# Collisional Transfer of Rotational Energy and Spectral Lineshapes

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## 1 Introduction

Molecular collisions are an unavoidable occurrence in the gaseous state of matter. They influence greatly a wide range of observable properties of the gas. These properties include pressure-induced absorption of radiation,[1-3] induced optical birefringence,[4] pressure-broadening of spectral lines,[5-7] ultrasonic relaxation,[8] nuclear-spin relaxation,[9] dielectric properties,[10,11] transport properties,[12] temperature variation of virial coefficients,[12,13] abnormal rotational distribution of molecules in the interstellar space,[14] *etc.* A satisfactory explanation of these properties requires a thorough understanding of the collisions. Attempts to study the collisions experimentally have developed along two lines. In the first one, any of the properties mentioned above is studied experimentally and a back calculation is made to derive certain parameters of the forces of collisional interaction.[15] In the other, specially devised experiments[16-21] are

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[1] M. F. Crawford, H. L. Welsh, and J. L. Locke, *Phys. Rev.*, 1949, **75**, 1607.
[2] A. A. Maryott and G. Birnbaum, *J. Chem. Phys.*, 1962, **36**, 2026, 2032.
[3] N. H. Rich and A. R. W. McKellar, 'A bibliography on collision-induced absorption', National Research Council of Canada publication number 15, 1975, p. 145.
[4] A. D. Buckingham, *J. Chem. Phys.*, 1959, **30**, 1580; see also *Adv. Chem. Phys.*, 1967, **12**, 107.
[5] G. Birnbaum, *Adv. Chem. Phys.*, 1967, **12**, 487.
[6] Krishnaji, *J. Sci. Ind. Res., India*, 1973, **32**, 168.
[7] H. Rabitz, *Ann. Rev. Phys. Chem.*, 1974, **25**, 155.
[8] T. L. Cottrell and J. C. McCoubrey, 'Molecular Energy Transfer in Gases', Butterworth, London, 1961.
[9] M. Bloom and I. Oppenheim, 'Intermolecular Forces' ed. J. O. Hirschfelder, Wiley, New York, 1967, p. 549.
[10] D. R. Johnson, G. J. Oudemans, and R. H. Cole, *J. Chem. Phys.*, 1960, **33**, 1310.
[11] T. K. Bose and R. H. Cole, *J. Chem. Phys.*, 1970, **52**, 140.
[12] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, 'Molecular Theory of Gases and Liquids', Wiley, New York, 1954.
[13] S. Kielich, *Physics*, 1962, **28**, 511.
[14] T. Oka, *Mém. Soc. Roy. Science Liège* 1972, 6, III, 37.
[15] Krishnaji and V. Prakash, *Rev. Mod. Phys.*, 1966, **38**, 690.
[16] A. P. Cox, G. Flynn, and E. B. Wilson, jun., *J. Chem. Phys.*, 1965, **42**, 3094.
[17] T. Oka, *J. Chem. Phys.*, 1966, **45**, 752, 754.
[18] T. Oka, 'Advances in Atomic and Molecular Physics' ed. D. R. Bates and I. Estermann, Academic Press, New York, 1973, Vol. 9, p. 127.
[19] T. Carrington, *J. Chem. Phys.*, 1959, **31**, 1418.
[20] J. P. Toennies, *Discuss. Faraday Soc.*, 1962, **33**, 96; *Z. Physik.*, 1957, **182**, 257; *Z. Physik.*, 1966, **76**, 193. See also J. P. Toennies, *Chem. Soc. Rev.*, 1974, **3**, 407.
[21] M. Cavallini, M. G. Dondi, A. Scoles, and U. Valbusa, *Chem. Phys. Lett.*, 1971, **10**, 22.

performed to study the collisions in a more direct manner. Experiments of the first kind have been successful in yielding the desired parameters within reasonable limits of uncertainty, but they do not give any information about the precise effect of a collision on the state of a molecule. Experiments of the second kind were devised to extract this information but they have, as yet, been only partially successful. What most of these experiments observe, is the over-all effect of a large number of collisions producing various changes in the state of the molecule; it is difficult to devise an experiment which will single out one collision or one type of collision and study its consequences in detail. This situation is also no better from the theoretical point of view. A theoretical investigation of collisions depends on a knowledge of the forces of interaction between molecules and on a subsequent formulation of a rigorous theory which relates to the experimental results. Unfortunately, the finer details of interaction potential are only partially understood.[22] The formulations of rigorous theories for most of the collisional phenomena have been done, but they have the drawback that they are not in an easily computable form so as to make them more meaningful. The theories which have been put in computable form, involve certain approximation methods which have limited validity. The problem is further complicated due to the possibility of simultaneous collision between three or more molecules. Thus molecular collisions present a challenging problem to experimentalists as well as to theoreticians.

Discussion in this paper will be restricted to binary or two-body collisions and to the way they influence lineshapes in pure rotational spectra at low pressures. The term collision will be used to refer to the subtle encounters where two molecules pass each other with a fairly large distance between them and while doing so, they undergo a change either in their translational state of motion or in their internal energy state, which is expressed in terms of the electronic state, the vibrational state, and the rotational state. Most molecular collisions at room temperature or moderate temperatures are very low energy collisions and are not able to produce any electronic or vibrational excitation of the molecule. They do, however, induce changes in the rotational states of colliding molecules and are sometimes accompanied by small changes in their translational motion. Rotational changes occur in two forms:

(i) the rotational phases of the molecules may be changed while their rotational energies may remain unchanged; these collisions are known as *elastic* or *adiabatic* collisions.

(ii) the rotational energy may change as a result of a transition from one rotational state to another; these collisions are known as *inelastic* or *non-adiabatic* collisions.

