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# QUARTERLY REVIEWS

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## THE INTERACTIONS OF SLOW ELECTRONS WITH MOLECULES

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### 1. Introduction

CHEMISTS have for long been interested in the behaviour of charged species: Faraday's laws of electrolysis, for example, are among the foundations of the subject. In time, however, although the study of electrical phenomena in solution became an important part of physical chemistry, the study of electrical phenomena in gases became largely the concern of physicists.<sup>1,2</sup> Present knowledge relating to one aspect of electrical phenomena in gases, the interaction of slow electrons with molecules, appears to have implications for our understanding of molecular behaviour which make it of interest to chemists. In particular, two phenomena, one first observed in the nineteen-twenties and the other in the nineteen-sixties, depend on the nature of molecular electronic states in a way which might lead to greater understanding of them, or at least provide additional tests for theories of molecular structure. These are first the Ramsauer-Townsend effect, in which certain gases are found to be remarkably transparent to electrons of specific (and quite low) energy, and secondly the existence of resonances with short-lived compound states of a molecule and an electron which may decay purely elastically, as with noble-gas atoms, or to give vibrationally excited molecules, as with carbon monoxide and nitrogen. We here give an introductory Review of the whole field of the interaction of slow electrons with molecules.

By slow electrons, we understand electrons with insufficient energy to cause ionisation. Such electrons may, in colliding with molecules, excite molecular electronic, vibrational, and rotational states, or may simply be deflected, leaving the molecule unchanged.

Although the picture of a molecule as a hard sphere with a constant cross-section is useful in considering many molecule-molecule collisions, it is inappropriate for electron-molecule interactions. This is because such interactions have a longer range than molecule-molecule interactions, and because the de Broglie wavelength of the electron (about a hundred times greater than that of a molecule with the same energy) is comparable with the range of the interaction. Thus the collision cross-section depends not only on the properties of the molecule but also on the velocity of the

<sup>1</sup> H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena", Oxford Univ. Press, London, 1952.

<sup>2</sup> J. B. Hasted, "Physics of Atomic Collisions", Oxford Univ. Press, London, 1964.

electron. Crudely, a fast electron and a slow electron "see" the molecule as having different sizes. An electron-molecule collision has been defined as follows: "An electron-molecule collision is said to have taken place if any physical change can be detected in the system after the distance between the electron and molecule has first decreased and then increased."

Collisions in which ions are not found can be divided into three kinds: (a) *elastic collisions*, in which the internal state of the molecule remains unchanged. Only kinetic energy is exchanged between electron and molecule, and conservation of momentum requires that the fractional energy lost by electrons (mass  $m$ ) in such collisions with molecules (mass  $M$ ), is about  $2m/M$ , or  $10^{-4}$ ; (b) *inelastic collisions*, in which the molecule gains internal energy from the electron; and (c) *superelastic collisions*, in which the reverse process occurs.

The probability of collision, as defined above, is expressed in terms of *collision cross-section*. Thus the probability,  $p$ , that an electron (of given velocity) will undergo a collision in travelling a distance  $x$  through a gas of number density  $N$  is given by

$$p = Q_T N x \quad (1)$$

where  $Q_T$  has the dimensions of area and is known as the total collision cross-section.  $Q_T$  may be split into elastic and inelastic components which are similarly defined and combine additively:

$$Q_T = Q_{el} + Q_{inel} \quad (2)$$

If one is interested in the angle of deflection of the electron, one can define a differential cross-section  $I(\Omega)d\Omega$  for scattering into an element of solid angle  $d\Omega$ . If  $\theta$  is the polar scattering angle and  $\phi$  the azimuthal angle,  $d\Omega = \sin \theta d\theta d\phi$ , and the total cross-section is just the differential cross-section integrated over the range of solid angle:

$$Q_T = \int_0^\pi \int_0^{2\pi} I(\theta, \phi) \sin \theta d\theta d\phi \quad (3)$$

The momentum transfer cross-section,  $Q_D$ , is defined by

$$Q_D = \int_0^\pi \int_0^{2\pi} I(\theta, \phi) (1 - \cos \theta) \sin \theta d\theta d\phi \quad (4)$$

When scattering is isotropic, that is, when  $I(\theta)$  is constant, which is true for sufficiently slow electrons,  $Q_D = Q_T$ . If there is preferential forward scattering  $Q_D < Q_T$  and if backward scattering predominates  $Q_D > Q_T$ . In some experiments,  $Q_D$  rather than  $Q_T$  is the measurable quantity.

These cross-sections describe an electron-molecule collision. Experiments are designed to measure them, and theories are conceived to predict or interpret them.

## 2. Methods of Study

Two main types of experimental technique are used to study electron-molecule interactions. These are electron-beam and electron-swarm methods.

