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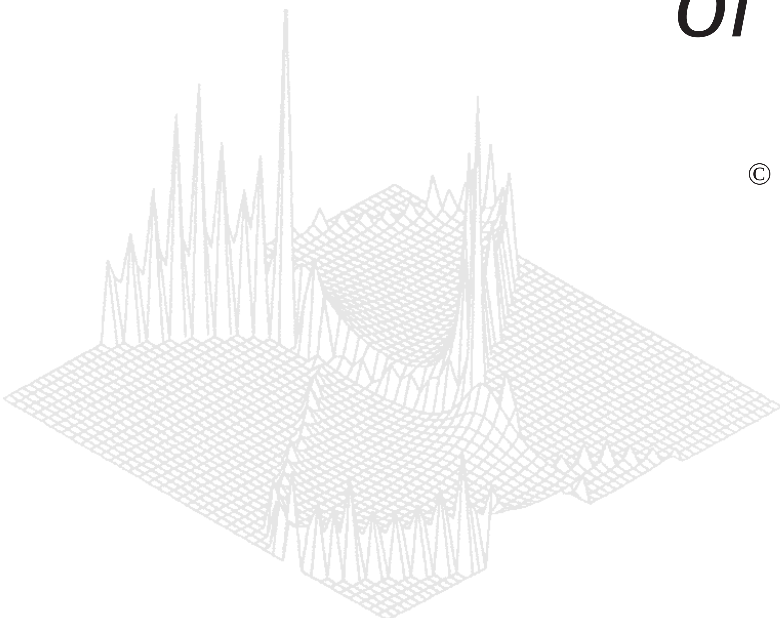

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A Critical Comparison of Electron Scattering Cross Sections measured by Single Collision and Swarm Techniques*

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Abstract

Electron scattering cross sections (elastic, rotational and vibrational excitation) for a number of atomic and (relatively) simple molecular systems are examined. Particular reference is made to the level of agreeement which is obtained from the application of the completely different measurement philosophies embodied in 'beam' and 'swarm' techniques. The range of energies considered is generally restricted to the region below 5 eV.

1. Introduction

A number of powerful techniques have been developed over the past thirty years for the study of the interaction of low energy charged particles with atoms and molecules and the subsequent derivation from these studies of scattering cross sections and reaction rates. In general these techniques are broadly classified into those where single collisions between individual scattering partners are examined—the so-called 'beam' measurements, and those where the derived quantities are extracted from observations of the collective motion of a large number of charged particles undergoing many collisions—the so-called 'swarm' technique.

It is fair to say that these two experimental camps have shared a studied but mutual antipathy towards one another for many years. In part this is due to a number of early, and in some cases long-lived, discrepancies which have existed between measurements from each camp of scattering cross sections for simple atomic and molecular species—these will be discussed in some detail in the following sections. In addition to these underlying discrepancies, the two techniques are so conceptually different and they have so little in common either in terms of practice or terminology, that much of the mutual doubt arises from ignorance amongst the practitioners of one for the details of the other. This is particularly the case for the swarm experiments where the derivation of scattering cross sections from measured transport coefficients is a complex and convoluted task requiring an understanding of transport theory which is beyond the call of duty for most practitioners of the beam technique.

* Dedicated to Professor Robert W. Crompton on the occasion of his seventieth birthday.

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Like all experimental approaches the various manifestations of these techniques have their strengths and weaknesses and it is not our intention to further document those here. Detailed discussions of the experimental techniques can be found in a number of books and articles (e.g. Huxley and Crompton 1974; Trajmar *et al.* 1983; Nickel *et al.* 1989; Crompton 1994; Trajmar and McConkey 1994). In this article we will focus on a discussion of the underlying problems associated with a comparison between beam and swarm-derived cross sections and illustrate these by a critical comparison of some of the recent results from both techniques.

2. Comparison Techniques

A major source of the confusion surrounding comparisons between beam and swarm experiments arises from the very nature of the cross sections which are derived from these experiments. For example for elastic scattering from atomic systems at low incident energies (below the first excitation threshold) swarm experiments yield transport parameters (drift velocity, diffusion coefficients) from which the elastic momentum transfer cross section ($\sigma_{\rm m}$) is derived via an analysis using the Boltzmann equation. On the other hand beam experiments, either of a direct attenuation or crossed beam nature, yield total elastic ($\sigma_{\rm e}$) or elastic differential ($\mathrm{d}\sigma/\mathrm{d}\Omega$) cross sections respectively, and the way in which one can draw comparisons between these quantities, particularly the integral cross sections, is not generally apparent. In terms of the scattering phase shifts η_l these cross sections are given, in atomic units, by

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{1}{4k^2}\left[\left(\sum_{l=0}^{\infty}(2l+1)\sin 2\eta_l\, P_i(\cos\theta)\right)^2 + \left(\sum_{l=0}^{\infty}(2l+1)(1-\cos 2\eta_l)P_l(\cos\theta)\right)^2\right],$$

$$\sigma_{\rm e} = \frac{4\pi}{k^2}\sum_l (2l+1)\sin^2\eta_l = 2\pi\int_0^{\pi}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\sin\theta\,\mathrm{d}\theta\,,$$

$$\sigma_{\rm m} = \frac{4\pi}{k^2}\sum_l (1+1)\sin^2(\eta_l-\eta_{l+l}) = 2\pi\int_0^{\pi}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\sin\theta(1-\cos\theta)\,\mathrm{d}\theta\,,$$

where k is the electron momentum, θ the electron scattering angle, $P_l(\cos\theta)$ the l^{th} order Legendre polynomial and l the projectile orbital angular momentum.

As a result there is an obvious problem if one, for instance, wishes to compare measurements of the total elastic cross section from an attenuation measurement and the elastic momentum transfer cross section derived from a swarm measurement. This is because they are only generally equivalent under the restricted, and relatively uninteresting, conditions that either the scattering energy is zero or the scattering is isotropic. Indeed in general, these two cross sections are sensitive to different angular regions of the differential cross section and can show a markedly different dependence on the phase shifts, particularly at relatively low incident energies. Thus, as we shall see, some caution must be exercised when applying schemes which facilitate their comparison and in drawing conclusions from these comparisons.

Several techniques which assist in the comparison of these integral elastic scattering cross sections, at non-zero energies, have been developed over the years. One straightforward method is to use theoretical phase shifts to calculate the ratio of the total elastic and elastic momentum transfer cross sections as a function of energy and then to use this ratio to convert from one measured cross section to the other. This has been used quite successfully, for example, in the case of low energy electron scattering from helium (Buckman and Lohmann 1986) where accurate theoretical phase shifts (Nesbet 1979) were available. These results will be discussed in detail in a later section.

A more general technique which has proved extremely useful for the comparison of σ_{m} and σ_{e} for the heavier rare gases (Ne, Ar, Kr, Xe) and some simple, essentially spherically symmetric molecules such as CH_4, is the use of a phase-shift analysis technique based on modified effective range theory (MERT) as formulated for electron–atom scattering. This approach, a parametrisation of the energy dependence of the scattering phase shifts in terms of the dipole polarisability, effective range and scattering length, was first applied to problems in atomic physics by O'Malley and co-workers (O'Malley *et al.* 1961; O'Malley 1963). At that time however it was used mainly as a technique to extrapolate low energy integral cross sections to zero energy in order to obtain the scattering length. Subsequently it has been extensively used as a technique to compare beam and swarm-derived cross sections and a summary of its early use has been provided by Buckman and Mitroy (1989). In such cases the measured total (or momentum transfer) cross section is fit with (typically) a four- or five-parameter MERT expansion of the s- and p-wave phase shifts and the fitting parameters are then used to derive the alternate momentum transfer (or total) scattering cross section. Higher order phase shifts are given by the Born approximation. Recent applicants of this technique have been cautious in their conclusions as the range of energies over which it can be considered valid was not well understood, but it has rarely extended above 1 eV (e.g. see Buckman and Mitroy 1989). In addition, at low energies in the heavier rare gases Ar, Kr and Xe, both σ_{e} and σ_{m} are dominated by a deep Ramsauer–Townsend minimum. In σ_{e} the position of this feature depends to first order only on the s-wave phase shift whilst in σ_{m} it depends on both the s- and p-waves. Consequently, in this energy regime, phase-shift analysis procedures such as MERT are likely to be sensitive not only to the range of energies over which they are applied but also to the type of cross section which is being fitted (Buckman and Mitroy 1989). These authors also provided some general guidelines regarding the use of MERT (with rare gas atoms) as a means of comparison between integral cross sections obtained by swarm and beam methods.