In general, both the collision-induced phase shifts and the collision-induced transitions influence various gaseous properties mentioned in the beginning, although their relative importance varies in each case. There has not been any

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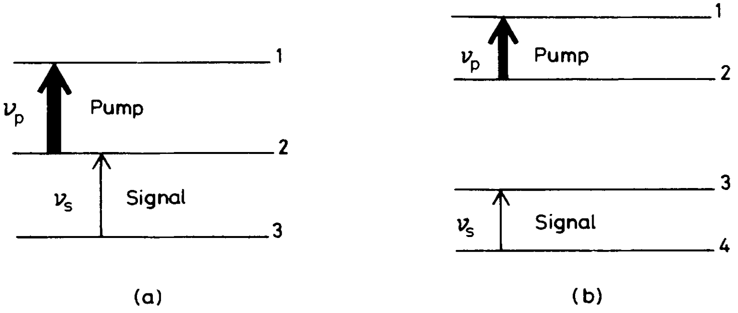
[22] J. O. Hirschfelder, *J. Chem. Phys.*, 1965, **43**, S199.

direct study of collision-induced phase shifts. Direct studies of collision-induced transitions have, of course, been attempted in recent years. A brief description of these experiments and their important conclusions is given in the following section.

## 2 Collision-induced Transitions

Consider an assembly of gaseous molecules. The molecules are constantly undergoing collisions and, in general, making transitions. However, the system as a whole is in a steady state having an equilibrium distribution of molecules among various rotational states. As such, these transitions can not be monitored directly. However a disturbance can be introduced into one of the rotational levels, where its effect on the neighbouring levels can be monitored and ascribed to collision-induced transfer of molecules. Two such methods have been developed. They are based on four-level double resonance studies[16,17] and optical fluorescence studies.[19] Besides these, another very elegant method involving molecular beams[20,21] has been used for a direct study of collision-induced transitions.

**A. Four-level Double Resonance Experiments.**—In a double resonance experiment[23,24] resonance absorptions due to two different transitions are observed simultaneously. Two types of double resonance experiments have been carried out: a three-level double resonance [Figure 1(a)], in which the two transitions have one energy level in common, and a four-level double resonance [Figure 1(b)] in which the four levels involved in the two transitions are all different.



(a) (b)

**Figure 1** *Energy level scheme used in a double resonance experiment (a) Three-level double resonance (b) Four-level double resonance*

In both cases, the experiment consists in pumping one of the transitions with high power radiation and observing its effect on the intensity of absorption due to the other transition. In the three-level double resonance experiments, the common energy level provides the necessary coupling between the two transitions. In the four-level double resonance experiment, however, the two

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[23] A. Battaglia, A. Gozzini, and E. Polacco, *Nuovo Cimento*, 1959, **14**, 1076.
[24] T. Yajima and K. Shimoda, *J. Phys. Soc. Japan*, 1960, **15**, 1668.

transitions do not have any common level and the only way they may be coupled is by means of collision-induced transitions. Pumping the transition 2 → 1 of frequency, say $\nu_p$, results in a highly non-Boltzmann population in levels 1 and 2. In the extreme case of saturation, the populations in levels 1 and 2 are equalized. This non-Boltzmann population is partially transferred to the neighbouring levels by way of collision-induced transitions until a new steady state is reached. Under these conditions, populations in levels 3 and 4 become $(n_3 + \delta n_3)$ and $(n_4 + \delta n_4)$ respectively where $n_3$ and $n_4$ are the normal Boltzmann populations and $\delta n_3$ and $\delta n_4$ are the deviations introduced by the pumping. The intensity $I$ of the signal transition 4 → 3 which depends on the population difference between levels 4 and 3, also changes by an amount $\Delta I$ such that

$$\frac{\Delta I}{I} = \left\{ \frac{\delta n_4 - \delta n_3}{n_4 - n_3} \right\}. \qquad (1)$$

Although the deviations $\delta n_4$ and $\delta n_3$ are small compared to $n_4$ and $n_3$, the value of $(\Delta I/I)$ can be relatively large because the denominator in equation (1) is also small.

An attempt to measure this ratio was first made by Cox, Flynn, and Wilson[16] in 1965, but it was unsuccessful because of an unsuitable choice of the levels and the low sensitivity of the instrument. The first successful experiment was done by Oka[17] in 1966 for the $C_2H_4O$ molecule, and was followed by a series of experiments[18,25-38] for a very wide variety of systems.

Figure 2 shows the block diagram of the apparatus used in Oka's experi-

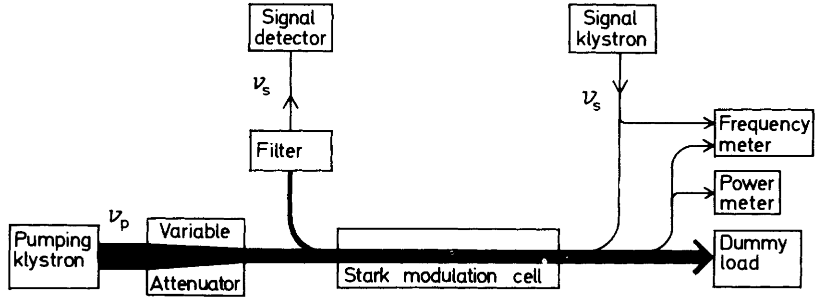

**Figure 2** *Block diagram of a double resonance apparatus*

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[25] T. Oka, *J. Chem. Phys.*, 1967, **47**, 13.
[26] T. Oka, *J. Chem. Phys.*, 1967, **47**, 4852.
[27] T. Oka, *J. Chem. Phys.*, 1968, **48**, 4919.
[28] T. Oka, *J. Chem. Phys.*, 1968, **49**, 3135.
[29] R. M. Lees and T. Oka, *J. Chem. Phys.*, 1969, **51**, 3027.
[30] P. W. Daly and T. Oka, *J. Chem. Phys.*, 1970, **53**, 3272.
[31] A. R. Fabris and T. Oka, *J. Chem. Phys.*, 1972, **56**, 3168.
[32] J. M. Roger, S. M. Freund, K. M. Evenson, and T. Oka (private communication).
[33] A. M. Ronn and E. B. Wilson, jun., *J. Chem. Phys.*, 1967, **46**, 3262.
[34] G. Roussy, J. Demaison, and J. et Baniol, *Compt. rend.*, 1969, **269**, 1080.
[35] M. Takami and K. Shimoda, *Japan. J. Appl. Phys.*, 1971, **10**, 658.
[36] P. J. Seibt, *J. Chem. Phys.*, 1972, **57**, 1343.
[37] L. Frenkel, H. Marantz, and T. Sullivan, *Phys. Rev. (A)*, 1971, **3**, 1640.
[38] J. B. Cohen and E. B. Wilson, jun., *J. Chem. Phys.*, 1973, **58**, 442; 1973, **58**, 456.

ments.[17,25] A high power microwave source provides the pumping radiation. Signal radiation is fed in the opposite direction from one of the standard low power microwave sources. The signal detector directly records the relative change in the intensity of signal line. It might be mentioned that effective pumping and good filtering of signal power from pump power are crucial to the success of the experiment. For further details of the experiment, reference can be made to the original papers, cited previously. However, the important results and conclusions are summarized below.