In beam experiments, an electron beam with as small an energy spread as possible is passed through the gas under "single collision" conditions; that is, the gas pressure and the electron path are chosen so that no electron makes more than one collision. Measurement of attenuation of the beam leads to total cross-sections; measurement of scattered electron currents leads to differential cross-sections; and energy analysis of scattered electrons leads to inelastic cross-sections, which may also sometimes be detected by observation of excited molecules.

Beam experiments lead fairly directly to absolute or relative cross-sections, but they are particularly difficult to do at the low energies of interest in the molecular field. Even the best "monoenergetic" beams of energy of a few electron-volts (ev) have a spread of 0.04 ev (as much as 400  $\text{cm}^{-1}$  in optical terms). For single-collision conditions, a gas pressure of  $10^{-4}$ — $10^{-5}$  torr (mm.Hg) is required, which demands the use of the best high vacuum techniques, with pumping systems capable of  $10^{-9}$  torr. Moreover, single-collision conditions mean that most of the electrons do not suffer a collision at all, so that the observable effects are small.

In swarm experiments, an electron swarm or pulse travels through a gas under the influence of an electric field, under multiple-collision conditions. Information about collisions is derived from the transport properties of the swarm. Such experiments are simpler to do, but the interpretation of the measured quantities in terms of single-collision interactions is complicated.

Consider an electron swarm in a gas, electrons and molecules being in thermal equilibrium. An electric field is now applied. The electrons gain energy from the field. Because  $m/M$  is small, only a small fraction of this energy is transferred to a molecule in a collision. The electron energy therefore increases, until a steady state is reached, in which the energy loss in collisions balances the energy gain from the field. The average electron velocity,  $\bar{u}$  is then given by

$$\frac{1}{2}m \bar{u}^2 = k \frac{1}{2}M \bar{V}^2; k \geq 1 \quad (5)$$

where  $m$ ,  $\bar{u}$ , refer to electrons and  $M$ ,  $\bar{V}$ , to molecules. Electron energy, at constant gas temperature, is found to depend only on the ratio of the applied field,  $E$ , to the gas pressure,  $P$ . The field, if D.C., not only heats up the electrons but causes them to move in its own direction with an average drift velocity,  $\bar{W}$ , which also depends on  $E/P$ .  $\bar{W}(E/P)$  is directly measurable, and  $\bar{u}(E/P)$  is closely related to measurable quantities: the problem is to relate these velocities to the cross-sections for individual collisions. A greatly simplified analysis follows.

The equation of motion for an electron in the  $x$ -direction (that of the field) is

$$Ee = m \cdot d^2x/dt^2 \quad (6)$$

If the average velocity in the  $x$ -direction immediately after a collision is zero (scattering assumed isotropic), and the time between collisions is  $\tau$ , then the drift velocity will be half the velocity at time  $\tau$ , or

$$\bar{W} = Ee\tau/2m \quad (7)$$

If  $N$  is the molecule density,  $l$  the electron mean free path,  $Q$  the collision cross-section,

$$\tau = l/\bar{u} = 1/NQ\bar{u} \quad (8)$$

and 
$$\bar{W} = \frac{Ee}{2m} \cdot \frac{1}{N} \cdot \frac{1}{Q\bar{u}} = \frac{(E/P)e}{2m} \cdot \frac{1}{N_0 Q \bar{u}} \quad (9)$$

where  $N_0$  is the molecule density at unit pressure. This equation relates  $\bar{W}$  and  $\bar{u}$  at any  $E/P$  to the collision cross-section.

The average fractional energy loss by an electron per collision,  $\lambda$ , can also be derived. Under steady-state conditions the energy lost to molecules equals energy gained from the field:

$$\frac{1}{2} \lambda m \bar{u}^2 = \frac{1}{2} m (2\bar{W})^2 \quad (10)$$

or 
$$\lambda = \frac{4\bar{W}^2}{\bar{u}^2} \quad (11)$$

This treatment ignores the distribution of electron velocities, the dependence of  $Q$  on electron velocity, and the angular dependence of the scattered electrons. Detailed calculations give

$$\bar{W} = \frac{E}{P} \cdot \frac{e}{3mN_0} \cdot \frac{1}{\bar{u}^2} \frac{d}{d\bar{u}} \left( \frac{\bar{u}^2}{Q_D} \right). \quad (12)$$

Use of  $Q_D$ , the momentum transfer cross-section, takes into account the angular distribution. The distribution of  $u$ , and the dependence of  $Q_D$  on  $u$ , is required for the evaluation of this expression. These in turn depend on the nature of the individual collision processes.