On the other hand, measurements of the elastic differential cross section (DCS) in a crossed-beam configuration can, in principle, be used to generate integral cross sections which also may be compared with either the attenuation or swarm measurements. Whilst this route is obviously extremely attractive there can be many problems associated with extrapolation of the DCS to the (unmeasurable) forward and backward angular regions, which ultimately limits the accuracy of the derived integral cross sections. In some cases, for example the lighter rare gases, phase shift analysis techniques can be applied at the DCS level by fitting the measured angular distribution with a function of the form of equation (1) to obtain the dominant, low-order phases. These can then be used to both extrapolate the DCS and to calculate directly the integral elastic scattering cross sections. This technique is generally applied at low energies, below the first excitation threshold, to both limit the number of phases required for the fit and to avoid the complication of complex phase shifts. This technique was first applied by Andrick and Bitsch (1975) and since then there have been many further applications, and these will be discussed in the next section.

Another possible way to extrapolate a measured DCS to 0 and 180° in order to derive an integral cross section is to use the results of a reliable theoretical calculation. In such a case only the shape of the theoretical cross section is required and, for many simple atomic systems, recent theoretical advances in both R-matrix and convergent close coupling techniques make this a viable option. Unfortunately, in many cases such theoretical guidance is not available and one must resort to 'eyeball' extrapolation.

Without doubt the most difficult area for the comparison of beam and swarm results has been electron–molecule scattering. There are a number of reasons for this. Firstly, phase-shift analysis techniques such as MERT are not generally applicable and, where they have been applied, the energy range can be rather restricted (Fabrikant 1984; Isaacs and Morrison 1992). Thus there is no method with a sound physical basis which can be used to compare total elastic and momentum transfer cross sections. Secondly, whilst electron–molecule scattering calculations have made great advances in recent years they do not approach the level of sophistication or accuracy obtained in the electron–atom case (Tennyson 1995). Thus the use of theoretical cross sections for extrapolation of electron–molecule DCS must be approached with considerable caution. Thirdly, and most importantly, the opening of inelastic channels such as rotational and vibrational excitation at low incident energies poses severe problems for the analysis of swarm experiments. As a result the cross section 'set' that is derived from an analysis of transport parameters is not unique if more than one inelastic channel is open. Also, with the exception of a few simple diatomic systems, rotational excitation cannot easily be resolved by conventional crossed-beam electron spectrometers, and most results from these experiments for vibrational excitation involve a sum over rotational excitation.

Finally, we note a potential technical limitation with the beam technique, particularly in relation to the measurement of inelastic DCS. Most such cross sections are measured relative to the elastic DCS, and the establishment of the relative detector response as a function of scattered electron energy is of prime importance. Whilst procedures have been developed in various laboratories to experimentally determine this response function there are still many inherent uncertainties which are usually apparatus specific. An alternative approach to this problem was proposed by LeClair *et al*. (1996) who designed and developed a time-of-flight spectrometer for measuring inelastic to elastic differential cross section ratios in the energy range extending from threshold to several eV above the inelastic threshold, for electron–gas scattering. This approach, in principle, eliminates the need for the complicated calibration procedures currently used to determine the analyser response when using conventional electrostatic electron energy-loss spectroscopy. At this stage, however, its major limitation is that with an energy resolution of $0\cdot7$ eV it is mainly applicable to the case of electron–atom scattering, and only rarely will excited electronic states in molecules have their vibrational bands isolated by such an amount. Thus, as Trajmar and McConkey (1994) recently noted: 'This is an outstanding problem to which a reliable and convenient solution does not exist at the present time.' Notwithstanding the above, there are many examples of electron–molecule collision cross sections where results from these two techniques are available and these will be discussed in the following sections.

3. Specific Results

3·1 Atomic Systems

3·1·1 Helium

Electron–helium scattering is one of the outstanding successes of low energy electron–atom collision physics and was the first example of the high accuracy that is obtainable for elastic scattering measurements using the swarm technique. However, the early history of the comparison between swarm and beam derived results is not entirely a happy one. With the exception of the very early measurements of Ramsauer and Kollath (1929), the earliest beam measurements of the total elastic cross section for helium were by Golden and Bandel (1965), whilst there were a number of derivations of the momentum transfer cross section (e.g. Frost and Phelps 1964; Crompton *et al*. 1967; Crompton *et al*. 1970) from swarm experiments. Golden made the first attempt to compare these cross sections via the use of effective range theory and found that the total cross section measurements were incompatible with all of the swarm-derived momentum transfer cross sections. These differences simmered for some time and almost all subsequent measurements and theory in the early and mid 1970s disagreed with the Golden and Bandel result. A full discussion of this topic is given by R. K. Nesbet in an accompanying article in this issue (see p. 473).

In the late 1970s a number of events finally put the helium controversy to rest. Firstly, the swarm experiments were repeated by Milloy and Crompton (1977) with little change to the derived σ_{m} and accurate total scattering cross sections were measured between $0\cdot5$ and 50 eV by Kennerly and Bonham (1978). These were closely followed by *ab initio* variational calculations of electron–helium elastic scattering at energies below the first excitation threshold ($19\cdot82$ eV) by Nesbet (1979), who was prompted to do so by the (renowned) insistence of R. W. Crompton. These cross sections, and later refinements to the experimental values by Jones and Bonham (1982), indicated a consistent set of results with the swarm and beam experiments in excellent agreement with the theory for both σ_{m} and σ_{e} respectively. Since then there have been several further total cross section measurements (e.g. Ferch *et al*. 1980; Buckman and Lohmann 1986) which have extended σ_{e} to much lower energies ($\approx$100 meV) and absolute DCS measurements at energies as low as $1\cdot5$ eV (Brunger *et al*. 1992). The latter have been phase-shift analysed to yield an integral cross section which is also in excellent agreement with the theory and the previous total scattering measurements. We compare the total elastic cross sections in Fig. 1 where, for convenience, we have expressed the swarm-derived results of Milloy and Crompton as an integral elastic cross section, these values being obtained by multiplying their σ_{m} by the theoretical (Nesbet 1979) ratio for $\sigma_{\mathrm{e}}/\sigma_{\mathrm{m}}$. Clearly there is excellent agreement between these various cross sections. It is worth noting here that difficulties in the use of MERT in helium as a means of transferring from $\sigma_{\rm m}$ to $\sigma_{\rm e}$ and *vice-versa* have been pointed out by both Buckman and Lohmann (1986) and Buckman and Mitroy (1989) and these are discussed in further detail in the next section.

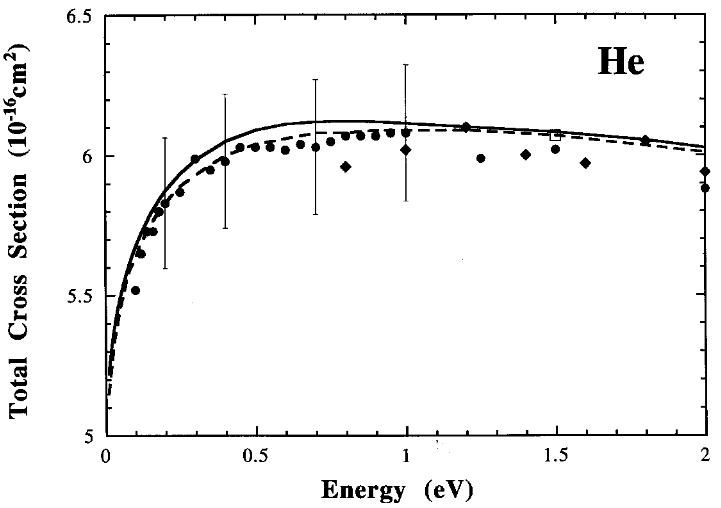

Fig. 1. Total electron scattering cross section (10^{-16} cm^2) for helium between 0 and 2 eV: Crompton *et al.* (- - -), Nesbet (—), Jones and Bonham (◆), Buckman and Lohmann (●) Brunger *et al.* (□). Note that the zero of the x-axis has been displaced.

In Fig. 2 the DCS measurements of Brunger *et al.* (1992) at 1·5 eV are compared with the theory of Nesbet and the recent convergent-close-coupling calculation of Fursa and Bray (1995). Once again the agreement is excellent.

The importance of these results for helium cannot be stressed too much. The convergence of absolute measurement and *ab initio* calculation has provided a benchmark and calibration standard for electron atomic physics upon which many of the present day measurements, for a wide range of atomic and molecular gases, rely.

3·1·2 Neon

The situation in neon regarding cross section comparisons is also rather healthy, perhaps even as good as that in helium. Comprehensive summaries of contemporary low energy work have been given in two recent crossed-beam studies (Shi and Burrow 1992; Gulley *et al.* 1994), so we will not repeat those details here. Also, given the relatively large number of cross section measurements available in the literature, we will be somewhat selective in our choice of comparisons and largely concentrate on the recent measurements.