**Table 1** *Observed values of* $(\Delta I/I)$ *for some systems*[a]

| *Molecule* | *Pumping transition* | *Signal transition* | $\Delta I/I$ (%) |
|---|---|---|---|
| $H_2CO$ | $10_{29} \rightarrow 10_{28}$ | $9_{29} \rightarrow 9_{28}$ | $-30.7 \pm 2$ |
| | | $8_{27} \rightarrow 8_{26}$ | $-14.5 \pm 2$ |
| | $18_{3,16} \rightarrow 18_{3,15}$ | $17_{3,15} \rightarrow 17_{3,14}$ | $-22.0 \pm 2$ |
| | | $16_{3,14} \rightarrow 16_{3,13}$ | $-8.8 \pm 2$ |
| HDCO | $15_{3,13} \rightarrow 15_{3,12}$ | $14_{3,12} \rightarrow 14_{3,11}$ | $-21.3 \pm 2$ |
| | | $13_{3,11} \rightarrow 13_{3,10}$ | $-16.9 \pm 2$ |
| | $22_{4,19} \rightarrow 22_{4,18}$ | $21_{4,18} \rightarrow 21_{4,17}$ | $-14.4 \pm 2$ |
| | | $20_{4,17} \rightarrow 20_{4,16}$ | $-5.7 \pm 2$ |
| HCN | $J = 12$ doublet | $J = 11$ doublet | $-31.6 \pm 3$ |
| | | $J = 10$ doublet | $-21.0 \pm 3$ |
| | | $J = 9$ doublet | $-19.4 \pm 3$ |
| | | $J = 8$ doublet | $-14.0 \pm 3$ |
| DCN | $J = 13$ doublet | $J = 12$ doublet | $-26.4 \pm 2$ |
| | | $J = 11$ doublet | $-19.3 \pm 2$ |
| | | $J = 10$ doublet | $-17.7 \pm 2$ |
| | | $J = 9$ doublet | $-14.5 \pm 2$ |
| $H_2CCO$ | $13_{1,13} \rightarrow 13_{1,12}$ | $12_{1,12} \rightarrow 12_{1,11}$ | $-20.7 \pm 2$ |
| | | $11_{1,11} \rightarrow 11_{1,10}$ | $-13.8 \pm 2$ |
| | | $10_{1,10} \rightarrow 10_{19}$ | $-7.6 \pm 2$ |
| | | $9_{19} \rightarrow 9_{18}$ | $-5.4 \pm 2$ |

[a] Ref. 25

Experimentally measured values of the relative change in intensity $(\Delta I/I)$ for some of the systems studied by this method are given in Tables 1 and 2. An examination of these and other values listed in the original papers leads us to the following conclusions:

(i) collisions do provide substantial coupling between molecular rotational levels as is clear from the large values of $(\Delta I/I)$ for many systems;

(ii) collisional transitions are not random, but have definite preferences;

(iii) the preference varies from system to system resulting in a positive $\Delta I$ for some systems and negative for others;

**Table 2** *Calculated transition-rates and* $(\Delta I/I)$ *for the four-level systems in ammonia*

| *System* $(J, K)_p$–$(J', K')_s$ | *Transition-rate* (MHz/Torr)[a] | | | | | | | $(\Delta I/I)$ (%) | |
|---|---|---|---|---|---|---|---|---|---|
| | $k_{\alpha}\uparrow$ | $k_{\alpha'}\downarrow$ | $k_{\beta}$ | $k\gamma\uparrow$ | $k\gamma'\downarrow$ | $k_{\xi 1}$ | $k_{\xi 2}$ | *Calc.*[a] | *Exptl.*[b] |
| (4, 1)–(3, 1) | 14.75 | 11.50 | 23.37 | 4.51 | 5.44 | 6.62 | 9.44 | 9.83 | 8.22 ± 0.5 |
| (5, 2)–(4, 2) | 13.91 | 14.28 | 37.76 | 7.09 | 9.80 | 3.06 | 7.79 | 4.87 | 4.62 ± 0.5 |
| (6, 3)–(5, 3) | 10.83 | 15.39 | 48.52 | 7.31 | 12.96 | 1.66 | 5.01 | 2.17 | 1.91 ± 0.4 |
| (5, 1)–(4, 1) | 17.06 | 18.76 | 16.47 | 3.79 | 5.75 | 3.73 | 12.74 | 13.14 | 8.81 ± 0.5 |
| (8, 2)–(7, 2) | 9.41 | 22.58 | 22.16 | 2.97 | 8.02 | 0.89 | 5.10 | 6.24 | 3.75 ± 0.5 |
| (8, 1)–(7, 1) | 11.03 | 27.00 | 9.90 | 1.64 | 4.38 | 1.01 | 6.22 | 11.95 | 7.40 ± 1 |
| (3, 1)–(2, 1) | 11.84 | 7.40 | 36.81 | 5.83 | 6.18 | 10.53 | — | 5.01 | 4.4 ± 0.2 |
| (4, 2)–(3, 2) | 12.72 | 8.64 | 54.83 | 8.93 | 8.55 | 5.23 | — | 2.34 | 2.5 ± 0.2 |
| (5, 3)–(4, 3) | 12.06 | 10.78 | 64.65 | 10.16 | 11.87 | 2.66 | — | 1.01 | 2.0 ± 0.2 |
| (6, 4)–(5, 4) | 9.60 | 11.77 | 72.59 | 9.10 | 13.89 | 1.45 | — | 0.24 | 1.6 ± 0.2 |
| (7, 5)–(6, 5) | 8.46 | 11.01 | 79.48 | 8.60 | 13.44 | 0.86 | — | −0.06 | 0.9 ± 0.2 |
| (8, 6)–(7, 6) | 5.90 | 10.83 | 85.95 | 6.29 | 13.64 | 0.55 | — | −0.17 | 0.6 ± 0.2 |
| (2, 1)–(1, 1) | 10.77 | — | 74.56 | 9.00 | — | 13.22 | — | 0.95 | 1.5 ± 0.2 |
| (3, 2)–(2, 2) | 11.00 | — | 94.29 | 11.06 | — | 8.22 | — | −0.03 | 1.2 ± 0.2 |
| (4, 3)–(3, 3) | 12.14 | — | 104.50 | 13.36 | — | 4.38 | — | −0.49 | 1.1 ± 0.2 |
| (5, 4)–(4, 4) | 11.95 | — | 112.28 | 13.90 | — | 2.36 | — | −0.72 | 0.8 ± 0.2 |
| (6, 5)–(5, 5) | 9.92 | — | 119.08 | 11.87 | — | 1.35 | — | −0.69 | 0.63 ± 0.2 |
| (7, 6)–(6, 6) | 8.77 | — | 124.32 | 10.74 | — | 0.87 | — | −0.67 | 0.35 ± 0.2 |

