfer of quantum of vibrational energy from mode ν_1, plus the necessary increment of translational energy to give $0 \rightarrow 1$ excitation of the mode ν_2, with relaxation time β_{12}.

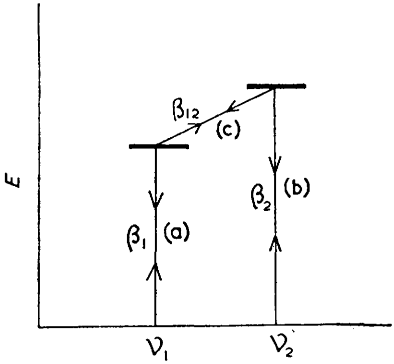

FIG. 1. *Energy-level diagram showing possible transitions for a molecule with two active vibrational modes.*

For the majority of polyatomic molecules which have been investigated experimentally a single relaxation time is observed, corresponding to relaxation of the whole of the molecular vibrational energy. This means that $\beta_2 \gg \beta_1 \gg \beta_{12}$. Vibrational energy thus enters the molecule *via* process (*a*), which is rate-controlling, and rapidly flows in complex collisions *via* process (*c*) to the second mode (and any other higher modes). Process (*b*) is too slow to play any rôle. This mechanism is characterised by a single overall relaxation time, β, which can be shown to be related to β_1 by the equation $\beta_1 = (C_1/C_s)\beta$, where C_1 is the specific-heat contribution due to mode ν_1 alone, and C_s the total vibrational specific heat. The general picture is that rapid vibration–vibration transfer maintains continuous equilibrium of vibrational energy between the various fundamental modes of the molecule, and that the whole of this energy relaxes in a single vibration–translation transfer process *via* the lowest mode.[5]

For a few molecules, in all of which there is a large difference between ν_2 and ν_1, the rate of the complex process (*c*) is much slower and the condition $\beta_2 \gg \beta_{12} > \beta_1$ applies. Process (*b*) is again too slow to play any rôle, but process (*a*) is now faster than process (*c*). A double relaxation phenomenon results. The vibrational energy of ν_2 (and any upper modes) relaxes *via* complex process (*c*), followed by the faster process (*a*). Process (*c*) is thus the rate-determining step, and the vibrational energy of the upper modes is transferred with a relaxation time β_{12}. The vibrational energy of the lowest mode, ν_1, relaxes independently by process (*a*) with the shorter relaxation time β_1. This behaviour has been observed for only three gases, SO_2,[6] CH_2Cl_2,[7] and C_2H_6.[5] The experimental data

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[5] J. D. Lambert and R. Salter, *Proc. Roy. Soc.*, 1959, *A*, **253**, 277.

[6] J. D. Lambert and R. Salter, *Proc. Roy. Soc.*, 1957, *A*, **243**, 78; P. G. Dickens and J. W. Linnett, *ibid.*, 1957, *A*, **243**, 84.

[7] D. Sette, A. Busala, and J. C. Hubbard, *J. Chem. Phys.*, 1955, **23**, 787.

are summarised in Table 1. Two relaxation times are observed, β_1 and β_{12}, enabling calculation of the collision numbers Z_{10} and Z_{12}, corresponding to processes (*a*) and (*c*) respectively. For all these molecules, $\nu_2 > 2\nu_1$, and theoretical considerations show that the complex step (*c*) is a transfer of energy between one quantum of mode ν_2 and two or three quanta of mode ν_1. (The frequency gap between ν_2 and the remaining upper modes is small in all cases, and transfer between these is rapid.)

Table 1 *Experimental collision numbers for intramolecular vibrational energy transfer at* 300°K

Substance	ν_1 (cm.$^{-1}$)	ν_2 (cm.$^{-1}$)	i	$\Delta\nu$ (cm.$^{-1}$)	Z_{12}	Z_{10}
SO_2	519	1151	2	110	2390	390
CH_2Cl_2	283	704	2	140	460	30
C_2H_6	290	820	3	50	74	20

Z_{12} is the collision number for vibration–vibration transfer between i quanta of mode ν_1 and one quantum of mode ν_2.

The general conclusion may be drawn that intramolecular vibration–vibration energy transfer between modes is usually faster than vibration–translation transfer from the lowest mode. In a few cases, where there is a large frequency discrepancy between modes, so that multiple quantum transfers are involved, vibration–vibration transfer is slower.