Swarm measurements in neon have been carried out by Robertson (1972) and Koizumi (1984). Recently, absolute DCS have been measured by Shi and Burrow (1992) and Gulley *et al.* (1994) and these, in conjunction with the earlier measurements of Williams (1979), provide an extensive set of data for comparison below 5 eV. There have also been many low energy total elastic cross section

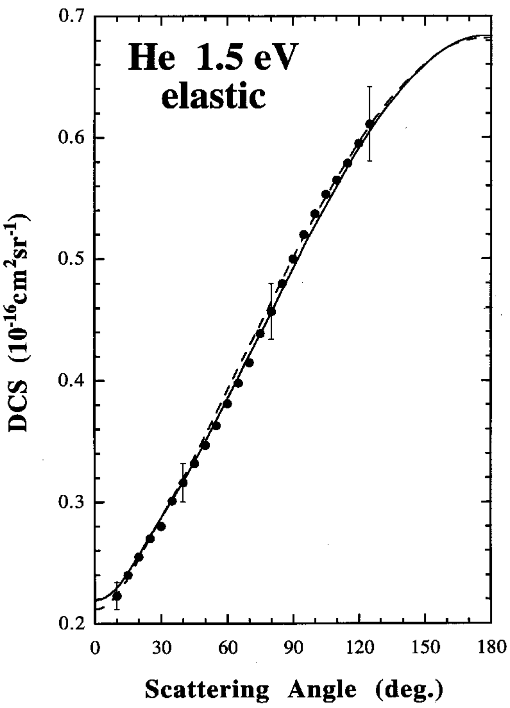

Fig. 2. Differential cross section (10^{-16} cm^2 sr^{-1}) for elastic electron scattering from helium at an incident energy of $1 \cdot 5$ eV: Nesbet (—), Brunger *et al.* (●) and Fursa and Bray (- - -).

measurements for neon, the most recent being those of Gulley *et al.* using a time-of-flight (ToF) electron spectrometer. In addition, the experimental transport data of Robertson have been analysed by O'Malley and Crompton (1980), using MERT, to extract phase shifts from which $\sigma_{\rm m}$, $\sigma_{\rm e}$ and some low energy elastic DCS have been derived. This analysis only involved the parametrisation of the s-wave phase shift, the form of the p- and d-waves being derived, and fixed, from a MERT-based fit to the phase shifts of Williams. As is the case in helium, the p- and d-wave phase shifts are small and they have a very weak energy dependence below about 1 eV. Thus, while an accurate four or five parameter MERT fit to the neon integral ($\sigma_{\rm m}$ or $\sigma_{\rm e}$) cross sections is readily achieved below 1 eV, the higher order phase shifts are so poorly determined that the derivation of the alternate integral cross section ($\sigma_{\rm e}$ or $\sigma_{\rm m}$) from this process is plagued with uncertainty (Buckman and Mitroy 1989). Nonetheless, comparisons can still be made of the various cross sections, as well as with those from multiconfiguration Hartree–Fock (Saha 1989, 1990) and polarised orbital (McEachran and Stauffer 1985) calculations, in a number of ways.

In Fig. 3 we show the momentum transfer cross section for neon where we compare the experimental results of O'Malley and of Crompton and Gulley *et al.* with the theoretical values of Saha and of McEachran and Stauffer at energies below $2 \cdot 5$ eV. There are two sets of results from the beam measurements of Gulley *et al.* Firstly their DCS measurements have been phase-shift analysed and, from the derived phase shifts, the momentum transfer cross section has been calculated at 0·75, 1·0, 1·3 and 2·2 eV. Secondly, their σ_e from the ToF measurements has been converted to a σ_m by using the ratio of these two cross sections from the calculation of Saha. It is immediately apparent that the level of agreement between all of these data is excellent.

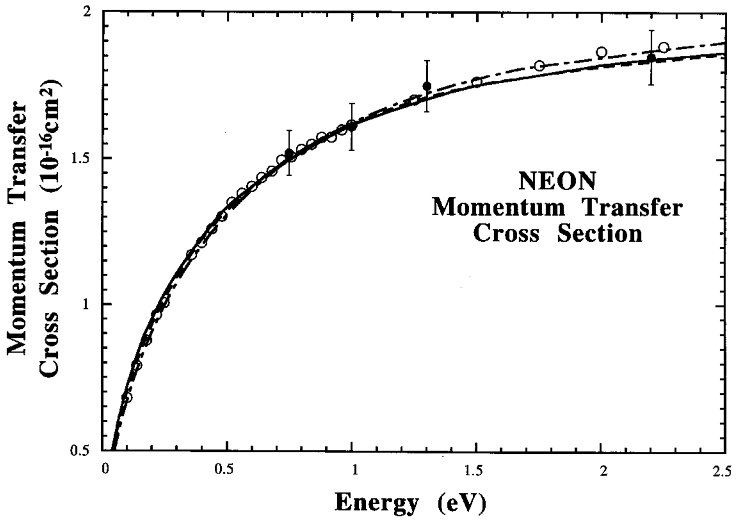

Fig. 3. Momentum transfer cross section (10^{-16} cm^2) for neon between 0 and 2·5 eV: Robertson (- - -), McEachran and Stauffer (— - —), Saha (—), Gulley *et al.* ToF (○) and Gulley *et al.* DCS-derived (●).

At the DCS level we are able to make a rather unique comparison between swarm and beam results as O'Malley and Crompton have used their MERT-derived phase shifts to calculate elastic DCS which can be compared with the recent measurements of Shi and Burrow and Gulley *et al.* as well as with the above calculations. This is done in Figs 4*a* and 4*b* for incident electron energies of 0·25 and 1·0 eV. In both cases the swarm result and the theory of Saha are essentially indistinguishable across the entire angular range. At 0·25 eV the DCS measurements of Shi and Burrow are in relatively good agreement with the swarm result and theory, although consistently higher by about 3–5% at most angles. At 1·0 eV both DCS measurements, the swarm result, and the theory of Saha and that of McEachran and Stauffer, are all in excellent agreement. Given the circumstances, on the one hand the low incident electron energies involved which mitigate strongly against accurate crossed-beam experiments and on the other, a swarm-derived *differential* cross section obtained directly from a phase-shift analysis of the elastic momentum transfer cross section, we feel that the level of agreement is amazingly good.

3·1·3 Argon

Argon is the first of the rare gases where the appearance of the Ramsauer–Townsend (RT) minimum at low incident energies serves to substantially complicate the energy dependence of the elastic cross section. However, in some respects this

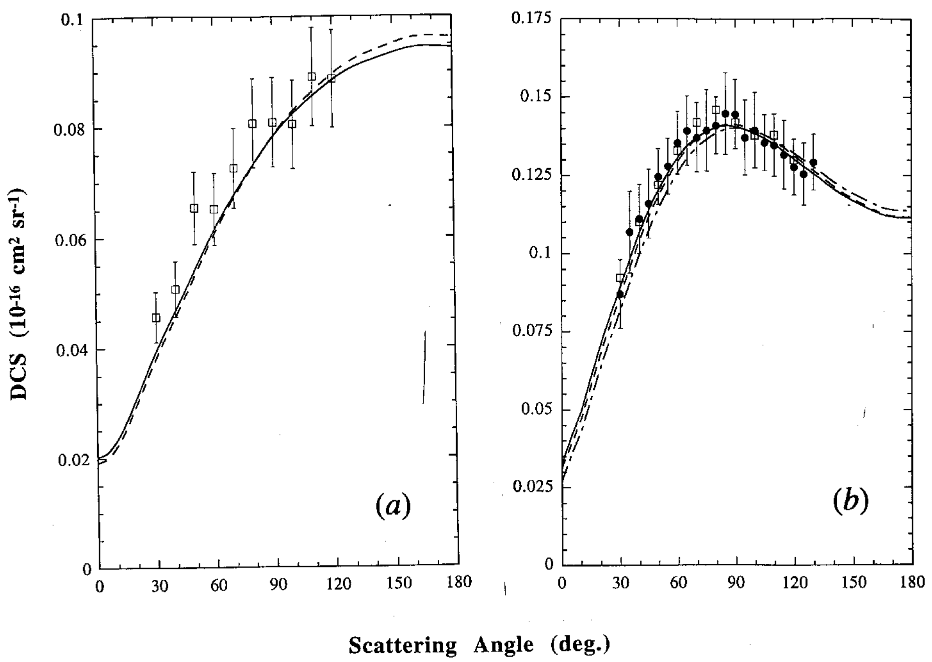

Fig. 4. Differential cross section (10^{-16} cm^2 sr^{-1}) for elastic electron scattering from neon at an incident energy of (*a*) 0·25 eV, O'Malley and Crompton (- - -), Saha (—), Shi and Burrow (□) and (*b*) 1·0 eV, O'Malley and Crompton (- - -), McEachran and Stauffer (—-—), Saha (—), Shi and Burrow (□), Gulley *et al.* (●).

complication compensates for some of the problems experienced in the lighter rare gases, as it is beneficial to the use of phase-shift analysis techniques at the integral cross section level. In fact it is the first example in the rare gas atoms where MERT can be used independently, and with reasonable accuracy, to provide a comparison between σ_{e} and σ_{m} (see for example Haddad and O'Malley 1982; Buckman and Mitroy 1989; Petrović *et al.* 1995). It is also another gas where early comparisons between beam and swarm results for low energy integral cross sections and the scattering length were at odds for many years with the culprit, unfortunately from our perspective, being the beam result.