[a] Ref. 39, [b] Ref. 27.

[39] V. Prakash and J. E. Boggs, *J. Chem. Phys.*, 1974, **60**, 2163.

(iv) collisional transitions with $|\Delta J| > 1$ can also occur even though their probabilities may be small;

(v) probabilities of collisional transitions depend on the collision-partners-rotational states involved *etc.*

These experiments establish the existence of certain selection rules for collision, induced transitions and indicate the dependence of transition matrix elements on the collision-partners, rotational states *etc.* In order to gain more specific information regarding these selection rules and the probabilities of allowed transitions, experimental studies must be supplemented by some theoretical calculations. The general procedure followed is to assume an interaction potential and a set of selection rules, calculate the values of $(\Delta I/I)$, and compare them with the measured values. These calculational methods have been developed and used by Prakash and Boggs.[40]

The energy level scheme commonly employed for such experiments consists of symmetrically split levels (*e.g.* *l*-type doublets in HCN and DCN, *k*-type doublets in $H_2CO$, $H_2CCO$ *etc.*, inversion doublets in ammonia, rotation-tortion doublets in $CH_3OH$ *etc.*) as shown in Figure 3. Assuming that the colli-

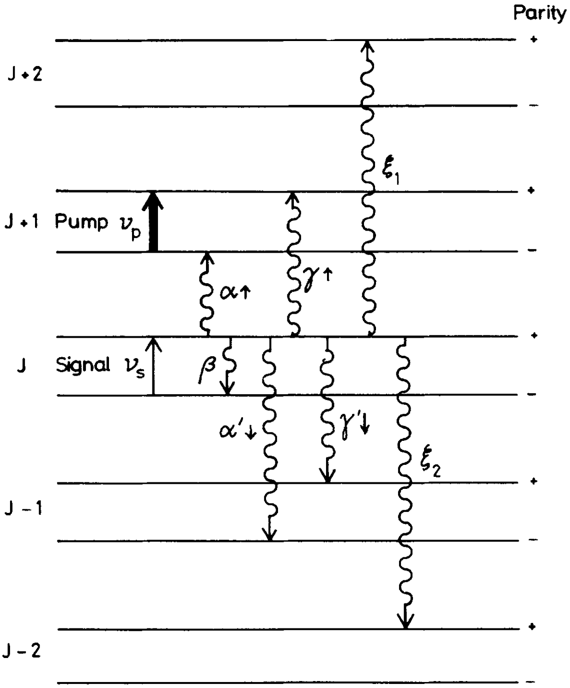

**Figure 3** *Energy level scheme relevant to a four-level double resonance experiment. Collisional transitions are shown by wavy arrows, while radiative transitions by solid arrows*

[40] V. Prakash and J. E. Boggs, *J. Chem. Phys.*, 1972, **57**, 2599.

sion-induced transitions obey the same selection rules as the radiation-induced transitions, the allowed collisional transitions for dipolar interaction are shown as $\alpha\uparrow$, $\alpha'\downarrow$ and $\beta$ corresponding to $\Delta J = +1, -1$, and 0, parity $+ \rightarrow -$. The relative intensity change $(\Delta I/I)$ can be expressed in terms of the rates at which these transitions occur and is given by[25]

$$\frac{\Delta I}{I} = \frac{\nu_p}{\nu_s} \cdot \frac{k_{\alpha\uparrow}}{k_{\alpha\uparrow} + k_{\alpha'\downarrow} + 2k_\beta}, \tag{2}$$

where $k$'s represent various transition rates. These rates can be calculated theoretically[40] provided that the transition matrix elements are known. The values of $(\Delta I/I)$ derived from equation (2) using theoretical values of transition rates totally disagreed with experimental values. This suggests the possibility of additional transitions which might be induced by a collision perhaps as a second order effect. The second order transitions that have been considered are those with $\Delta J = \pm 1$, parity $\pm \rightarrow \pm$ and those with $\Delta J = \pm 2$, parity $\pm \rightarrow \pm$. These transitions are shown in Figure 3 as $\gamma\uparrow$, $\gamma'\downarrow$, $\xi_1$ and $\xi_2$, respectively. Considering these additional transitions, equation (2) is modified to

$$\frac{\Delta I}{I} = \frac{\nu_p}{\nu_s} \cdot \frac{k_{\alpha\uparrow} - k_{\gamma\uparrow}}{k_{\alpha\uparrow} + k_{\alpha'\downarrow} + k_{\gamma\uparrow} + k_{\gamma'\downarrow} + 2k_\beta + k_{\xi1} + k_{\xi2}} \tag{3}$$

The mechanism for second-order transitions is not completely known. They can occur by one or more of the following processes:

(i) two successive dipolar transitions occurring in quick succession so as to take place within the duration of one collision;

(ii) one single transition caused by the quadrupolar interaction;

(iii) one single transition caused by an induction interaction.