3 Intermolecular Transfer of Vibrational Energy

A. Ultrasonic Dispersion in Mixtures.—Much more information about vibration–vibration transfer can be derived from ultrasonic measurements on binary mixtures. If a relaxing gas A is mixed with a non-relaxing gas B, such as helium, there are two collision processes by which vibration–translation energy transfer can occur:

(1) $A^* + A \rightarrow A + A$ (vib. → trans.)
(2) $A^* + B \rightarrow A + B$ (vib. → trans.).

Since (1) and (2) will have different collision efficiencies, the result will be a composite relaxation time for A given by

$$\frac{1}{\beta_A} = \frac{1-x}{\beta_{AA}} + \frac{x}{\beta_{AB}} \tag{4}$$

where x is the mole fraction of B in the mixture, β_{AA} is characteristic of process (1), and β_{AB} of process (2).[3] This can be represented graphically by a *linear* plot of reciprocal relaxation time, $1/\beta_A$, against mole fraction x.

If both A and B are polyatomic relaxing gases, there will also be two collision processes, corresponding to (1) and (2), for vibration–translation energy transfer from B* in homomolecular and heteromolecular collisions. In addition there can be a vibration–vibration transfer between A* and B*, making five transfer processes in all:

(1) $A^* + A \rightarrow A + A$ (vib. → trans.)
(2) $A^* + B \rightarrow A + B$ (vib. → trans.)
(3) $A^* + B \rightarrow A + B^*$ (vib. → vib. ± trans.)
(4) $B^* + B \rightarrow B + B$ (vib. → trans.)
(5) $B^* + A \rightarrow B + A$ (vib. → trans.).

If process (3), vibration–vibration transfer, does not occur the mixture will show a double relaxation process, characterised by two relaxation times β_A and β_B, which will both be related to molar composition by equations of type (4), each giving a linear plot of $1/\beta$ against composition. If vibration–vibration transfer does occur, the picture is completely altered. Suppose, for convenience, that pure A relaxes slowly, and pure B rapidly, so that processes (4) and (5) are both much faster than processes (1) and (2); there are now two alternative possibilities for the overall relaxation process.

If vibration–vibration transfer is much faster than all the other processes, (3) will maintain the vibrational energy of the whole system ($A^* + B^*$) in continuous equilibrium, and the total vibrational heat content of both components will relax *via* the faster of processes (4) or (5). There will thus be a single relaxation time, involving the total vibrational energy. The rate-controlling process will be either (4) or (5). If (4) plays the predominant rôle, as is likely, this will give rise to a near *quadratic* dependence of overall reciprocal relaxation time on mole fraction of B, since the rate of process (4) is proportional to x^2, and eqn. (4) no longer applies. This mechanism is closely analogous to the relaxation behaviour shown by pure polyatomic gases giving single dispersion, discussed in Section 2. The *near-resonant* collision process, involving transfer of vibrational energy from mode ν_x, of molecule A to mode ν_y of molecule B plays exactly the same rôle as the *complex* collision process, involving transfer of vibrational energy from mode ν_x to mode ν_y of a single molecular species.

Alternatively, if process (3) is slower than (4) or (5), but faster than (1) or (2), A will again relax by the route: (3) followed by (4) or (5), but now (3) will be rate-determining. This will give a *linear* dependence of $1/\beta_A$ on x. B will relax independently, and more rapidly *via* (4) and (5), with linear dependence of $1/\beta_B$ on x. There will thus be a double relaxation process with two relaxation times, β_A involving only the vibrational heat capacity of A, and β_B only that of B; both showing linear concentration-dependence. This mechanism is analogous to the relaxation behaviour of those polyatomic gases discussed in Section 2 which show double dispersion because vibration–vibration transfer between modes is *slower* than vibration–translation transfer from the lowest mode.