There have been a large number of determinations of elastic differential, integral and momentum transfer cross sections for argon at energies below 5 eV and it is not our intention to summarise them all here, as this has been done recently by Gibson *et al.* (1996*a*). Rather we once again present a somewhat subjective selection of these measurements to illustrate the state of play for this gas. The early transport measurements of Milloy *et al.* (1977) and Robertson (1977) have provided the basis for a number of subsequent MERT-based analyses by Haddad and O'Malley and Petrovic *et al.* From a 'beam' perspective there have been measurements of the total cross section by Ferch *et al.* (1985) and Buckman and Lohmann (1986) amongst many others, as well as DCS measurements by Williams (1979), Srivastava *et al.* (1981), Weyhreter *et al.* (1988), Furst *et al.* (1989) and Gibson *et al.* (1996*a*). There have been many theoretical calculations of these cross sections over the years but we shall restrict ourselves to a comparison with the recent multiconfiguration calculation of Saha (1995) and the polarised orbital approach of McEachran and Stauffer (1996). The latter calculation is a variation of the earlier polarised orbital work by these authors where dynamic distortion and relativistic effects are also accounted for.

Before embarking on a comparison of the swarm and beam integral cross sections for argon it is worth summarising the findings of an extensive investigation into the reliability of MERT as a comparison standard by Buckman and Mitroy (1989). They applied various MERT fits to integral elastic cross sections ($\sigma_{\rm e}$) which were calculated from published theoretical phase shifts and randomly 'smeared' by a few percent to mimic 'typical' experimentally measured values. The phase shifts derived from such a fit were then used to calculate $\sigma_{\rm m}$ and the result compared to the $\sigma_{\rm m}$ calculated directly from the phase shifts. This procedure indicated that for argon, either a four- or five-parameter MERT fit, up to a maximum energy of 1 eV, would permit a reasonably accurate (5–10%) means of comparison between the two cross sections derived from the two different types of experiment.

In Fig. 5 we provide a summary of the integral cross section results for argon by comparing the swarm-derived $\sigma_{\rm m}$ of Haddad and O'Malley with a $\sigma_{\rm m}$ derived from a MERT fit to the $\sigma_{\rm e}$ of Buckman and Lohmann, a $\sigma_{\rm m}$ derived by multiplying the $\sigma_{\rm e}$ of Buckman and Lohmann by the theoretical $\sigma_{\rm m}/\sigma_{\rm e}$ ratio from McEachran and Stauffer's calculation, and the calculated $\sigma_{\rm m}$ of McEachran

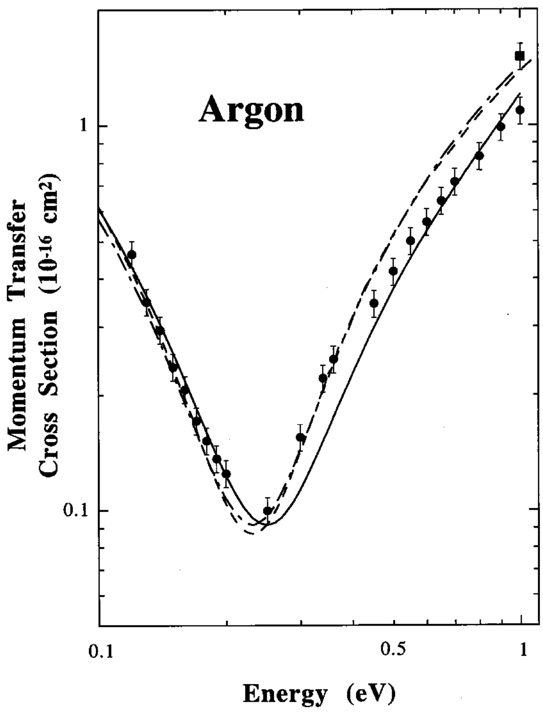

Fig. 5. Momentum transfer cross section (10^{-16} cm^2) for argon between 0·1 and 1·0 eV: Haddad and O' Malley (- - -), McEachran and Stauffer (—-—), Buckman and Lohmann—MERT (—), Buckman and Lohmann—from theory ratio (●) and Gibson *et al.* (■).

and Stauffer. Also shown is a lone point at 1 eV which is derived from the recent elastic DCS measurements of Gibson *et al*. Noting that we have now gone to a logarithmic scale for this figure in order to highlight the stong energy dependence of the cross section, the overall level of agreement here is not as good as exhibited for either helium or neon. Nonetheless it is still reasonable, given the difficulties, outlined above, that are associated with the comparison. In particular, at energies below the RT minimum, the level of agreement is extremely good.

In Fig. 6 we show a number of experimental and theoretical results for the elastic DCS at an energy of 1·0 eV. The experimental results are those of Haddad and O'Malley (1982) which have been calculated from phase shifts derived from a MERT-based fit to the swarm transport data of Milloy *et al*. (1977) and Robertson (1977), the DCS of Weyhreter *et al*. (1988) and the most recent DCS values of Gibson *et al*. (1996). The calculations of Saha and McEachran and Stauffer are also shown. The crossed-beam measurements and the theory are all in excellent agreement whilst the DCS derived from the swarm measurements are larger in magnitude at the cross section peak and the structure is shifted to smaller scattering angles. We note that this disagreement does *not* necessarily reflect on either the quality of the swarm transport measurements or the integral cross sections that are derived from them. Rather it is perhaps a reflection of the uncertainties inherent in the calculation of a *differential* cross section from phase shifts which have been derived from a fit to an *integral* cross section, the latter being less sensitive to the phase shifts than the former.

3·1·4 Scattering Lengths for the Rare Gases

As mentioned previously, one point where beam and swarm experiments can be compared is at zero energy where both are equivalent and can be expressed, in terms of the scattering length A, as

$$\sigma_{\mathrm{e}} = 4\pi A^2 = \sigma_{\mathrm{m}}\,, \qquad \text{for} \quad E = 0\ \mathrm{eV}\,.$$

Whilst it is not possible within either technique to directly measure the zero-energy cross section, the values are usually obtained by extrapolation of a measured cross section to zero energy using a technique such as MERT. To complete our discussion on the rare gases we show, in Table 1, a comparison of scattering lengths for He, Ne and Ar from swarm and beam measurements and from theory. Once again it is immediately apparent that the level of agreement for this parameter is extremely good for each of these gases, the largest discrepancies (4–5%) occuring in the case of neon where the theoretical value is larger than both the beam and swarm results.

3·1·5 Miscellaneous Atomic Systems

A number of other atomic systems have been, or are possible, subjects for the comparison of cross sections determined from swarm and beam experiments. Three possible candidates are the heavier rare gases krypton and xenon, and mercury. However, it is apparent that the level of agreement which exists between the various measurements of total cross sections, momentum transfer cross sections, and between theoretical calculations, is nowhere near as good as

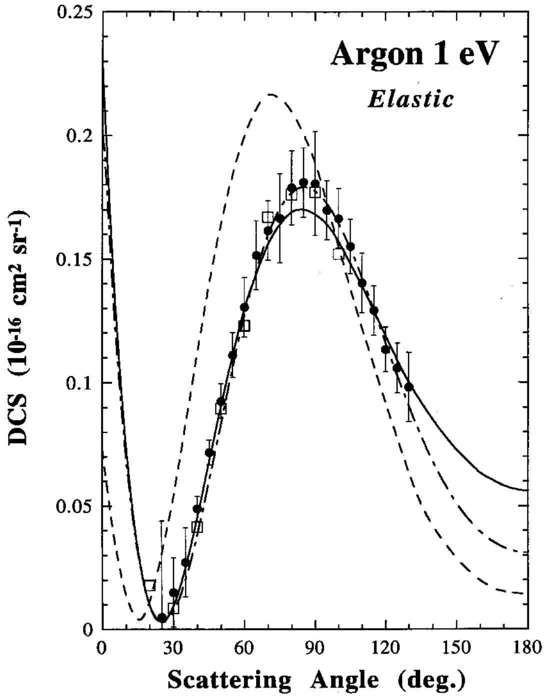

Fig. 6. Differential cross section (10^{-16} cm^2 sr^{-1}) for elastic electron scattering from argon at an incident energy of 1·0 eV: Haddad and O'Malley (- - -), Weyhreter *et al.* (□), Saha (—), McEachran and Stauffer (—-—) and Gibson *et al.* (●).