In general, all the three processes will contribute to the second-order transitions. Using a second-order perturbation theory, Rabitz and Gordon[41] have estimated for HCN that the first process is the dominant one. It has been assumed that this is also a valid assumption for other molecules. Thus, for example, a collision-induced transition from a state $J = 4$ to a state $J = 6$ is treated by using a matrix element which is a product of the dipole matrix elements for $J = 4 \rightarrow 5$ and for $J = 5 \rightarrow 6$.

The values of transition rates and $(\Delta I/I)$ calculated from equation (3) for four level systems in pure ammonia are given in Table 2 along with the experimental values of $(\Delta I/I)$. It is seen that the agreement is very good in some cases, satisfactory in others while completely unsatisfactory in others still. An overall review of the results suggests the following conclusions.

The collision-induced transitions do not seem to obey very rigid selection rules.

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[41] H. A. Rabitz and R. G. Gordon, *J. Chem. Phys.*, 1970, **53**, 1831.

Those transitions which are allowed by the selection rules for relevant radiation-induced transitions, are preferentially induced. For example, if collisional interaction involves the dipole moment of the molecule, the dipolar transitions $\Delta J = 0, \pm 1$, parity $\pm \rightarrow \mp$ have a preference. However, if the collision is strong enough, other transitions, *e.g.* $\Delta J = \pm 1$, parity $\pm \rightarrow \pm$ and $|\Delta J| > 1$ may also be weakly allowed. The transitions with $|\Delta J| > 1$ have been experimentally observed using the methods of triple resonance[42] and multiple resonances.[29] Theoretically also the matrix element for a multistep transition $n \rightarrow m \rightarrow k$ *etc.* is not negligibly small in many cases.

**B. Optical Fluorescence Experiment**[19,43–51]—It is possible to produce molecules in a single quantum state with specified electronic, vibrational, and rotational quantum numbers by absorption of monochromatic radiation which could be either a sharp emission line or a laser line that happens to coincide with the molecular absorption line. These excited molecules undergo a series of collisions with each other and with the molecule of their thermal bath. At each collision, they make transitions to other vibrational and rotational levels within the same electronic state. The sequence is terminated when the molecule loses its electronic excitation in a strong collision or by spontaneous emission giving fluorescence radiation. The whole process is shown in Figure 4.

The wavelength of fluorescence radiation will depend on the rotational and vibrational state from which the emission takes place and its intensity will depend on the population in that state. Thus from an analysis of the fluorescence spectrum, it is possible to determine the population distribution among various rotational and vibrational states of the excited electronic state. It has been found that the probability of collisional transfer of rotational energy is much more than that of vibrational energy even in the excited electronic state.

The observed distribution of molecules among various rotational states has to be attributed to collisional transitions and it can be interpreted in terms of various transition rates. This, in general, is a very difficult task, mainly because transitions are not restricted to nearest neighbour jumps. The practical approach followed in these studies is to assume a set of collisional transitions, calculate the rotational distribution on this basis and compare it with the observed distribution.

It was found that the observed rotational distributions are not consistent with the optical selection rule $\Delta J = 0 \pm 1$ and transitions with $|\Delta J| > 1$ are also

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[42] R. M. Lees and T. Oka, *J. Chem. Phys.*, 1968, **49**, 4234.
[43] T. Carrington, *J. Chem. Phys.*, 1961, **35**, 807.
[44] H. P. Broida and T. Carrington. *J. Chem. Phys.*, 1963, **38**, 136.
[45] J. I. Steinfeld and W. Klemperor, *J. Chem. Phys.*, 1965, **42**, 3475.
[46] K. M. Evenson and H. P. Broida, *J. Chem. Phys.*, 1966, **44**, 1637.
[47] C. Ottinger, R. Velasco, and R. N. Zare, *J. Chem. Phys.*, 1970, **52**, 1636.
[48] C. Ottinger and D. Poppe, *Chem. Phys. Letters*, 1971, **8**, 513.
[49] D. L. Akins, E. H. Fink, and C. B. Moore, *J. Chem. Phys.*, 1970, **52**, 1604.
[50] E. H. Fink, D. L. Akins, and C. B. Moore, *J. Chem. Phys.*, 1972, **56**, 900.
[51] K. Sakurai, S. E. Johnson, and H. P. Broida, *J. Chem. Phys.*, 1970, **52**, 1625.

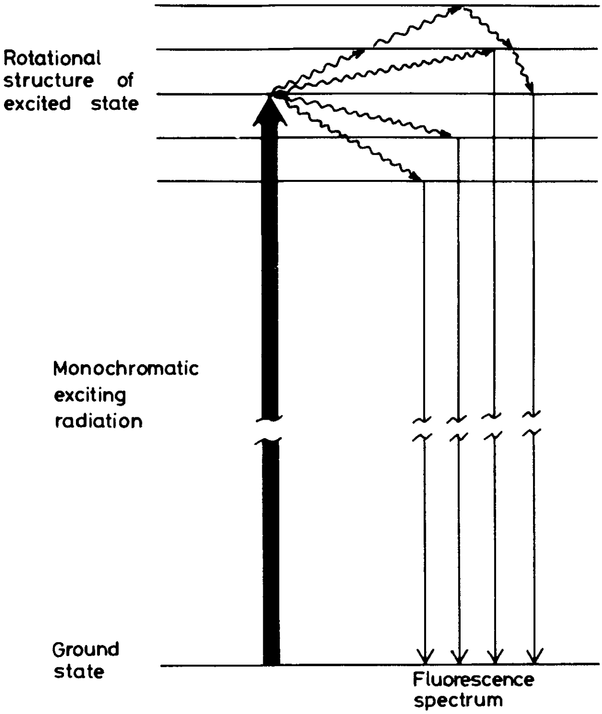

**Figure 4** *Monochromatically excited fluorescence spectrum. Collisional transitions are shown by wavy arrows while radiative transitions by solid arrows*

important. In some systems, transitions with $|\Delta J|$ as large as 5 are also indicated. More definite selection rules are difficult to derive from these studies.

These studies are complementary to the studies described in the previous section in the sense that they enable us to study the collisional transitions in the excited electronic state and also to study non-polar molecules. Practical difficulties in these experiments arise due to the exact coincidence required between the molecular absorption line and the monochromatic exciting radiation. With the advent of tunable lasers, it should be possible to overcome this difficulty. The other drawback in the method is that the lifetime of the excited state cannot be controlled. If this is too long, some of the molecules might undergo many collisions before giving out fluorescence radiation. Further, all molecules do not undergo the same number of collisions. In such cases, the detailed features of the collision-induced transitions do not show up in the fluorescence spectrum.