The nature of the overall relaxation process for mixtures (whether single or double), and the concentration-dependence of the relaxation times, are thus determined by the relative rates of processes (1)—(5). Observations of ultrasonic dispersion in the two pure gases A and B, and in a series of mixtures extending over the whole concentration range, enable a diagnosis to be made of which type of mechanism is followed. The rates of processes (1) and (4) are obtained from the measurements on the pure components, and the rates of processes (3) and (5) which give the best fit to the experimental observations can be estimated by trial and error. The results for a series of mixtures are given in Table 2.[8]

Table 2 *Experimental collision numbers for intermolecular vibrational energy transfer at* 300°K

A	B	ν_A (cm.$^{-1}$)	ν_B (cm.$^{-1}$)	i	$\Delta\nu$ (cm.$^{-1}$)	Z_{AB}	Z_{AA}	Z_{BB}
Singly dispersing mixtures								
SF_6	$CHClF_2$	344	369	1	25	50	1005	122
C_2H_4	C_2H_6	810	821·5	1	11·5	40	970	74
Doubly dispersing mixtures								
CCl_2F_2	$CH_3{\cdot}O{\cdot}CH_3$	260	250	1	10	5	73	<3
CH_3Cl	$CH_3{\cdot}O{\cdot}CH_3$	732	250	3	18	70	421	<3
SF_6	$CH_3{\cdot}O{\cdot}CH_3$	344	164	2	16	80	1005	<3
CHF_3	C_2F_4	507	507	1	0	50	1500	5·5
SF_6	C_2F_4	344	190	2	36	70	1005	5·5
CF_4	C_2F_4	435	220	2	5	110	2330	5·5
Spectroscopic data								
$NO(A^2\Sigma^+)$	N_2	2341	2330	1	11	790	—	—
$NO(X^2\pi)$	CO	1876	2143	1	267	10,000	—	—
$NO(X^2\pi)$	N_2	1876	2330	1	454	500,000	—	—
CO	CH_4	2143	1534	1	609	33,000	—	—

Z_{AB} is the collision number for vibration–vibration transfer between one quantum of mode ν_A of molecule A and i quanta of mode ν_B of molecule B. (Frequencies, ν_A and ν_B, are for 0—1 vibrational transition.)

Mixtures were chosen for which near-resonant vibration frequencies in the two components would be expected to give rise to rapid vibration–vibration transfer (small value of Z_{AB}). It will be seen that where Z_{AB} lies *below* the collision numbers for vibrational relaxation of the pure components, Z_{AA} and Z_{BB}, single dispersion is observed; where Z_{AB} lies *between* Z_{AA} and Z_{BB}, double dispersion is observed.

The actual experimental results for one singly dispersing mixture, SF_6 + $CHClF_2$, are shown in Figure 2. The lowest vibrational modes of the two molecules lie close enough for rapid vibration–vibration transfer, and single dispersion is observed, with near-quadratic concentration-dependence of $1/\beta$. This indicates that the homomolecular relaxation of $CHClF_2$ (B) [process (4)] is the rate-controlling step, and is faster than the heteromolecular relaxation [process (5)]. The curve calculated for concentration-dependence of $1/\beta$ was obtained by setting up the detailed energy and temperature-relaxation equations developed by Tanczos,[9] and solving over the whole concentration range on an

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[8] J. D. Lambert, D. G. Parks-Smith, and J. L. Stretton, *Proc. Roy. Soc.*, 1964, *A*, **282**, 380.
[9] F. I. Tanczos, *J. Chem. Phys.*, 1956, **25**, 439.

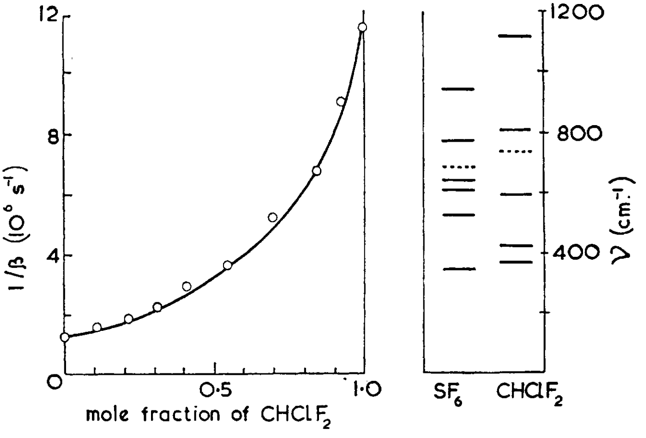

FIG. 2. *Reciprocal relaxation times and energy level diagram for* $SF_6 + CHClF_2$ *mixtures.* ○, *observed points;* ————, *curve calculated from theory.*
(Reproduced by permission, from *Proc. Roy. Soc.*, 1964, *A*, **282**, 380)

electronic computer. The value of Z_{AB} in Table 2 was estimated to give the best fit, and may be taken as 50 ± 15. Similar behaviour is shown by the mixture $C_2H_4 + C_2H_6$, investigated experimentally by Valley and Legvold.[10] This case is complicated by the double dispersion shown by pure ethane (Section 2), but the torsional (290 $cm.^{-1}$) mode of ethane relaxes independently of the upper modes in both pure gas and mixtures. A preliminary report has recently been made of a third mixture, $CO_2 + C_2H_4O$, showing single dispersion.[11]