Table 1. Summary of beam, swarm and theoretical results for the scattering lengths (in Å^2) for He, Ne and Ar

	Technique	Authors	Scattering length
He	Swarm	Crompton *et al.*	1·19
	Beam	Buckman & Lohmann	1·16
	Theory	Nesbet	1·183
Ne	Swarm	O'Malley & Crompton	0·214
	Beam	Gulley *et al.*	0·212
	Theory	Saha (1990)	0·222
Ar	Swarm	Petrovic *et al.*	−1·459
	Beam	Buckman & Lohmann	−1·442
		Ferch *et al.*	−1·449
	Theory	McEachran & Stauffer	−1·441

in the lighter rare gases considered above (e.g. Buckman and Lohmann 1987). It is also apparent that comparison approaches such as MERT are not as readily applicable in the heavier rare gases (e.g. Buckman and Mitroy) and probably not at all in the case of Hg.

3·2 Diatomic Molecular Systems

A selection of the available momentum transfer cross sections for electron scattering from oxygen (O_2), carbon monoxide (CO), nitric oxide (NO), hydrogen (H_2) and nitrogen (N_2) is provided in Table 2. These particular molecules were specifically chosen for consideration because of their general importance in upper atmospheric physics, the physics of gaseous electronic devices in which they are constituents, laser physics applications and plasma physics (Itikawa 1994). In addition, while H_2 provides the fundamental test case for the application of various scattering theories to electron–molecule collisions systems (Morrison *et al*. 1987), the others in this list also, in some sense, represent prototypical systems. For example, while O_2 is a homonuclear diatomic molecule like H_2 and N_2, it represents an open-shell electron–molecule scattering system, but without the further complicating factor of having a permanent dipole moment. Similarly, NO can then be thought of as an extension of this as, while it is an open-shell molecule, it is a heteronuclear diatomic with a permanent dipole moment.

As is apparent from Table 2 there have already been extensive studies, both beam and swarm based, into O_2, CO, H_2 and N_2, the glaring exception being NO where only the crossed-beam work of Mojarrabi *et al*. (1995) is known to us. We now consider H_2, N_2 and CO in more detail below.

3·2·1 H_2

The vexed problem of low energy electron scattering from molecular hydrogen has been dealt with in some detail in another paper in this volume but it is (unfortunately) clear that one cannot approach a topic such as the present without giving it due consideration.

H_2 is one of the few molecules where the comparison process between beam and swarm measurements, of rotational excitation, can be made with reasonable accuracy and reliability. This is due to several factors. Firstly, the energy spacing of the rotational levels is reasonably large, enabling their resolution with state of the art crossed-beam spectrometers and, secondly, the first vibrational threshold occurs at a relatively high energy allowing swarm analyses to yield rotational cross sections which can be essentially free of uniqueness problems for energies below about 0·5 eV. A number of recent publications (e.g. Morrison *et al*. 1987) have shown the good agreement which exists between beam experiments, swarm experiments and theory for both the momentum transfer cross section and the low energy rotational (0–2, 1–3) excitation cross sections and we shall not go into that detail here. However, as is now well known amongst the afficionados of the field, the situation regarding near threshold vibrational (0–1) excitation is anything but well resolved and has been perhaps the longest standing discrepancy between beam and swarm measurements of scattering cross sections. Much has been written about this topic in the literature and it is not our intention to re-visit it too extensively but rather to summarise the situation as it presently stands, taking into account some of the recent developments.

The magnitude of the near-threshold $\nu = 0$–1 vibrational excitation cross section has been the subject of considerable uncertainty and debate for many years. This uncertainty arose initially due to the disagreement between total cross sections derived from swarm (Crompton *et al*. 1970; England *et al*. 1988) and single collision (Ehrhardt *et al*. 1968; Linder and Schmidt 1971) experiments. At energies below a few eV these cross sections disagreed with each other by as much as 60%, with the 'beam' cross sections being larger than the swarm. This discrepancy, although important, received little further attention until the 1980s when advances in electron–molecule scattering theory were such that attention was focussed on rotational and vibrational excitation of this fundamental diatomic system. Firstly, Morrison and co-workers (Morrison *et al*. 1987) carried out a number of vibrational close coupling calculations on electron–hydrogen scattering and, whilst we will not discuss the theory in any detail here, their calculations for the integral $\nu = 0$–1 cross section largely agreed with the crossed-beam experiments and not the swarm-derived values. Further swarm studies were undertaken by Crompton and colleagues during the 1980s using techniques involving the measurement of

Table 2. Summary of the available momentum transfer cross sections for crossed-beam and swarm studies of electron–diatomic molecule scattering

Molecule	Technique	Authors	Energy range (eV)
O_2	Swarm	Hake and Phelps (1967)	0·01–100
	Swarm	Lawton and Phelps (1978)	0·01–100
	Crossed beam	Shyn and Sharp (1982)	2–200
	Swarm	Hayashi (1987)	0·6–1000
	—	Shimamura (1989)	0–1000
	Crossed beam	Sullivan *et al*. (1995)	1–30
	Swarm	Hayashi (1995)	1–2000
CO	Swarm	Pack *et al*. (1962)	0·003–0·04
	Swarm	Hake and Phelps (1967)	0·001–10
	Crossed beam	Tanaka *et al*. (1978)	3–100
	Swarm	Land (1978)	0–100
	Swarm	Haddad and Milloy (1983)	0·4–4
	Crossed beam	Gibson *et al*. (1996)	1–30
NO	Crossed beam	Mojarrabi *et al*. (1995)	1·5–40
H_2	Swarm	Frost and Phelps (1962)	0·01–100
	Swarm	Crompton *et al*. (1969)	0–2
	Swarm	Gibson (1970)	0·01–0·48
	Crossed beam	Srivastava *et al*. (1975)	3–75
	Crossed beam	Shyn and Sharp (1981)	2–200
	Crossed beam	Nishimura *et al*. (1985)	2·5–200
	Crossed beam	Khakoo and Trajmar (1986)	15–100
	Swarm	Hayashi and Niwa (1987)	15–1000
	Swarm	England *et al*. (1988)	0–5
	Crossed beam	Brunger *et al*. (1991)	1–5
	Swarm	Schmidt *et al*. (1994)	0·01–2
N_2	Swarm	Frost and Phelps (1962)	0·004–10
	Swarm	Englehardt *et al*. (1964)	0·001–20
	Crossed beam	Srivastava *et al*. (1976)	7–75
	Swarm	Taniguchi *et al*. (1978)	0·1–500
	Crossed beam	Cartwright (1978)	10–60
	Crossed beam	Shyn and Carignan (1980)	1·5–400
	Swarm	Haddad (1984)	0–10 eV
	Swarm	Phelps and Pitchford (1985)	0–1000
	Crossed beam	Sohn *et al*. (1986)	0·1–1·5
	Swarm	Hayashi and Niwa (1987)	0–1000
	Swarm	Ohmori *et al*. (1988)	0·05–500
	Crossed beam	Sun *et al*. (1995)	0·55–10

transport parameters in gas mixtures and, although these experiments resulted in small differences in the final swarm cross section set (England *et al.* 1988) the overall conclusion regarding the above discrepancy between beam and swarm measurements was unchanged. In addition, the use of a numerical optimisation technique to find the optimal hydrogen cross section set which was compatible with the transport parameters of England *et al.* did not reveal any major differerences in the cross sections (Morgan 1993).

A series of absolute elastic scattering and vibrational excitation measurements as well as further scattering calculations were undertaken by Brunger *et al.* (1990, 1991) and Buckman *et al.* (1990) with a specific aim to address this discrepancy. These measurements were placed on an absolute scale by use of the relative flow technique for the elastic channel and it is important to note that a careful characterisation of the relative analyser transmission for elastic and inelastic electrons was also made. At those energies where the discrepancy between the former beam and swarm measurements was largest, around $1 \cdot 5$ eV, the integral cross sections derived from the new crossed-beam results were in good agreement with the older crossed-beam studies and with the vibrational close coupling calculations, but still substantially ($\approx$60%) larger than the swarm-derived cross section. Importantly, the angular differential scattering cross sections were also in good agreement with the theory in both magnitude and shape.

There has been one other recent theoretical investigation of the $\nu = 0$–1 excitation cross section. The Kohn variational technique has been applied to the problem by Rescigno *et al.* (1993) and the calculated cross sections are in excellent agreement with the recent (and old) beam measurements for both differential and total cross sections at energies between $1 \cdot 0$ and 5 eV. All of the recent results for the total vibrational cross section at energies between threshold and 5 eV are illustrated in Fig. 7 where they are also contrasted with the original swarm and beam cross sections. There is little doubt that the new experimental and theoretical values clearly favour a vibrational excitation cross section which is higher than that provided by the swarm analysis of Crompton and colleagues (e.g. England *et al.*). However, the reasons for this discrepancy, which has been extensively studied over the past ten years from both an experimental and theoretical point of view, still remain elusive.