**C. Molecular Beam Experiments.**[20,21]—In this method, the collision cross-section for a single specified rotational transition is measured in a molecular beam apparatus. The schematic arrangement is shown in Figure 5. An inhomogeneous electrostatic field set up by a four pole[20] acts as a state selector. With

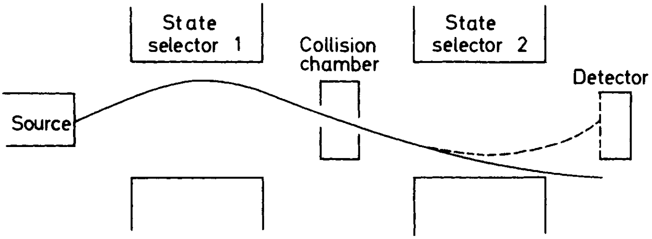

**Figure 5** *Schematic diagram of a molecular beam apparatus for the study of collision-induced rotational transitions*

this field, molecules in a specified rotational state are separated out of a molecular beam. These are then focused into a collision chamber containing another gas. Molecules which are scattered by a small angle are then collected in a second inhomogeneous field and are analysed for their rotational states. The main advantage of this method is that the analysis yields a single transition probability. However, the experimental difficulties involved in the technique limit the applicability of this method.

## 3 Rotational Lineshapes at Low Pressures

Out of the various collisional phenomena mentioned in the introduction, spectral lineshapes have received wide attention because practical engineering applications as well as basic physical interests are involved. The subject has been reviewed from time to time.[5-7] This section will, therefore, emphasize only the recent developments with brief critical remarks about the previous work.

Rotational lineshapes under most laboratory conditions are attributable to molecular collisions. The collisions, in general, induce rotational transitions as well as rotational phase shifts. However, since the average kinetic energy of molecules at room temperature exceeds the rotational splittings in the microwave region, collisional transitions in microwave region are highly probable and should account for the dominant contribution to the microwave linewidths. This implies that the selection rules for collision-induced transitions must be known before any specific calculation of lineshapes can be made. Theories show that the linewidth of any transition $i \rightarrow f$ does not involve the probabilities of individual transitions $i \rightarrow i'$ or $f \rightarrow f'$, but the sum of probabilities of transitions from $i$ and $f$ to all possible levels $i'$ and $f'$, *i.e.*, the sum $\sum_{i'f'} \{\langle P_{ii'}\rangle + \langle P_{ff'}\rangle\}$. Thus only the total probability of transition out of a certain level is needed. Under these conditions, the assumption of optical selection rules for collisional transitions is a reasonable approximation as explained below. The various transitions are competitive; one occurs at the cost of the other. As such, considering only the first-order transitions would amount to neglect of higher order transitions while overestimation of the first-order transitions; the total transition probability out of the level might not be substantially altered. Therefore, considering only the first-order transitions has been the universal practice in linewidth calculations.

The theories for low pressure lineshapes can be divided into two groups:

(i) perturbation theories,

(ii) non-perturbative theories.

Perturbation theories have the advantage that they can be put in an easily computable form. The two theories which have been mostly used are the Anderson theory[52-54] and the Murphy–Boggs theory.[55,56] The details of these theories can be seen either in the original papers or in the previous reviews.[5-7,57] Anderson's theory has the advantage of incorporating collision-induced transitions as well as collision-induced phase shifts in the theory. The width is given as[7]

$$\Delta\nu = \frac{1}{4\pi}\,\rho\,[\langle v\sigma_i\rangle + \langle v\sigma_f\rangle] + \rho\langle v\sigma_{if}\rangle\,, \tag{4}$$

where $\rho$ is the number density of perturber molecules, $\sigma_i$ and $\sigma_f$ are the total cross-sections for transitions out of the levels $i$ and $f$, respectively, and $\sigma_{if}$ is related to the phase shifts. This theory, however, has a drawback that an arbitrary interpolation scheme has to be used for the interruption function $S_2(b)$ in the regions where perturbation theory is not valid. Anderson suggested three different schemes:

(1) $\{1 - \cos[2\,S_2(b)]^{\frac{1}{2}}\}$ to be used in place of the function $S_2(b)$,

(2) The perturbation theory expression for $S_2(b)$ is used for $b$ from $\infty$ down to $b_0$ defined by $S_2(b_0) = 1$. From $b_0$ to 0, $S_2(b)$ is assumed to be unity.

(3) $\{1 - \exp[-2\,S_2(b)]\}$ is used in place of the function $S_2(b)$. The second scheme has been almost always used even though none of the three has any rigorous justification. An analysis of the expression will show that it can exceed unity at small $b$ values and is likely to oscillate in that region.[7] With this in mind, scheme (1) is qualitatively more correct. Johri and Srivastava[58] have recently suggested an alternative interpolation scheme in which the function

$$\{1 - \exp[-S_2(b)]\}$$

is used in place of the function $S_2(b)$. They used this scheme to calculate the foreign gas broadening of OCS and $CH_3{}^{81}Br$ lines by nonpolar perturbers[59] and obtained better agreement with experiments. Their scheme is better in the

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[52] P. W. Anderson, *Phys. Rev.*, 1949, **76**, 647.

[53] C. J. Tsao and B. Curnutte, jun., *J. Quant. Spectroscopy. Radiative Transfer*, 1962, **2**, 41.

[54] Krishnaji, Research Report No. 3, Microwave Laboratory, Department of Physics, University of Allahabad, India (December 1964).

[55] J. S. Murphy and J. E. Boggs, *J. Chem. Phys.*, 1967, **47**, 691; 1967, **47**, 4152; 1968, **49**, 3333; 1969, **50**, 3320; 1969, **51**, 3891; 1971, **54**, 2443.

[56] J. E. Boggs, 'Molecular Spectroscopy: Modern Research' ed. K. Narahari Rao and C. Weldon Mathews, Academic Press, New York, 1972, p. 49.

[57] P. R. Berman, *Appl. Phys.*, 1975, **3**, 283.