The mixtures of the second section in Table 2, which were investigated earlier (when erroneous conclusions were drawn),[12] all show double dispersion. The details for one mixture, $SF_6 + C_2F_4$, are shown in Figure 3. There is near-resonance between the lowest (344 $cm.^{-1}$) mode of SF_6 and the first harmonic of the lowest (190 $cm.^{-1}$) mode of C_2F_4. Perfluoroethylene shows very efficient homomolecular vibration–translation transfer ($Z_{BB} = 5{\cdot}5$), and the estimated vibration–vibration transfer rate ($Z_{AB} = 70$) falls between this and the slower vibration–translation transfer rate of sulphur hexafluoride ($Z_{AA} = 1005$). Double dispersion is observed, with the predicted linear concentration-dependence of the two relaxation times. The remaining mixtures in this section, all of which involve B components whose homomolecular relaxation is very rapid, behave similarly.

B. Spectroscopic Evidence.—Information about vibration–vibration transfer involving diatomic molecules with comparatively high vibrational frequencies

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[10] L. M. Valley and S. Legvold, *J. Chem. Phys.*, 1962, **36**, 481.

[11] T. Seshagiri Rao and E. Srinivasachari, *Nature*, 1965, **206**, 926.

[12] J. D. Lambert, A. J. Edwards, D. Pemberton, and J. L. Stretton, *Discuss. Faraday Soc.*, 1962, **33**, 61.

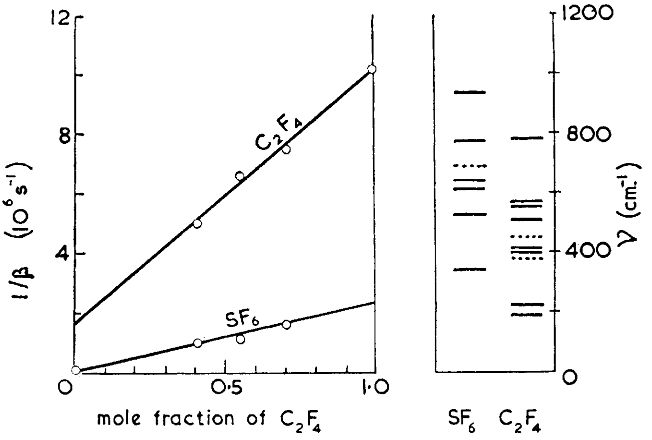

FIG. 3. *Reciprocal relaxation times and energy level diagram for* $SF_6 + C_2F_4$ *mixtures.* ○, *observed points.*

(Reproduced by permission, from *Discuss. Faraday Soc.*, 1962, **33**, 61)

has been obtained by flash-photolytic and spectroscopic techniques. Callear showed that vibrationally excited NO in the ground electronic state, $NO(X^2\pi)$ can be produced by flashing NO mixtures with ultraviolet light, and the rate of relaxation in collision with N_2 or CO followed spectroscopically.[13] He also observed the more rapid rate of vibration–vibration transfer between electronically excited $NO(A^2\Sigma^+)$ and N_2 by observing the quenching of resonance fluorescence.[14] The quenching of infrared resonance fluorescence of CO in the presence of CH_4 has been used by Millikan to measure the rate of vibration–vibration transfer for this mixture.[15] The values of Z_{AB} obtained for all these mixtures are included in Table 2.

In the fluorescence quenching experiments on mixtures of $NO(A^2\Sigma^+) + N_2$, the former was produced in vibrational levels $v = 3$, 2, and 1, vibration transfers involving all three levels were followed.[13] More than 85% of the transfers involved exchange of a *single* quantum, *e.g.*,

$$NO[A^2\Sigma^+(v = 2)] + N_2(v = 0) = NO[A^2\Sigma^+(v = 1)] + N_2(v = 1)$$

which gives a collision number designated by Z_{01}^{21}, and the values obtained for the three possible transfer were: $Z_{01}^{10} = 790$; $Z_{01}^{21} = 440$; $Z_{01}^{32} = 200$, which are in the approximate ratio 3 : 2 : 1. Thus vibration–vibration transfer usually involves a single quantum, but the efficiency of transfer increases almost proportionately with increase in vibrational quantum number.[16]

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[13] A. B. Callear, *Discuss. Faraday Soc.*, 1962, **33**, 28.