### 3. Total Collision Cross-sections

Attempts to measure the total collision cross-section of molecules for slow electrons were first made at the beginning of this century. One of the most successful methods was introduced by Ramsauer in 1921, and his results formed the basis for much thinking about electron scattering. In his apparatus, shown diagrammatically in Figure 1, electrons photoejected from a zinc plate are accelerated by a potential  $V$  applied to plate  $A$ . A magnetic field  $H$  causes the electrons to describe a circular path of

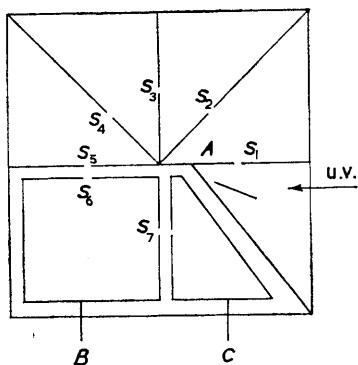


FIG. 1. Ramsauer's apparatus for measurement of total collision cross-sections for electrons in gases (from ref. 1).

radius  $r$  through the slits  $S_1$  to  $S_7$ . This defines the electron energy.  $B$  and  $C$  are two collectors insulated from the cell and each other. The cell is filled with the gas at a pressure of about  $10^{-1}$ – $10^{-3}$  torr. All electrons colliding with gas molecules between  $S_6$  and  $S_7$  (a distance  $x$ ) fail to get through  $S_7$  to  $C$ . By measuring the current to  $B$  and  $C$  together ( $j$ ) and the current to  $C$  alone ( $i$ ) at two gas densities  $N_1$  and  $N_2$ , it is possible to obtain  $Q_T$  from the easily derived relationship

$$Q_T = \frac{1}{x(N_1 - N_2)} \ln \frac{j_1 i_2}{i_1 j_2} \quad (13)$$

Some cross-sections measured in this way are shown in Figure 2. They are, as expected, of the order of molecular dimensions.

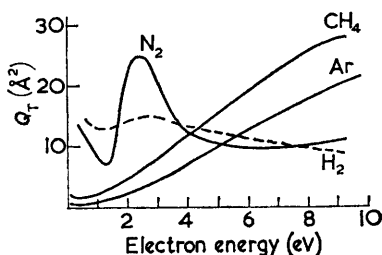


FIG. 2. Total collision cross-sections for electrons in Ar, H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>.

The cross-sections for the noble gases are purely elastic in the energy region shown. Those for polyatomic molecules may include inelastic components. Figure 2 shows that even  $Q_{el}$  depends on the energy of the incident electron.

The deep minimum in  $Q_T$  shown in Figure 2 for argon and methane is known as the Ramsauer-Townsend effect. It can be explained simply

in terms of the wave-mechanical theory of scattering. The molecule may be considered to act as a potential well of depth  $D$  and range  $a$ , so that  $U(r) = -D$  for  $r < a$ , and  $U(r) = 0$  for  $r \geq a$ . A long way from the molecule, the electron has its de Broglie wavelength  $\lambda = h/mu$ . When it comes into the attractive potential, it is speeded up and  $\lambda = h/\sqrt{(m^2u^2 + 2Dm)}$ . These two waves must join smoothly at  $r = a$ . To do this, and keep the amplitude finite at the origin, a phase shift must be introduced into the electron wave relative to the phase that the wave would have if the potential well did not exist. This phase shift is, in principle, what allows an observer to detect the scattering. If the phase shift should happen to be  $2\pi$  or  $2n\pi$  there would be no detectable effect: as far as an observer is concerned, the electron would be unaffected by the molecule.

Detailed scattering theory shows that the cross-section is a function of the phase shift:

$$Q_T = \frac{4\pi}{k^2} \sum_l (2l + 1) \sin^2 \eta_l \quad (14)$$

where  $k = 2\pi/\lambda$  and  $\eta_l$  is the phase shift for an electron of angular momentum quantum number  $l$ : that is, an electron for which the angular momentum about the molecule,

$$mub = (h/2\pi)\sqrt{l(l+1)}$$

where  $b$  is the distance between the initial line of motion of the particle and the centre of the potential well. For a slow electron  $mub$  is small, and thus for an electron to have even unit angular momentum about the molecule,  $b$  must be fairly large (for a 0.1 eV electron,  $b \sim 9 \text{ \AA}$ ; for a 1 eV electron,  $b \sim 3 \text{ \AA}$ ). If  $b$  is larger than the effective range of the electron-molecule interaction, then  $\eta_l = 0$  for all  $l > 0$ , so that

$$Q_T = (4\pi/k^2) \sin^2 \eta_0 \quad (15)$$

and  $Q_T = 0$  if  $\eta_0 = n\pi$ . In any case, if the interaction falls off fairly rapidly with distance,  $\eta_l$  is likely to be small for higher  $l$  values. A Ramsauer-Townsend effect is then to be expected in a system in which only head-on collisions are important and in which the attractive field is strong enough to introduce a phase shift of  $n\pi$ .

A similar argument concerning the relative unimportance of collisions with  $l > 0$  leads to the conclusion that scattering of slow electrons should be isotropic.

