

# Analyses of Recent Experimental and Theoretical Determinations of e-H<sub>2</sub> Vibrational Excitation Cross Sections: Assessing a Long-Standing Controversy

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## Abstract

During the last four years, we have undertaken a major effort to resolve a serious, long-standing discrepancy between various experimental and theoretical determinations of the cross section for the  $v_0 = 0 \rightarrow v = 1$  vibrational excitation of H<sub>2</sub>. This effort has involved crossed electron-beam molecular-beam measurements of relative angular distributions, measurements of transport coefficients in mixtures of H<sub>2</sub> and various rare gases, and *ab initio* theoretical calculations using a vibrational close-coupling formalism with an exact treatment of non-local exchange effects. The discrepancy remains unresolved—a fact with potentially wide-ranging consequences for beam experiments, theory, and the unfolding of inelastic electron-molecule cross sections from swarm data. New analyses of the transport data and the application of a new method of extrapolating angular distributions beyond the range of measurement sheds light on this disagreement and its implications.

## 1. Introduction and Background

Rotational and vibrational excitations of molecules play an important role in many gas discharge phenomena. Hence, cross sections for these processes are vital to developing and modelling devices which incorporate some such discharge (see, for example, Hunter and Christophorou 1984; Christophorou and Hunter 1984). These inelastic phenomena have therefore attracted considerable theoretical and experimental interest during the past several decades. (For a recent review see Morrison 1988.) Most of this work has emphasised resonant processes, for determining the structure of cross sections near a resonance energy (usually at a few eV) not only challenges experimentalists but also stimulates theorists to examine more closely the physical underpinnings of these phenomena (Domcke 1991). But this emphasis has led to the neglect of direct excitations, in spite of their importance as energy-loss processes.

Some reluctance to measure directly rotational and vibrational cross sections at very low energies is understandable. The threshold energies (and associated energy losses) for rotational excitation are typically a few meV at most, and for vibrational excitation, a few tenths of an eV. Such small thresholds pose formidable problems for direct measurements, e.g. in a crossed-beam apparatus.

Swarm experiments provide an alternative way to determine these cross sections: the analysis of data taken in these experiments leads indirectly to a set of inelastic and momentum-transfer cross sections that are consistent with the observed 'transport properties', quantities which describe the behaviour of a swarm of electrons drifting and diffusing through a molecular gas of known density under the influence of an external electric field of known strength (Huxley and Crompton 1974). But problems also confront this approach: in most electron-molecule systems so many inelastic processes are energetically accessible even at very low energies that the interpretation of transport data is difficult and sometimes ambiguous—and, apart from exceptional circumstances, the resulting set of cross sections may not be unique.

Equally formidable difficulties attend *ab initio* theoretical calculations of low-energy cross sections, especially at near-threshold energies (Lane 1980; Morrison 1983). First, in representing the electron-target potential one must include important non-local interactions (short-range exchange and bound-free correlation) as well as induced second-order effects (long-range polarisation). Second, in formulating the collision dynamics one must cope with the non-spherical nature of the electron-molecule Coulomb potential and the large number of diverse target states that may participate in the scattering. Finally, one must be sure that any simplifications one uses in solving the continuum Schrödinger equation accurately describe the effect of the nuclear motion on the scattering function.

The most widely studied electron-molecule system is electron-hydrogen. From a theoretical standpoint, hydrogen—with its closed-shell structure, few electrons, lack of sharp low-energy resonances, and weak electron-nuclear attraction—is the simplest neutral molecule. From an experimental standpoint, the sparseness of its ro-vibrational spectrum makes this system ideal for the determination of near-threshold rotational and vibrational cross sections via transport analysis of swarm data (for details see Morrison *et al.* 1987*a*). Moreover, the comparatively large threshold energies (and energy losses) for vibrational excitation of H<sub>2</sub> make feasible accurate direct measurements of vibrational cross sections in crossed-beam experiments. Nevertheless, experimental difficulties often limit the accuracy of, and confidence in, these cross sections, while very few *ab initio* theoretical studies have sought high accuracy at near-threshold energies. Consequently our knowledge of near-threshold inelastic cross sections for this simple system has remained fraught with questions and discrepancies.

One of the most vexing of these discrepancies concerns the  $v_0 = 0 \rightarrow v = 1$  cross section. Many years ago Ehrhardt *et al.* (1968) and Linder and Schmidt (1971) reported crossed-beam measurements of this cross section. About the same time, Crompton *et al.* (1969, 1970*a*) reported a determination of  $\sigma_{0 \rightarrow 1}^{(v)}$  by comparing calculated transport coefficients with measured values whose uncertainties were at most a few percent. Over the energy range from threshold to about 1.5 eV, these beam- and swarm-derived cross sections disagreed by amounts greatly in excess of the errors and uncertainties claimed for each result. Moreover, until the last decade few theorists had focused on vibrational excitation at these energies. So by 1980 this large and unacceptable disparity remained a mystery.