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

[15] R. C. Millikan, *J. Chem. Phys.*, 1965, **42**, 1439.

[16] A. B. Callear, *J. Appl. Optics*, Supplement on Chemical Lasers, 1964.

4 Factors Determining the Efficiency of Energy Transfer

The general significance of the collision numbers recorded in Tables 1 and 2 can be discussed in terms of quantum mechanical theory. For all mixtures listed in Table 2, except the last three, the exchanging vibrational frequencies lie close to exact resonance, 36 cm.$^{-1}$ being the largest energy discrepancy. An equation derived by Tanczos for resonant-energy exchange should be applicable.[9] This is based on the quantum mechanical theory of Schwartz, Slawsky, and Herzfeld (S.S.H.)[17] and gives the probability P(a, b) for resonant energy exchange in a collision between two molecules, a and b, as

$$P(\mathrm{a, b}) = P_{\mathrm{O}}(\mathrm{a})P_{\mathrm{O}}(\mathrm{b})V^2(\mathrm{a})V^2(\mathrm{b})\,\frac{64\pi^2\mu kT}{\alpha^2 h^2}\,\exp - (\phi_{\mathrm{O}}/kT) \qquad (5)$$

P_{O}(a) and P_{O}(b) are geometrical orientation factors. V^2(a) and V^2(b) are 'vibration factors' for the quantum jumps involved in each molecule; they depend on the detailed physical nature of the process and the intramolecular force constants, and contain terms in the intermolecular repulsion parameter, and the inverse of v, the vibrational frequency of the mode involved. They result in the probability's being enhanced by a steep intermolecular repulsion potential, and decreased for modes of high frequency. The vibration factors are also smaller for multiple quantum jumps, and this lowers the probability of transfers involving harmonics of fundamental modes. α is an intermolecular force constant, μ is the reduced mass of the collision pair, ϕ_{O} is the minimum value of the intermolecular potential function used.

Insufficient data are available on intramolecular force constants and intermolecular potentials for most of these polyatomic molecules to make quantitative *a priori* calculations of P(a, b) possible. But the general trends produced by various factors are well illustrated in Tables 1 and 2. The first striking conclusion is that resonant vibration–vibration exchanges do not have unit efficiency, as has often been assumed. This is illustrated experimentally by the mixture $CHF_3 + C_2F_4$, where both components have vibrational modes of identical frequency, 507 cm.$^{-1}$, and the estimated value for Z_{AB} is 50. The efficiency of near-resonant collisions decreases with rising frequency of the exchanging modes. Were all other factors equal, Z_{AB} should be proportional to the square of ν. This is illustrated by the increase in Z_{AB} from 5 for interchange between CCl_2F_2 ($\nu_{\mathrm{A}} = 260$ cm.$^{-1}$) + $CH_3{\cdot}O{\cdot}CH_3$ ($\nu_{\mathrm{B}} = 250$ cm.$^{-1}$) to 790 for the mixture NO($A^2\Sigma$) ($\nu_{\mathrm{A}} = 2341$ cm.$^{-1}$) + N_2 ($\nu_{\mathrm{B}} = 2330$ cm.$^{-1}$), where the vibration frequencies increase by a factor of approximately 10, and Z_{AB} by a factor of rather more than 100. Z_{AB} values for the other single quantum near-resonant exchanges:

CHF_3 (507 cm.$^{-1}$) + C_2F_4 (507 cm.$^{-1}$)
SF_6 (344 cm.$^{-1}$) + $CHCl_2F_2$ (369 cm.$^{-1}$)
C_2H_4 (810 cm.$^{-1}$) + C_2H_6 (821·5 cm.$^{-1}$)

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[17] R. N. Schwartz, Z. Slawsky, and K. F. Herzfeld, *J. Chem. Phys.*, 1952, **20**, 1591.

which have intermediate frequencies, all lie in the neighbourhood of 50. The other factor, which is important, is the relative inefficiency of multiple quantum transfers. This is illustrated by the remaining near-resonant mixtures in Table 2, all of which involve 2- or 3-quantum transitions and show values of Z_{AB} ranging from 70 to 110. The intramolecular 3-quantum transfer between the 290 cm.$^{-1}$ and 820 cm.$^{-1}$ modes of ethane (Table 1), with a value of $Z_{12} = 74$, also falls into this class. For all the mixtures of this group there is no apparent correlation between the size of the energy discrepancy, $\Delta\nu$, and Z_{AB} which justifies the approximation of treating all these energy exchanges as resonant.