Detailed application of scattering theory to molecules is very complicated.  $Q$  can still be expressed in terms of the phase shifts, but for dipolar molecules, for example, the interaction will be sufficiently long range for higher-order phase shifts to be significant and a Ramsauer-Townsend effect will be forbidden. Methane appears to be an exception: its high symmetry means that there are no long-range charge-dipole or charge-quadrupole effects, and a Ramsauer-Townsend effect has been observed.

The prediction of such an effect has been used as a criterion for electronic wave-functions for methane.

Another important effect in the total collision cross-sections for the noble gases has also been observed in a Ramsauer-type experiment, although it was first found in another beam experiment.<sup>3-5</sup> It is most clearly shown in helium (which does not show a Ramsauer-Townsend effect), where a narrow dip of about 15%, followed by a slightly broader rise, occurs in the total cross-section at 19.3 eV (Figure 3). The lowest

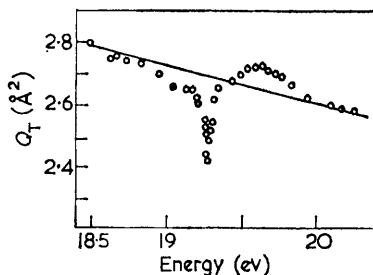


FIG. 3. Total collision cross-section for electron-helium impacts showing the sharp resonance at 19.3 eV (from ref. 4).

excited state of helium,  $^3S(1s, 2s)$  has an energy of 19.8 eV above the ground state, so what is observed is the appearance of sharply defined structure in the elastic cross-section. Analogy with similar effects in nuclear physics suggests that this type of resonance effect is related to the formation of an unstable compound state of the atom and the electron, and indeed the energy of the first excited state of  $\text{He}^- (1s, 2s^2)$  is expected to be in this region. Such resonance processes involving compound states of electrons and molecules are thought to play an important part in inelastic electron-molecule processes which will be discussed later.

It has already been mentioned that  $\bar{W}$  and  $\bar{u}$ , the electron drift velocity and the electron random velocity in an electron swarm, are related to  $Q_D$ , the momentum transfer cross-section, which is itself related to the total collision cross-section, and a simplified account of the relationship has been given. If, in equation (12),  $Q_D$  is considered to vary slowly with  $u$ , and the distribution of  $u$  is Maxwellian, we have

$$Q_D = \frac{2}{3} \frac{E e}{P m N_0} \cdot \frac{\bar{u}^{-1}}{\bar{W}} \quad (16)$$

and thus an approximate value of  $Q_D$  if  $\bar{W}(E/P)$  and  $\bar{u}(E/P)$  are known.

There are several methods for determining  $\bar{W}$ , but the best in the low-energy region is the shutter method. The apparatus is shown diagrammatic-

<sup>3</sup> G. J. Schulz, *Phys. Rev.*, 1964, **136**, A650.

<sup>4</sup> D. E. Golden and H. W. Bandel, *Phys. Rev.*, 1965, **138**, A14.

<sup>5</sup> C. E. Kuyatt, J. A. Simpson, and S. R. Mielczarek, *Phys. Rev.*, 1965, **138**, A 385.

ally in Figure 4. Electrons from a photocathode *C* move in an electric field through the electron shutters *S*<sub>1</sub> and *S*<sub>2</sub> to the anode *A*. Each shutter consists of fine wires mounted on an insulating frame, alternate wires being connected so that a potential difference may be applied between adjacent wires. Electrons pass through the shutters only when the field between

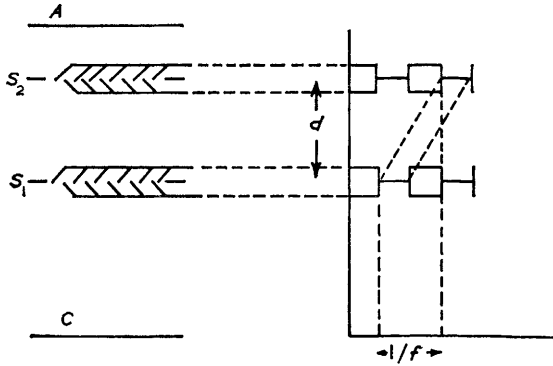


FIG. 4. *Electron-shutter apparatus for measurement of electron drift velocities through gases.*

the wires is zero, or nearly so. An alternating, in phase, potential is applied to the wires so that the shutters are alternately open and closed to electrons. *S*<sub>1</sub> acts as a chopper, cutting the electron stream into a series of pulses which drift towards the anode. They arrive at the anode only if *S*<sub>2</sub> is open when they reach it, that is, if they cover the distance *d* in a time equal to  $1/f$ , where *f* is the frequency of the switching potential. In the experiment, *f* is varied till the anode current is a maximum (at  $f_m$ ) and  $W = d \cdot f_m$ . Current maxima also appear at  $2f_m, 3f_m, \dots, n f_m$ , corresponding to *S*<sub>2</sub> opening and shutting (*n*-1) times while the pulse covers the distance *d*.