3·2·2 N_2

Despite the fact that low energy electron scattering by N_2 has been the subject of more experimental investigations than any other molecule, there is only minor scope for comparison between beam and swarm experiments as there has been little overlap between these two techniques for both elastic scattering or rotational/vibrational excitation. There are a number of reasons for this. Firstly, whilst there have been many measurements of both momentum transfer and total cross sections, the means for comparison between these two cross sections in N_2 is not well established. Secondly, and perhaps more importantly, the overwhelming majority of low energy crossed-beam studies has been preoccupied with the unravelling of the collision dynamics associated with the strong $^2\Pi_g$ resonance spanning the energies from 2–5 eV. A summary of low energy collision cross sections in N_2 and an extensive comparison between beam-derived cross sections and theory has recently been given by Sun *et al.* (1995).

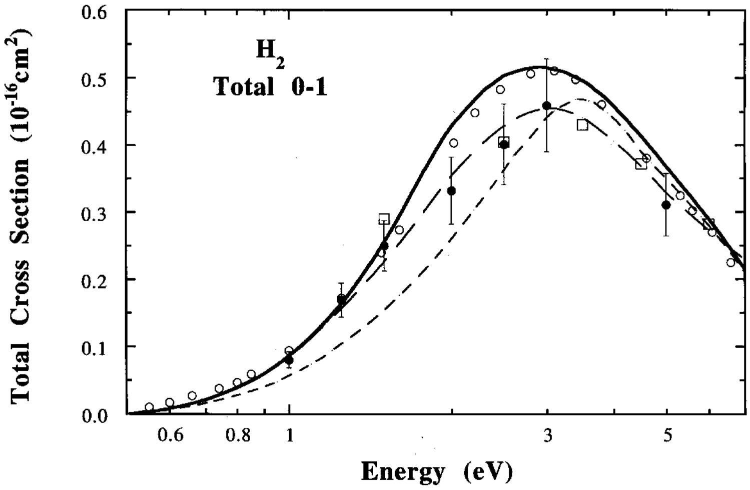

Fig. 7. Total vibrational excitation (0–1) cross section (10^{-16} cm^2) for low energy electron scattering from H_2: Ehrhardt *et al.* (○), Linder and Schmidt (□), Morrison *et al.* (—), England *et al.* (- - -), Brunger *et al.* (●) and Rescigno *et al.* (— —).

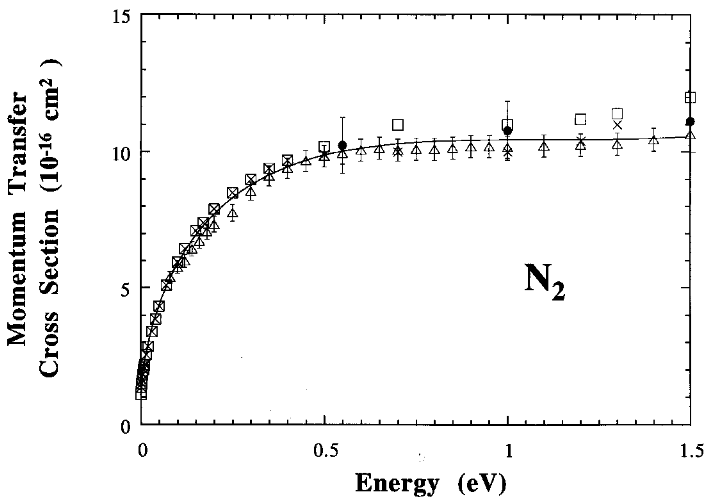

Fig. 8. Momentum transfer cross section (10^{-16} cm^2) for N_2 between 0 and 1·5 eV: Shyn and Carignan (+), Haddad (□), Phelps and Pitchford (x), Morrison *et al.* (—), Sun *et al.*—DCS-derived (●) and Sun *et al.*—ToF measurement of total converted with theory (△).

Nonetheless, it is possible to make comparisons between momentum transfer cross sections derived from swarm measurements with those which arise from low energy crossed-beam measurements of elastic scattering and those from recent theory. This is done in Fig. 8 where we compare the swarm-derived $\sigma_{\rm m}$ of Haddad

(1984) and Phelps and Pitchford (1985) with the crossed beam measurements of Shyn and Carignan (1980), and both the crossed beam and ToF measurements of Sun *et al.* (1995) as well as with the very recent theory of Morrison and co-workers (Morrison *et al.* 1996). Note that the ToF measurements of Sun *et al.* are of the *total* cross section and they have been converted to $\sigma_{\rm m}$ by the use of the ratio of $\sigma_{\rm m}/\sigma_{\rm t}$ from the theoretical calculations of Morrison *et al.* The comparison in Fig. 8 is somewhat limited in that it only extends to an energy of $1\cdot5$ eV, to avoid the complications caused by the resonance, but the agreement in this energy range is clearly extremely good between the beam, swarm and theoretical cross sections.

3·2·3 CO

A summary of the published momentum transfer cross sections for electron scattering from CO can be found in Table 2. Of the available data we have plotted the swarm-derived $\sigma_{\rm m}$ of Land (1978) and Haddad and Milloy (1983) and the crossed-beam derived $\sigma_{\rm m}$ data of Tanaka *et al.* (1978) and Gibson *et al.* (1996*b*) in Fig. 9. Also in this figure we show the theoretical results of Jain and Norcross (1992), Morgan and Tennyson (1993) and Morgan (1995).

In the energy region where they overlap, the data of Gibson *et al.* and Haddad and Milloy are in quite good agreement, given the uncertainty on the beam data. The exception to this is at the cross section peak around 2 eV, the peak arising due to the enhancement of the cross section by the strong $^2\Pi$ shape resonance. Here the results of Gibson *et al.* are some 50% lower than those of Haddad and Milloy. This discrepancy is possibly due, at least in part, to the fact that the $\sigma_{\rm m}$ of Haddad and Milloy includes contributions from all open rotational and vibrational channels as well as the elastic channel. Both these measurements do, however, find the resonance peak to be at about $1\cdot9$ eV. A similar picture also emerges when the $\sigma_{\rm m}$ of Gibson *et al.* is compared to that of Land. In this case, however, the swarm-derived $\sigma_{\rm m}$ of Land predicts the resonance peak to occur at an energy which appears to be too low. It is also apparent from Fig. 9 that the beam results for $\sigma_{\rm m}$ of Gibson *et al.* and Tanaka *et al.* (1978) are in reasonable agreement.

The *R*-matrix calculation of Morgan (1995) is found to be in good accord with the $\sigma_{\rm m}$ data of Gibson *et al.* for energies greater than $1\cdot9$ eV, while the earlier *R*-matrix result of Morgan and Tennyson predicts the maximum in the resonant cross section at a much lower energy. The work of Jain and Norcross (1992) clearly reproduces (see Fig. 9) the gross features of the momentum transfer cross section, although there are some differences in the fine detail when this calculation is compared to the cross sections of both Haddad and Milloy and Gibson *et al.* At higher energies (not shown in the figure) the calculation of Jain *et al.* (1984) is in reasonable accord with the data of Tanaka *et al.*

The recent crossed-beam results of Gibson *et al.* have helped clarify the level of agreement between beam and swarm determinations of $\sigma_{\rm m}$ in e^-+CO scattering. At this stage the remaining major source of concern, at lower beam energies, relates to the magnitude of $\sigma_{\rm m}$ at the $^2\Pi$ resonance peak. More sophisticated theoretical calculations are still required to provide an adequate description of this collision system

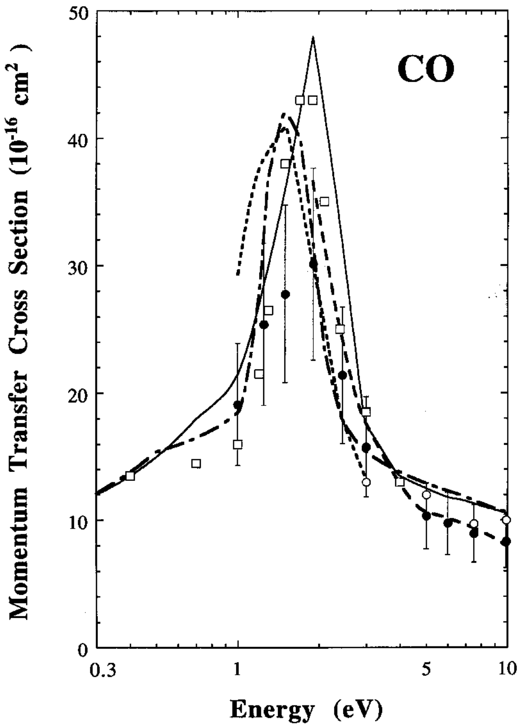

Fig. 9. Momentum transfer cross section (10^{-16} cm^2) for CO between 0·3 and 10 eV: Land (—-—), Haddad and Milloy (□), Tanaka *et al.* (○), Jain and Norcross (—), Morgan and Tennyson (- - -), Morgan (– – –) and Gibson *et al.* (●).