The remaining vibration–vibration transfers recorded in Tables 1 and 2 show energy discrepancies, ranging from 110 to 609 cm.$^{-1}$, and can no longer be regarded as approximately resonant. They should follow a more complicated expression than eqn. (5), involving an exponential term in the energy discrepancy, $\Delta\nu$.[17,18] Callear has shown that for the transfers between NO, N_2, and CO, recorded in Table 2, where all three components are diatomic molecules with similar molecular weights, and would be expected to show similar gas-kinetic collision parameters, the value of log Z_{AB} shows a linear plot against $\Delta\nu$ as predicted.[13] The higher transfer efficiency of CH_4 as a collision partner for CO, in spite of the large energy discrepancy ($\Delta\nu = 609$ cm.$^{-1}$) is due to its lower molecular weight, and to the fact that vibrations which involve *hydrogen atoms* show a large amplitude, owing to the small mass of the hydrogen atom.[19] This results in a substantial increase in the vibration factors (cf. eqn. 5), and is the likely explanation for the comparatively high transfer efficiencies shown by hydrogen-containing molecules in vibration–translation,[5] as well as in vibration–vibration transfers. Finally, the relatively inefficient intramolecular transfers, given in Table 1 for SO_2 and CH_2Cl_2, involve both sizeable energy discrepancies and double quantum jumps.

For *simple* polyatomic molecules, where reliable molecular parameters are available, *a priori* quantum mechanical calculations by the S.S.H. method have shown reasonable success with homomolecular relaxation processes.[18] Similar calculations have recently been carried out on a number of O_2 mixtures, for which some experimental results are available for comparison.[20] The calculated Z_{AB} values are shown in Table 3; they must be regarded as only approximate, but are in qualitative agreement with the experimental findings. The latter have all been made with very low concentrations of additive ($\leqslant 2\%$) and are insufficient for exact interpretation. It is clear that vibration–vibration transfer can give a satisfactory explanation for the striking 'catalytic' effect on the vibrational relaxation of O_2 shown by many polyatomic additives. The trends shown in the values of Z_{AB} in Table 3 are of the same kind as those discussed above for Tables 1 and 2. The striking efficiency of H_2O is an example of the 'hydrogen effect', combined with a near-resonant collision. [The even more striking value of Z_{BB} for H_2O is due to the strong dipole–dipole interaction

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[18] J. L. Stretton, *Trans. Faraday Soc.*, 1965, **61**, 1053.
[19] D. G. Jones, J. D. Lambert, and J. L. Stretton, *J. Chem. Phys.*, 1965, **43**, 4541.
[20] D. G. Jones, J. D. Lambert, and J. L. Stretton, *Proc. Phys. Soc.*, 1965, **86**, 857.

Table 3 *Calculated collision numbers for intermolecular vibrational energy transfer in oxygen mixtures at* 300°K

Additive (B)	ν_B (cm.$^{-1}$)	*i*	$\Delta\nu$ (cm.$^{-1}$)	Z_{AB}	Z_{BB}
CH_4	1534	1	20	170	11,600
CD_4	1092	1	462	16,000	4960
C_2H_4	1444	1	110	490	4050
C_2H_2	729	2	96	1800	490
H_2O	1596	1	42	80	*ca.* 1
D_2O	1178	1	376	1160	*ca.* 1
HDO	1402	1	152	140	*ca.* 1

Z_{AB} is the collision number for vibration–vibration transfer between one quantum of the fundamental mode of $O_2(\nu_A = 1554$ cm.$^{-1})$ and *i* quanta of mode ν_B of molecule B. For pure oxygen $Z_{AA} = 8{\cdot}31 \times 10^7$ (calc.).

between molecules, which leads to a very deep minimum in the intermolecular potential, so that the ϕ_0 term (cf. eqn. 5) takes control. Theoretical calculations giving such high transfer efficiencies are unreliable.]