[58] G. K. Johri and S. L. Srivastava, *Chem. Phys. Letters*, 1976, **39**, 579.

[59] G. K. Johri and S. L. Srivastava, *Ind. J. Pure Appl. Phys.*, 1976, **14**, 917.

sense that a theoretical justification[60] has also been obtained whilst the three schemes suggested in Anderson's original paper were quite arbitrary.

The Murphy–Boggs theory,[55] although not a conventional perturbation method, is a first-order treatment. The width is given as

$$\Delta\nu = \frac{1}{4\pi}\rho[\langle v\sigma_i\rangle + \langle v\sigma_f\rangle]\,. \tag{5}$$

The effects of collision-induced phase shifts are thus ignored. This has been considered as a reasonable approximation for pure rotational linewidths in the microwave region of the spectrum. However, a recent calculation[61] and several experimental observations of pressure-induced shifts in the microwave region clearly indicate that the effects of collision-induced phase shifts even in the microwave region are not completely negligible. The Murphy–Boggs theory has a clear advantage over the Anderson theory in that no arbitrary interpolation schemes are needed and a smooth transition from large $b$ to small $b$ is obtained as a natural consequence of the theory. The theory has recently been extended by Mehrotra and Boggs[62] to include the higher order multipole interactions and also to be applicable to the rotational lines in the excited vibrational states in the infra-red region.

Neither of the two theories discussed above is able to explain satisfactorily the quantum number dependence of rotational linewidths.[63]

Pressure-induced shifts of microwave spectral lines have received much less attention than widths, primarily because they are expected to be small and their measurement is difficult. Until 1971, the only measurements reported were those by Matsuura[64] and Shimoda[65] for the ammonia inversion line and these were detected while working with the ammonia maser. In 1971, Story *et al.*[66] reported systematic measurements of the shifts of $(J, K) = (12, 12)$ inversion line of $NH_3$ perturbed by $NH_3$, He, Ar, OCS, $CO_2$, $N_2$, $CH_3CN$, $CH_3F$, and $CH_4$. They used a highly sensitive microwave spectrometer designed for the purpose and obtained negative shifts ranging from 1—25% of the linewidth in the various cases. The shifts of rotational lines were first measured by Luijendijk[67] for $J\ 0 \rightarrow 1$ line of $CH_3Cl$ and $J\ 1 \rightarrow 2$ and $2 \rightarrow 3$ lines of OCS. Hewitt and Parsons[68] also measured the shifts of ammonia inversion lines* and $CH_3Cl$ and OCS rotational lines.

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* Shifts of ammonia inversion lines have also been measured (R. K. Kakar and R. L. Poyntor, *J. Mol. Spectroscopy*, 1975, **54**, 475), and calculated theoretically (K. Tanaka, S. C. Mehrotra, and J. E. Boggs, *J. Amer. Chem. Soc.*, in press).

[60] G. K. Johri and S. L. Srivastava, *Chem. Phys. Letters*, 1977, **45**, 364.

[61] J. Jarecki and R. M. Herman, *J. Quant. Spectroscopy. Radiative Transfer*, 1975, **15**, 707.

[62] S. C. Mehrotra and J. E. Boggs, *Indian J. Pure Appl. Phys.* (in press).

[63] See the earlier reviews on the subject or, for example, G. P. Srivastava and D. Kumar, *J. Phys. B; Atom. Molec. Phys.*, 1976, **9**, 651.

[64] K. Matsuura, Y. Sugiura, and G. M. Hatoyama, *J. Phys. Soc. Japan*, 1957, **12**, 314.

[65] K. Shimoda, *J. Phys. Soc. Japan*, 1957, **12**, 558.

[66] I. C. Story, V. I. Metchnik, and R. W. Parsons, *J. Phys. B; Atom. Molec. Phys.*, 1971, **4**, 593; *Phys. Letters (A)*, 1971, **34**, 59.

[67] S. C. M. Luijendijk, Ph.D. dissertation, University of Utrecht, The Netherlands (December 1973).

[68] P. L. Hewitt and R. W. Parsons, *Phys. Letters (A)*, 1973, **45**, 21.

MacGillivray[69] has very recently modified the spectrometer used by Story *et al.*[66] and has measured shifts of rotational lines of $CH_3Cl$, OCS, $CH_3I$, $CH_3CN$, and $CH_3OH$.

Parsons *et al.*[70] attempted to explain the observed shift of the ammonia inversion line on the basis of Anderson's theory. They found that this theory allows no contribution for lineshifts from multipolar interactions. The induction, dispersion, and exchange interactions do make a finite contribution provided that the dipole moment and/or polarizability of the ammonia molecule change when the molecule makes a transition.* Even after an approximate estimate of this change, experimental agreement is not good.

Frost[71] has recently extended Anderson's theory to permit calculations of shifts of spectral lines arising from multipolar interactions. The theory has been used to calculate the widths and shifts of several ammonia inversion lines broadened by $NH_3$, OCS, and $CH_3Cl$ and of self-broadened $CH_3Cl$ $J$ 0 → 1 and OCS 1 → 2 rotational lines. The agreement with measured widths and shifts is not good, though the sign and the order of magnitude of lineshifts have been correctly obtained. The disagreements have been attributed to the cut off procedure used for the interruption function $S_2(b)$.

A significant advance in the theoretical formulation for the lineshape problem has been made very recently by Mehrotra and Boggs.[72] This is a more general theory in which the effects of collision-induced transitions as well as collision-induced phase shifts have been considered in a more rigorous way. It was shown that the two earlier theories are limiting cases of this theory. This theory has been applied very successfully to the rotational transitions in OCS. Its success in explaining the quantum number dependence of OCS linewidths is particularly noteworthy. Further, the lineshifts have also been predicted to the correct order of magnitude.

The non-perturbative theories of lineshapes can be fully quantum-mechanical,[73] semiclassical,[74,75] or classical.[76] The quantum-mechanical theory is obviously the more appropriate one, but the calculations become much more involved and are not feasible except for the simplest systems. On the other hand, fully classical treatments have the disadvantage that any quantum effects do not show up. The semiclassical treatments constitute a compromise between the two. In all of these, the translational degrees of freedom are treated classically while the internal degrees of freedom are treated quantum mechanically. The recent treatment by Mehrotra and Boggs[75] reveals important information

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* This was later found to be incorrect by Frost (ref. 71).