3·3 Polyatomic Molecules

In Table 3 we provide a summary of the available experimental determinations for momentum transfer cross sections for eighteen polyatomic molecules. We do not claim this list is exhaustive but it does provide a fair overview for the current status of the field. It is clear from Table 3 that, with the notable exceptions of methane (CH_4) and to a lesser extent carbon dioxide (CO_2) and water (H_2O), there has not been a significant number of either swarm or crossed-beam studies of electron–polyatomic molecule scattering processes. Indeed for many of the molecules there has only been one or two swarm investigations, with most of these conducted prior to the mid-1980s. With regard to the crossed-beam measurements then we see the situation is quite unsatisfactory as in most cases there is only one cross section determination based on the relative-flow technique. Moreover, the reported swarm and crossed-beam elastic momentum transfer cross sections do not often have overlapping energy ranges. Consequently it appears that the field of electron–polyatomic molecule scattering provides fertile ground for further investigations by both beam and swarm experimentalists. Two specific examples, CO_2 and CH_4, are now discussed below to highlight this latter point.

Table 3. Summary of the available momentum transfer cross sections for crossed-beam and swarm studies of electron–polyatomic molecule scattering

Molecule	Technique	Authors	Energy range (eV)
CH_4	Crossed beam	Tanaka *et al.* (1982)	3–20
	Swarm	Haddad (1985)	0·01 –10
	Crossed beam	Sohn *et al.* (1986)	0·2 –5
	Swarm	Ohmori *et al.* (1986)	0·05 –50
	Crossed beam	Sakae *et al.* (1989)	75–700
	Swarm	Davies *et al.* (1989)	10–30
	Crossed beam	Shyn and Cravens (1990)	5–50
	Swarm	Schmidt (1991)	0·001 –2
	Crossed beam	Boesten and Tanaka (1991)	1·5 –100
	Swarm	Hilderbrandt (1996)	0–3
	Crossed beam	Bundschu *et al.* (1997)	0·6 –5·4
C_2H_6	Swarm	Duncan and Walker (1974)	0·01–2
	Swarm	McCorkle *et al.* (1978)	0·02–0·2
	Crossed beam	Tanaka *et al.* (1988)	3–100
C_3H_8	Swarm	Duncan and Walker (1974)	0·01–1
	Swarm	McCorkle *et al.* (1978)	0·02–0·3
	Crossed beam	Boesten *et al.* (1994)	2–100
C_2H_4	Swarm	Hayashi (1990)	0·01–100
C_2H_2	Swarm	Bowman and Gordon (1967)	0·01–0·06
OCS	—	—	—
N_2O	Swarm	Pack and Phelps (1961)	0·01–0·05
	Crossed beam	Marinkovic *et al.* (1986)	10–80
	Swarm	Hayashi and Niwa (1987)	0·01–1000
	Crossed beam	Johnstone and Newell (1993)	5–80
O_3	Crossed beam	Shyn and Sweeney (1993)	3–20
CO_2	Swarm	Hake and Phelps (1967)	0·01–100
	Swarm	Lowke *et al.* (1973)	0·04–100
	Crossed beam	Shyn *et al.* (1978)	3–90
	Crossed beam	Register *et al.* (1980)	4–50
	Crossed beam	Iga *et al.* (1984)	500–1000
CF_4	Swarm	Stefanov *et al.* (1988)	0·007–2
	Crossed beam	Sakae *et al.* (1989)	75–700
	Crossed beam	Boesten *et al.* (1992)	1·5–100
CF_3CI	—	—	—
CF_2CI_2	Swarm	Novak and Frechette (1985)	0–100
	Swarm	Hayashi and Niwa (1987)	0·01–100
$CFCI_3$	—	—	—
CCI_4	—	—	—
H_2S	Crossed beam	Gulley *et al.* (1993)	1–30
NH_3	Swarm	Pack *et al.* (1962)	0·01–0·08
	Swarm	Hayashi (1981)	0·01–100
	Crossed beam	Alle *et al.* (1992)	2–30
SO_2	Crossed beam	Orient *et al.* (1982)	12–200
	Swarm	Hayashi and Niwa (1987)	0·01–100
	Crossed beam	Trajmar and Shyn (1989)	5–50
	Crossed beam	Gulley and Buckman (1994)	1–30
H_2O	Swarm	Pack *et al.* (1962)	0·01–0·08
	Crossed beam	Danjo and Nishimura (1985)	4–200
	Crossed beam	Shyn and Cho (1987)	2·2–20
	Swarm	Hayashi (1989)	0·01–100
	Crossed beam	Johnstone and Newell (1991)	6–50

3·3·1 CO_2

In Fig. 10 the experimental elastic momentum transfer cross sections of Register *et al.* (1980), Lowke *et al.* (1973) and Shyn *et al.* (1978) are compared along with the theoretical results of Morrison *et al.* (1977). The level of agreement between the crossed-beam results of Shyn *et al.* and Register *et al.* is quite poor, over their common energy range of measurement. Shyn *et al.* did not perform a relative-flow-type measurement (Nickel *et al.* 1989) and they normalised their relative DCS data to the elastic helium calculation of LaBahn and Callaway (1970) which has been superseded in recent years. In addition to these concerns with their normalisation procedure, we also note that for other molecules e.g. H_2 and N_2 this group tends to find elastic DCS which are considerably larger in magnitude at backward angles than those of other laboratories. As the momentum transfer cross section is strongly weighted towards scattering at backward angles this may account for some of the discrepancy. On the other hand, as Register *et al.* used a relative flow technique to set the absolute scale of their DCS data, with reliable helium cross sections as the standard set, we would consider their cross section to be the more accurate of the two crossed-beam determinations for σ_m in the lower energy regime.

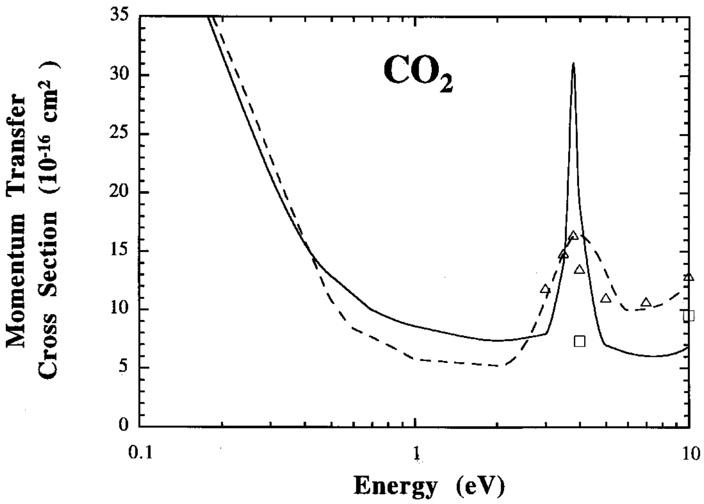

Fig. 10. Momentum transfer cross section (10^{-16} cm^2) for CO_2 between 0·1 and 10 eV: Lowke *et al.* (---), Morrison *et al.* (—), Shyn *et al.* (△) and Register *et al.* (□).

Somewhat paradoxically, the swarm-derived σ_m of Lowke *et al.* tends to favour the momentum transfer data of Shyn *et al.* over that of Register *et al.* For the reasons we have just described we believe this 'agreement' between Shyn *et al.* and Lowke *et al.* to be fortuitous, perhaps suggesting that both beam and swarm groups should revisit this scattering system for further study.

At very low energies (<0·4 eV) the calculation of Morrison *et al.* is in good accord with the swarm-derived result of Lowke *et al.* However it appears from Fig. 10 that in the region of the $^2\Pi_u$ resonance this calculation is clearly larger in magnitude than the swarm σ_m at the resonance peak.

In summary, the determination of σ_m for electron scattering from CO_2 provides further opportunities for both beam and swarm experimental studies and theory. In particular there is a definite need for another, systematic, crossed-beam elastic scattering investigation to be conducted at beam energies below 100 eV which also encompasses the $^2\Pi_u$ resonance.

3·3·2 CH_4

Methane provides a rather fertile patch for comparisons of beam and swarm cross sections. In addition to those momentum transfer cross sections derived by extrapolation and integration of crossed-beam elastic DCS data (Tanaka *et al.* 1982; Sohn *et al.* 1986; Sakae *et al.* 1989; Shyn and Cravens 1990; Boesten and Tanaka 1991; Bundschu *et al.* 1997) there is also a large number of swarm-derived σ_m for methane (Haddad 1985; Schmidt 1991; Davies *et al.* 1989; Hilderbrandt 1996). A selection of these data and a selection of the results of the calculations of Jain (1986), Yuan (1988), McNaughten *et al.* (1990), Nishimura and Itikawa (1994) and Gianturco *et al.* (1995) are plotted in Fig. 11.