5 The Rôle of Vibration–Vibration Transfers in Chemical Kinetics

Two factors of fundamental importance in unimolecular reaction kinetics are the efficiency of collisional activation and deactivation of molecules, and the efficiency of energy transfer between different vibrational modes in the molecule. The various conclusions about efficiency of vibration–vibration transfer, which have been discussed above, apply equally to homomolecular and heteromolecular collisions. The vibrational deactivation of molecules in homomolecular collisions can occur either by vibration–translation transfer, or by resonant vibration–vibration transfer. The efficiencies of both processes depend critically on the frequency of the lowest vibrational mode; the collision number for vibration–translation transfer varies *exponentially* with frequency; the collision number for resonant vibration–vibration transfer is roughly proportional to the *square* of the frequency. Comparison of the values for vibration–vibration transfer given above with those for vibration–translation transfer given by Lambert and Salter[5] shows that, for hydrogen-containing molecules with frequencies below about 500 cm.$^{-1}$, both processes have collision efficiencies ($1/Z_{AB}$) varying between 1/5 and 1/50, and there is little significant difference between them. For molecules containing no hydrogen atom, vibration–translation transfer will be substantially less efficient, even in this frequency range. As frequency rises above 500 cm.$^{-1}$, both efficiencies decrease, but vibration–vibration transfer quickly becomes much more efficient than vibration–translation. Thus, for O_2 ($\nu = 1554$ cm.$^{-1}$) resonant vibration–vibration transfer ($Z_{AB} =$ *ca.* 10^2) is several powers of ten more efficient than vibration–translation ($Z_{10} =$ *ca.* 10^7), and even a non-resonant collision with an energy discrepancy $\Delta\nu = 462$ cm.$^{-1}$ ($Z_{AB} =$ *ca.* 10^4) is much more efficient. The temperature-dependence of resonant vibration–vibration transfer is much weaker than that of vibration–translation transfer, so that the difference in efficiency will become less marked at higher temperatures.

The chemical implication of this is that for moderately complex organic molecules, which have torsional frequencies around 250 cm.$^{-1}$, homomolecular vibrational deactivation may be expected to occur by either process, and to have a collision efficiency of 1/3 to 1/5 (allowing for the slightly higher efficiency of transfer from upper vibrational levels). Heteromolecular deactivation by an additive with a suitable range of low vibrational frequencies for easy vibration–vibration transfer may well be somewhat more efficient than homomolecular deactivation. This is in accord with recent observations on the kinetics of thermal isomerisation of cyclobutenes.[21] Recent ultrasonic work has shown that for the straight-chain hydrocarbons n-pentane and n-hexane, which have even lower torsional frequencies ($\nu < 100$ cm.$^{-1}$), vibration–translation transfer occurs at approximately every collision,[22] and other flexible organic molecules may be expected to show the same high efficiency. In contrast, for all molecules containing no hydrogen atom, and for hydrogen-containing molecules with lowest vibrational frequencies above 500 cm.$^{-1}$, deactivation will occur mainly by vibration–vibration transfer, with collision efficiencies varying between roughly 1/50 and 1/500. For this group collisions with monatomic additives, which can only deactivate by vibration–translation transfer, will be much less efficient than self-collisions. Collisions with polyatomic additives can have slightly higher efficiency than self-collisions, but only where suitable vibrational frequencies for near-resonant transfer are present; complex organic molecules possessing a wide spectrum of frequencies are most likely to fulfil this criterion. Otherwise additive efficiencies will be lower. Relative collision efficiencies for deactivation derived from unimolecular reaction kinetics are in accord with these views.[2]

The different active vibrational modes of polyatomic molecules are usually fairly closely spaced, so that vibration–vibration transfer between modes will be near-resonant, and will show an efficiency of the same order as that of vibrational activation and deactivation. Transfer between modes which are widely spaced may be considerably less efficient.

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[21] H. M. Frey and D. C. Marshall, *Trans. Faraday Soc.*, 1965, **61**, 1715; C. S. Elliott and H. M Frey, *ibid.*, 1966, **62**, 895.

[22] R. Holmes, G. R. Jones, and R. Lawrence, *Trans. Faraday Soc.*, 1966, **62**, 46.