[69] W. R. MacGillivray, *J. Phys. B; Atom. Molec. Phys.*, 1976, **9**, 2511.

[70] R. W. Parsons, V. I. Metchnik, and I. C. Story, *J. Phys. B: Atom. Molec. Phys.*, 1972, **5**, 1221.

[71] B. S. Frost, *J. Phys. B; Atom. Molec. Phys.*, 1976, **9**, 1001.

[72] S. C. Mehrotra and J. E. Boggs, *J. Chem. Phys.*, 1977, **66**, 5306.

[73] C. O. Trindle and K. H. Illinger, *J. Chem. Phys.*, 1968, **48**, 4415.

[74] H. A. Rabitz and R. G. Gordon, *J. Chem. Phys.*, 1970, **53**, 1815.

[75] S. C. Mehrotra and J. E. Boggs, *J. Chem. Phys.*, 1975, **62**, 1453.

[76] H. J. Liebe, M. C. Thompson, jun., and T. A. Dillon, *J. Quant. Spectroscopy. Radiative Transfer*, 1969, **9**, 31.

regarding the transition probabilities during a strong collision. In a strong collision, as the molecules move closer, the transition probability out of the level increases rapidly until the population in the coupled states has increased sufficiently and the molecules are then transferred back into the initial state. Thus the transition probability out of the level, averaged over the entire trajectory of the molecule, could be small in a strong collision, contrary to the widely held assumption that it is unity. This could have a strong impact on the calculated linewidths and could perhaps explain the discrepancies between experimental and theoretical widths where strong collisions are involved.

Among the recent experimental developments for studying rotational lineshapes, mention may be made of microwave refraction spectroscopy,[76] balanced bridge spectrometry,[66] lineshape fit method,[77] and transient nutation spectroscopy.[78]

In refraction spectroscopy, the linewidth is derived from pressure-dependence of the real part of the refractive index of the gas. This method has several advantages[6] over the conventional absorption spectroscopy and has been used for finding the self- and foreign-gas broadened widths of $H_2O$ lines.[76,79,80]

In the balanced bridge spectrometer used by Story *et al.*,[66] a higher sensitivity is achieved by balancing out the effects of the standing waves in the absorption cell. Radiation from the klystron is passed through four identical waveguide cells in parallel. The cells are arranged in two pairs, one member of each pair being a dummy whose function is to balance out the effects of standing waves. In one of the other cells, the gas is introduced at a fixed pressure while in the fourth cell the pressure of the gas can be varied. The width is measured by the usual derivative method. The method is particularly suited for lineshift measurements which require high sensitivity. MacGillivray[69] has recently improved upon this spectrometer. Rectangular waveguide cells were used instead of the circular waveguide cells. This reduced the standing waves and the two dummy cells could be avoided without adversely affecting the sensitivity. Further, a double phase-lock-loop was used for stabilizing the klystron frequency. It has been claimed that with these improvements, shifts as small as 500 Hz could be measured at an operating frequency of 100 GHz.

The lineshape fit method approaches the problem in a more fundamental way. Most of the other methods assume a Lorentzian lineshape and then make use of one or two points on the observed line to compute the width. However, for a Lorentzian line, all the points on the line contain information about the lineshape parameters and it would be more appropriate to make use of all the points for deriving these parameters. The line can, therefore, be recorded point by point and fitted digitally to the Lorentzian lineshape function using the peak intensity and the linewidth as adjustable parameters for obtaining a least square fit. Some of the important sources of error in other measurements are the un-

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[77] D. S. Olson, C. O. Britt, V. Prakash, and J. E. Boggs, *J. Phys. B; Atom. Molec. Phys.*, 1973, **6**, 206.

[78] A. H. Brittain, P. J. Manor, and R. H. Schwendemann, *J. Chem. Phys.*, 1973, **58**, 5735.

[79] H. J. Liebe and T. A. Dillon, *J. Chem. Phys.*, 1969, **50**, 727.

[80] T. A. Dillon and H. J. Liebe, *J. Quant. Spectroscopy. Radiative Transfer*, 1971, **11**, 1803.

detected overlap of the observed line with neighbouring lines and with their stark lobes, excessive distortions due to the applied modulations *etc.* All these errors distort the lineshape and are readily detected if the entire line is fitted to the theoretical Lorentzian function though they might escape detection if only two points are being measured. The only difficulty with this method is that absorption has to be measured at a very large number of discrete frequencies. This is very time-consuming, however with the development of a computer-controlled spectrograph,[81] it should be possible to overcome this difficulty.

The experiments described earlier for lineshape studies are all in the frequency domain. A time-domain experiment has also been devised which can give information about the collisional relaxation. This is the transient-nutation spectroscopy in which the spectral line is monitored after passing a strong radiation pulse or after rapid stark switching of the spectral line through the frequency of observation. In either case, a damped ringing signal is observed. The damping is due to the collisional relaxation. It has been suggested that the transient-nutation decay rate is essentially the same as the linewidth although the measurements on OCS[78] and $NH_3$[82] show some discrepancy with the corresponding microwave determined timewidths. It needs to be ascertained whether the relaxation mechanisms involved in the two cases are the same.

*Note added in proof.* The good agreement obtained between perturbation theories and experimental results in several cases should be considered mainly as fortuitous. The perturbation theory involves underestimation of the function $S_2(b,v)$ for large impact parameters, the assumption of unity $S_2(b,v)$ is an overestimation as is clearly shown in the Mehrotra–Boggs theory.[75] Therefore, the two errors may cancel when averaging over all impact parameters. This may lead to very good agreement but the $J$-dependence and the temperature-dependence may still remain unexplained. The authors are thankful to Dr. S. C. Mehrotra for bringing out this point and for making his preprints available prior to publication.

[81] S. C. Mehrotra, Ph.D. dissertation, University of Texas, Austin, Texas, U.S.A. (May 1975).
[82] J. M. Levy, J. H. S. Wang, S. G. Kukolich, and J. I. Steinfeld, *Phys. Rev. Letters*, 1972, 29, 395.