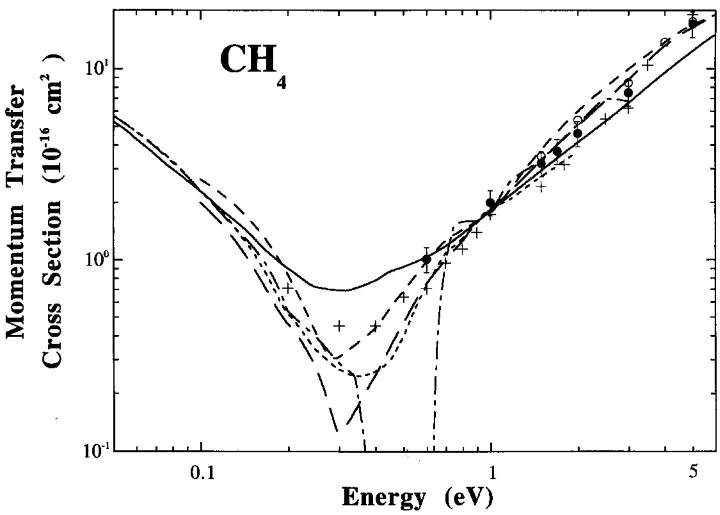

Fig. 11. Momentum transfer cross section (10^{-16} cm^2) for CH_4 between 0·05 and 6 eV: Haddad (—), Sohn *et al.* (+), Jain (- - -), Yuan (— —), Schmidt (- - -), Boesten and Tanaka (○), Hildebrandt (— - —) and Bundschu *et al.* (●).

At energies below about 0·1 eV and above about 0·8 eV, all three swarm determinations for σ_m are in quite good accord with one another. In the region of the Ramsauer–Townsend minimum, however, there are very large differences between all of these cross sections. The most recent and, in principle, most accurate result of Hildebrandt predicts a much deeper minimum in the cross section than did either Haddad or Schmidt. We believe this may be illustrative of the uniqueness problems, alluded to earlier, that can be associated with the swarm technique near, or above, newly opening channels. In particular the very deep minimum in σ_m of Hildebrandt may in some sense be compensated for by the large, resonantly enhanced, integral cross sections they find for the $\nu_{1,3}$ and $\nu_{2,4}$ composite vibrational excitation modes of CH_4 (see below).

With regard to the beam-derived results the magnitude of the σ_m of Sohn *et al.*, in the region of the RT minimum ($\approx 0 \cdot 3$ eV), lies between the swarm-derived values of Haddad and those of Schmidt. At $0 \cdot 6$ eV the recent crossed-beam result of Bundschu *et al.* favours the determination of Haddad, while that of Sohn *et al.*, at this same energy, is in better accord with the cross section of Schmidt. Thereafter, up to 4 eV, all the crossed-beam results (Tanaka *et al.*, Sohn *et al.*, Boesten and Tanaka and Bundschu *et al.*) are in quite good agreement with each other and with the swarm-derived results. For energies greater than 4 eV, and specifically in the region of the peak in σ_m (7–8 eV), the crossed-beam results of Sohn *et al.*, Boesten and Tanaka and Bundschu *et al.* are in good accord with each other but somewhat higher in magnitude than those of Tanaka *et al.*, Shyn and Cravens and Haddad, which are also in fair agreement with one another. As the most recent results of both Boesten and Tanaka and Bundschu *et al.* obtained their absolute scale by careful application of the relative flow technique, using helium as the standard gas, we believe their determination of σ_m, and that of Sohn *et al.* to be the more reliable. Furthermore, in their study Bundschu *et al.* assumed that methane can be approximated as a pseudo central-force scattering system, due to the nature of the (essentially) spherically symmetric electron charge distribution, so that a 'phase-shift analysis' of the elastic DCS could be undertaken. This allowed Bundschu *et al.* to quite accurately extrapolate their measured DCS to 0° and 180° before integrating to obtain the momentum transfer cross section, thereby minimising, to some extent, this problem which is inherent in crossed-beam measurements.

Finally, we note that from a theoretical perspective, the calculation of Jain (1986) appears to be superior to that of Yuan (1988) in predicting the depth of the RT minimum in σ_m. Notwithstanding this, for energies below $0 \cdot 1$ eV, the trend in the calculated cross section of Yuan suggests it would be in fair accord with the very low energy, swarm-derived data of Haddad, Schmidt and Hildebrandt.

There have also been several measurements of vibrational excitation of methane using both crossed-beam and swarm techniques. An example of these measurements for the lowest-lying composite bending ($\nu_{2,4}$) modes is shown in Fig. 12 where they are also compared with a recent theoretical result. Obviously there is a rather mixed level of agreement between recent experiments. Near threshold, and up to about 2 eV, the swarm results of Haddad (1985), Schmidt (1991) and Hilderbrandt (1996) differ substantially with the latter, in particular, demonstrating a number of very strong near-threshold peaks. Whilst threshold resonances have been demonstrated in vibrational excitation of these modes (Rohr 1980) we are not aware of any evidence from sensitive, high resolution crossed-beam experiments for such strong or numerous structures in this energy range nor can we place any sensible physical interpretation on them. The recent crossed-beam derived results of Bundschu *et al.* are in good agreement with the Hildebrandt cross section at 1 and 2 eV but unfortunately do not extend low enough in energy to provide a conclusive comparison with the apparent near-threshold structures. The crossed-beam data are significantly higher than the other two swarm cross sections at 1 eV, but in reasonable agreement with them both at 2 and 3 eV. At higher energies, the agreement between the cross section of Bundschu *et al.* and other crossed-beam studies (Tanaka *et al.*, Shyn) is marginal. On the other hand, the agreement between this latest crossed-beam data and the recent theoretical calculation of Althorpe *et al.* (1995) is quite good at all energies.

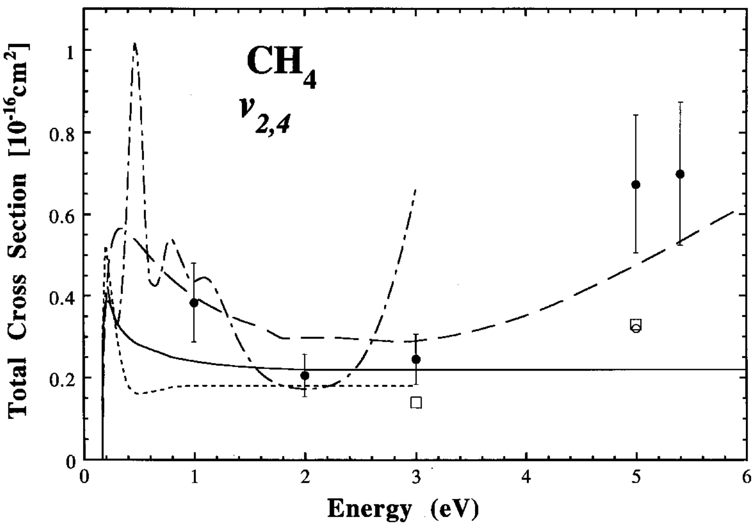

Fig. 12. Total vibrational excitation cross sections (10^{-16} cm^2) for the composite $\nu_{2,4}$ bending modes of CH_4: Tanaka *et al.* (□), Shyn (○), Haddad (—), Schmidt (---), Althorpe *et al.* (— —), Bundschu *et al.* (●) and Hildebrandt (—-—).

In summary, while the recent measurements of Bundschu *et al.* have clarified certain aspects of the momentum transfer cross section for CH_4, specifically in the energy range 0·6–5·4 eV, there is still further work required, particularly in relation to the position and depth of the RT minimum. These further investigations should ideally be conducted by beam, swarm and theoretical colleagues in close collaboration.

4. Conclusions

The above examples indicate that, despite the apparently common perception to the contrary, the situation regarding the comparison of cross sections derived from swarm and beam approaches, for simple atomic and molecular systems, is reasonably healthy. It is certainly true that the period since 1980 has seen the resolution of many of the discrepancies concerning the lighter atomic and molecular gases, with the exception of vibrational excitation in H_2. In fact this latter case, important as it is, has in our view clouded and polarised the issue somewhat and overshadowed the substantial gains made in many other cases. Whilst we have not dwelt too much on the relative experimental advantages of the two approaches, it is obvious to us that neither one individually provides a complete solution to the problems associated with collision cross section measurements at low incident energies. Rather it is important that they be treated as complementary approaches to a common problem and that their perceived strengths be applied appropriately, and in a collaborative fashion, in obtaining cross sections for a wide variety of processes from thermal to intermediate energies. It is also apparent that comparisons between the two techniques for molecular systems would benefit greatly from a more universally applicable version of MERT or something similar. Recent developments in this area (Isaacs and Morrison 1992; Morrison *et al.* 1996) are extremely encouraging.

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