The random velocity, *u*, can only be determined indirectly. The method, due to Townsend, involves measuring the sideways diffusion of electrons drifting through a gas. The spatial distribution of electrons under these circumstances depends on  $W/D$ , where *D* is the diffusion coefficient, which for an energy-independent  $Q_D$  and a Maxwellian distribution of velocities is related to *u* by

$$D = \frac{1}{3} \frac{\bar{u}}{N Q} \tag{17}$$

The apparatus for measurement of diffusion is shown in Figure 5. Electrons enter the diffusion chamber through a pin-hole in the cathode and are collected on the split anode *A*. The ratio of the current *i*<sub>a</sub> collected on the central disc of this anode to the total current *i*<sub>t</sub> is given, on solution of the diffusion equations with the appropriate boundary conditions, by

$$i_a/i_t = 1 - (h/d)\exp[-g(d - h)] \tag{18}$$



where  $g = W/2D$  and  $h$  and  $d$  are as shown in Figure 5. From equations (16) and (17)

$$\frac{W}{2D} = \frac{4E e \bar{u}^{-1}}{m \bar{u}} \quad (19)$$

so that  $\bar{u}(E/P)$  can be obtained from measurement of  $i_a/i_c$ . Knowledge of  $\bar{W}(E/P)$  and  $\bar{u}(E/P)$  give  $Q_D$  through equation (16).  $Q_D$  obtained in this way is compared with  $Q_T$  in Figure 6: the agreement is good, considering the approximations in the analysis.

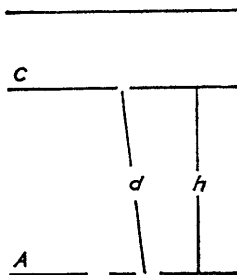


FIG. 5. Townsend's apparatus for obtaining the mean energy of an electron swarm in a gas.

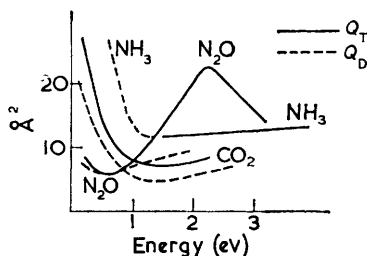


FIG. 6. Comparison of some electron-molecule collision cross-sections as measured directly ( $Q_T$ ) and as deduced from swarm data ( $Q_D$ ).

Swarm methods are important because they lead to cross-section results at very low energies, well below those obtainable in beam experiments. Considerable interest has recently been taken in low-energy inelastic processes (involving the excitation of molecular rotation and vibration) studied in this way.

Another method of evaluating momentum transfer cross-sections is from microwave absorption in a weakly ionised plasma. Such studies give reasonable agreement with swarm experiments.

Crossed-beam techniques can also be used to measure cross-sections, being particularly useful if high resolution of electron energy is required, or if reactive molecular species are being studied. Total cross-sections for electrons and atomic hydrogen have been measured in this way. An atomic

beam produced by a tungsten furnace was modulated by a low frequency chopping wheel before being crossed by an electron beam. The attenuation of the electron beam was observed as a low-frequency electron current, the frequency and phase of which was determined by the atomic beam chopper. Exact quantum-mechanical calculations on electron scattering by atomic hydrogen agreed well with experiment.

#### 4. Inelastic Cross-sections

Low-energy inelastic cross-sections are usually a small fraction of the total collision cross-section, which makes them more difficult to measure. Before discussing the nature of the processes, we describe some of the experimental methods.

(i) **Maier-Leibnitz Experiment.**—A typical apparatus for this swarm experiment, developed in the nineteen-twenties, is shown in Figure 7.

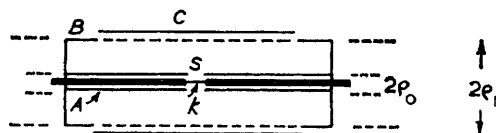


FIG. 7. *Maier-Leibnitz apparatus for study of inelastic electron-molecule collision processes (from ref. 1).*

A filament  $K$  is contained within a cylinder  $A$  of radius  $\rho_0$ , surrounded by a cylinder,  $B$ , radius  $\rho_1$ , constructed mainly of mesh. Electrons from  $K$  are accelerated by a potential  $V$  between  $K$  and  $A$  through a slit  $S$  into the field-free space containing the gas, through which they diffuse to  $B$ . They pass through  $B$ , and can be collected at  $C$ . A retarding-potential  $U$  (conveniently a fixed fraction of  $V$ ) is applied to  $C$ , so that electrons which have suffered appreciable energy loss are not collected. Because of this, it is found that if the current to  $C$  is measured as a function of  $V$ , there is a drop at the onset of an inelastic process. The current  $J_1$  which would have been observed had there not been an inelastic process is determined by extrapolation of the line before the drop, and the actual current  $J$  is expected to be related to it by  $J = J_1 \exp(-\mu Z)$ , where  $\mu$  is the fraction of inelastic collisions and  $Z$  is the total number of collisions suffered by an electron in going from  $A$  to  $B$ . Theoretical analysis of the diffusion process shows that

$$Q_{\text{inel}} = \mu Q_{\text{T}} = \frac{4}{3} \bar{u} Z Q_{\text{D}}^{-1} N^{-2} f(\rho_1, \rho_0) \quad (20)$$

where  $\mu Z$  is derived directly from experiment,  $Q_{\text{D}}$  and  $N$  have their usual meaning, and  $f(\rho_1, \rho_0)$  is a simple function of  $\rho_1$  and  $\rho_0$ .

This method has given electronic excitation cross-sections for the inert gases and detected vibrational excitation in nitrogen and hydrogen.

(ii) **Analysis of Swarm Experiments.**—The application of analysis of swarm experiments to the determination of  $Q_D$  has already been discussed. The appearance of inelastic processes in swarm experiments is indicated by a high value of  $W/\bar{u}$ , as suggested by equation (11). The fractional energy loss per collision,  $\lambda$ , should be  $2m/M$  for purely elastic processes, and greater than this for inelastic processes.  $\lambda$ , calculated from equation (11) with the coefficient 4 replaced by 2.46 (resulting from a better treatment of the averaging) is shown in Figure 8 for a number of gases. The

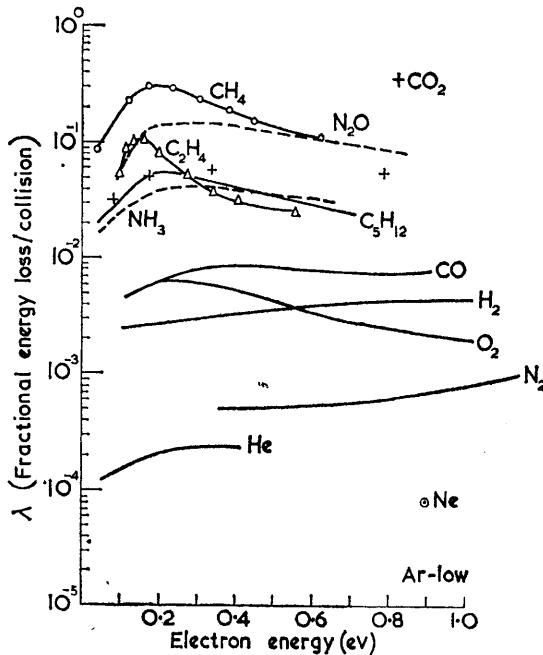


FIG. 8. Graph of fractional energy lost per collision by an electron colliding with gas molecules, as deduced from swarm data.

noble gases give the typical elastic values for  $\lambda$ , but molecular gases show much higher values, presumably because of excitation of molecular rotation and vibration.

A more sophisticated method of dealing with swarm data, which affords a greater knowledge of the actual cross-sections, is to calculate the electron energy distribution by the Boltzmann equation, taking into account the effect of inelastic processes by making assumptions about their cross-sections. Using this estimate of the electron-energy distribution, the drift velocity can be calculated exactly (equation 12) and compared with experiment. Adjustment of the assumed cross-sections to fit the experimental drift velocity over a wide range of  $E/P$  then gives a "best" set of

values which in many cases agree with those obtained by other methods (although at the lowest energies, this is the only method of attack).

The Boltzmann equation for the electron-energy distribution  $f(E_e)$ , where  $E_e = \frac{1}{2} m \bar{u}^2$ , is

$$\begin{aligned} \frac{E_e^2}{3} \frac{d}{dE_e} \left( \frac{E_e}{N_0 Q_D} \cdot \frac{df}{dE_e} \right) + \frac{2m}{M} \frac{d}{dE_e} (E_e^2 N_0 Q_D f) \\ + \frac{2mkT}{Ml} \frac{d}{dE_e} \left( E_e^2 N_0 Q_D \frac{df}{dE_e} \right) \\ + \sum_j (E_e + E_j) f(E_e + E_j) N_0 Q_{+j}(E_e + E_j) - E_e f(E_e) N_j \sum_j Q_{+j}(E_e) \\ + \sum_j (E_e - E_j) f(E_e - E_j) N_0 Q_{-j}(E_e - E_j) - E_e f(E_e) N_j \sum_j Q_{-j}(E_e) \\ = 0 \end{aligned}$$

where  $N_j$  is the number density of molecules in the  $j$ th state and the cross-sections  $Q_{\pm j}(E_e)$  are for processes in which electrons take up (+ $j$ ) and lose (- $j$ ) energy  $E_j$ . Cross-sections obtained in this way for hydrogen<sup>6</sup> are shown in Figure 9.

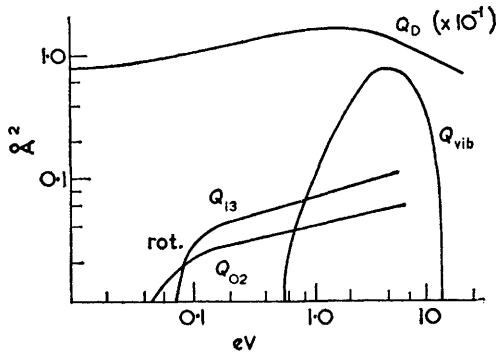


FIG. 9. Elastic and inelastic collision cross-sections for electrons in  $H_2$  as deduced from swarm data (from ref. 6).

(iii) **Electron Trap.**—The electron trap, which has given much information on low-energy processes, is shown diagrammatically in Figure 10. In this apparatus electrons of known energy pass through a gas under single-collision conditions. An arrangement of potentials and a magnetic field is so disposed that the electrons which suffer inelastic collisions are separately collected, and an estimate of the energy lost can also be obtained. The electron-energy selection is by the retarding potential difference (R.P.D.) method. The distribution of energy of electrons from the filament  $F$  is truncated by putting a potential  $V$  on to  $P$ , slightly negative with respect to  $F$ . If this potential is increased to  $V + dV$ , the energy distribution is

<sup>6</sup> A. G. Engelhardt and A. V. Phelps, *Phys. Rev.*, 1963, **131**, 2115.

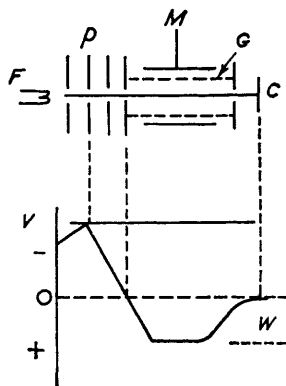


FIG. 10. *Schulz's electron trap for study of inelastic electron-molecule collision processes.*

truncated at a different point, and the difference in the events in the collision chamber in the two cases is due to electrons in the energy band  $dV$ . The electrons are accelerated into the collision chamber, which is at a uniform potential, by the potential  $V$ , and aligned by a magnetic field. The cylindrical walls of the collision chamber are of a grid mesh  $G$ , which allows electrons to pass through to the collector  $M$  which is maintained at a positive potential. A small part of the positive potential on  $M$  penetrates into the chamber, effectively creating a potential well of depth  $w$ , and an electron in the chamber then has energy  $V + w$ . If an electron collides inelastically, losing energy between  $V$  and  $V + w$ , it has insufficient energy to get out of the well and eventually arrives at  $M$ . Otherwise it passes through the chamber and is collected at  $C$ . Measurement of the trapped electron current at different  $V$  and  $w$  gives the relative probabilities of various inelastic processes.

(iv) **Double Electrostatic Analyser.**—If an electron of velocity  $u$  enters a region of radial electrostatic field at right angles to the lines of force it will describe a circular orbit of radius  $r_0$  given by  $mu^2/r_0 = -Ee$ . Electrons of the same velocity entering at angle  $\pm\alpha$  to the lines of force do not describe circular orbits, but their paths cross the circular arc at a point corresponding to an angular deflection of  $\pi/\sqrt{2}$  ( $127^\circ 17'$ ). Thus a focusing electron energy selector, the  $127^\circ$  analyser, can be built, and has given an energy resolution of 0.04 eV. Two such analysers can be used together to measure inelastic cross-sections. Electrons from the first analyser are crossed with a molecular beam, and the resulting electrons scattered in a chosen direction pass into a second analyser, which can be tuned to select electrons of different velocities. Thus the energies of the scattered electrons are measured directly. Hemispherical electrostatic analysers have also been employed as energy selectors.<sup>5,7</sup> This kind of apparatus is less sen-

<sup>7</sup> H. G. M. Heideman, C. E. Kuyatt, G. E. Chamberlain, *J. Chem. Phys.*, 1966, **44**, 355.

sitive than the electron trap, which collects all the inelastically scattered electrons, but it shows greater resolution.

(v) **Other Crossed-beam Experiments.**—When molecules are excited in a crossed electron–molecule beam it should be possible to detect the excited molecules directly, for example, by radiation from the excited state. However, the concentration of excited species is always low because of the low electron density (needed to avoid space-charge) and the low molecule density (needed for single-collision conditions) and because inelastic cross-sections are usually small. The method has however been used to measure electronic excitation cross-sections for hydrogen atoms.

(vi) **Experiments with Higher-energy Electrons.**—Higher-energy electrons, from 25 to 500 eV, are capable of ionising gases but they may also lose smaller quantities of energy in molecular excitation processes. The energy lost by the scattered electrons can be determined by a retarding-potential method. Experiments on wide-angle scattering at energies in the 25 eV region, and on forward scattering around 300 eV, have been carried out, to give “electron impact spectra” for electronic excitation.

## 5. Discussion of Excitation Processes

(i) **Electronic Excitation.**—Electronic transitions are readily caused by electrons of sufficient energy. Electronic excitation by electrons with several times the required energy closely resembles optical dipole excitations: the selection rules are the same, and the cross-sections are related to the optical intensities of absorption. This has been shown for a wide range of molecules with electrons in the 200–500 eV range by Lassette<sup>8</sup> and his co-workers. These cross-sections do fall with increasing energy above threshold, and, although they resemble optical processes as far as the selection rules are concerned, they differ in that while the optical processes involve resonance, the electron-induced processes do not in general do so, any excess of energy being easily removed by the electron.

However, when the electron energy is nearer the threshold, the possibility of exchange processes between incoming and molecular electrons arises. Then, the optical dipole selection rules do not apply and transitions involving change in multiplicity are possible. An electron-impact spectrum of ethylene obtained by Kuppermann and Raff is shown in Figure 11.<sup>9</sup> The incident electron energy was 40 eV. Two optically forbidden transitions appear. Distinction between exchange and other processes is relatively easy because the former gives a broader angular distribution of scattered electrons and a sharper fall-off in cross-section with increasing energy above threshold.

(ii) **Vibrational Excitation.**—“Direct” excitation of molecular vibration by slow-electron impact is ruled out by conservation of momentum, but

<sup>8</sup> E. N. Lassette *et al.*, *J. Chem. Phys.*, 1964, **40**, 1208.

<sup>9</sup> A. Kuppermann and L. M. Raff, *J. Chem. Phys.*, 1962, **37**, 2497.

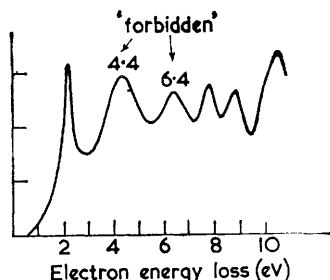


FIG. 11. *Electron-impact spectrum of C<sub>2</sub>H<sub>4</sub> for incident electrons of 40 eV. Two optically forbidden transitions appear.* (From Kupperman and Raff, *Discuss. Faraday Soc.*, 1963, 35, 30.)

experimental evidence has recently forced the realisation that another mechanism, vibrational excitation by way of a compound state (unstable molecular negative ion), is possible. Haas, in Maier-Leibnitz experiments, showed that, at 2 eV, 15% of electron-nitrogen encounters were inelastic and that the energy loss corresponded to vibrational excitation. Schulz, using the electron trap and also the double electrostatic analyser, confirmed this, and showed that 2.3 eV electrons excite several vibrational levels of N<sub>2</sub>. 1.7 eV electrons do the same to CO.

Swarm experiments with detailed analysis of the energy distribution show vibrational excitation of H<sub>2</sub>, D<sub>2</sub>, and N<sub>2</sub>; and a less detailed analysis of swarm results for a large number of gases strongly suggests vibrational excitation of methane and higher hydrocarbons.<sup>10</sup> It seems probable, therefore, that compound states play an important part in many slow-electron-molecule interactions.

(iii) **Rotational Excitation.**—It might appear at first sight that conservation of angular momentum might forbid "direct" rotational excitation of molecules by low-energy electrons: but the long-range nature of the interaction between electrons and dipolar or quadrupolar molecules means that electrons with quite high impact parameters, and therefore the necessary angular momentum, can interact sufficiently strongly to cause rotational excitation of polar molecules. Cross-sections calculated from this point of view agree quite well with those deduced from the analysis of low-energy swarm experiments.

## 6. Conclusion

The history of the study of electron-molecule interactions shows a period of activity, reaching a peak in the nineteen-twenties, followed by over twenty years of comparative quietude, and then, in the nineteen-fifties and -sixties, by an increasing number of papers. The reason for this pattern is two-fold. First, present-day techniques allow previously undetectable

<sup>10</sup> T. L. Cottrell and I. C. Walker, *Trans. Faraday Soc.*, 1965, 61, 1585.

quantities to be measured (as in beam experiments), and secondly, increase in theoretical understanding, particularly the notion of compound states, makes it easier for investigators to realise the significance of their results. The second is exemplified in vibrational excitation. About thirty years ago, workers in the field of electron swarms stated firmly that electrons excite vibrations in molecules. Because of the apparent theoretical implausibility, and because of the uncertainties in the analysis of swarm results, such statements were greeted with some scepticism. Now, theoretical conclusions borrowed from nuclear physics, and more definitive experimental techniques coupled with more sophisticated interpretation of old experimental techniques have shown that this is a fairly widespread effect.

Because of the existence of an excellent review<sup>1</sup> of the work up to about 1950, we have not given references to work before that date, and we have only given selected references to work published since then. The need for detailed references, even to work in the fifties, has been largely removed by the recent appearance of a book by Hasted<sup>2</sup> which covers much of the ground.