For these reasons, theorists at the University of Oklahoma and swarm experimentalists at the Australian National University undertook in the early 1980s a joint program aimed at determining total, momentum-transfer, rotational,

and vibrational e-H<sub>2</sub> cross sections of accuracy comparable to elastic cross sections for e-He scattering (Nesbet 1979). Essential to this program was the dovetailing of theory and experiment so as to effectively eliminate the uniqueness problem from transport analysis (Morrison *et al.* 1987a). By 1987, our calculations of *ab initio* theoretical cross sections and study of their implications for the analysis of swarm data led to the following situation (described at length in Crompton and Morrison 1986):

- (1) Morrison *et al.* (1984a,b) had calculated elastic and ro-vibrational e-H<sub>2</sub> cross sections using a composite dynamical theory consisting of converged close-coupling calculations (using a model exchange potential) for inelastic *S*-matrix elements and adiabatic-nuclei calculations (with an exact exchange potential) for elastic elements. The formulations used in these calculations were wholly independent of experimental cross sections.
- (2) The resulting theoretical rotational cross section  $\sigma_{0 \rightarrow 2}^{(r)}$  agreed with the swarm-derived result to within experimental error from threshold to 0.8 eV. (As the energy increases above this value the uncertainty in the swarm result increases too rapidly to warrant such comparisons.) The theoretical momentum-transfer cross section  $\sigma_{\text{mom}}$  agreed equally well with the swarm result. And the 'grand total cross section'  $\sigma_{\text{tot}}$  (the sum of cross sections for elastic scattering and *all* energetically accessible excitations) agreed with data taken in time-of-flight experiments.
- (3) Based on this agreement, we determined a new *vibrational* cross section  $\sigma_{0 \rightarrow 1}^{(v)}$  by using the shape of the theoretical rotational cross sections  $\sigma_{0 \rightarrow 2}^{(r)}$  and  $\sigma_{1 \rightarrow 3}^{(r)}$  to extrapolate the swarm-derived rotational cross sections to energies above 0.3 eV, the upper limit of high accuracy for the swarm analysis. (Doing so amounts to only a minor renormalisation of the theoretical curve.) The uncertainty in the vibrational cross section obtained via this procedure was considerably smaller than that in the earlier cross section of Crompton *et al.* (1969, 1970a).
- (4) To our astonishment, the resulting  $\sigma_{0 \rightarrow 1}^{(v)}$  was lower than the theoretical curve by as much as 40% (near 1 eV), a difference well outside the combined uncertainties of the scattering calculations and the unfolding of this cross section by transport analysis of swarm data.

So although we had used theoretical results to reduce significantly the uncertainty in  $\sigma_{0 \rightarrow 2}^{(r)}$ , we had not been able to resolve the long-standing disagreement between beam and swarm determinations of  $\sigma_{0 \rightarrow 1}^{(v)}$ . The new theoretical result supported the older beam data of Ehrhardt *et al.* (1968) and Linder and Schmidt (1971).

Since 1987 new initiatives have been undertaken on all three fronts: beam experiments, swarm experiments and their analysis, and *ab initio* theory. This paper reports a new analysis of the results of this effort and updates our earlier discussions of this conundrum (Crompton and Morrison 1986; Morrison *et al.* 1987a).

## 2. Synthesis of Recent Experimental and Theoretical Work

### 2.1. New Beam and Swarm Measurements

The major new component of this program was a complementary experiment in which Brunger *et al.* (1990, 1991) obtained absolute differential cross sections

using an electron–neutral beam apparatus specifically designed for this purpose. These authors measured angular distributions for both vibrationally elastic and inelastic ( $v_0 = 0 \rightarrow v = 1$ ) scattering which they normalised using the relative flow technique with elastic e–He cross sections as the benchmark (see, for example, Trajmar *et al.* 1984).

On the swarm front, experimentalists undertook new measurements involving dilute mixtures of  $\text{H}_2$  and rare gases and analyses of the resulting transport coefficients. Because the findings of these measurements bear directly on the vibrational discrepancy in hydrogen, we here summarise the philosophy of mixture experiments.

The addition of small traces of a *molecular* gas to a *monatomic* (rare) gas drastically alters the energy distribution of electrons in the swarm and, consequently, the transport coefficients (Bowe 1960; Robertson 1977). For example, in Fig. 1 we compare electron distribution functions for pure Ne and for an  $\text{H}_2$ –Ne mixture for a fixed ratio of electric field strength ( $E$ ) to gas number density ( $N$ ), i.e., for  $E/N = 0.3 \text{ Td}$  ( $1 \text{ Td} \equiv 10^{-21} \text{ V/m}^2$ ). The addition of only 1% of  $\text{H}_2$  reduces the mean energy of the swarm by about 50%. Consequently, the drift velocity  $v_{\text{dr}}$  (i.e. the velocity of the centroid of an isolated swarm of electrons drifting under the influence of an electric field) increases by more than 70%. These huge changes in the properties of the swarm do not arise from a change in the (aggregate) momentum-transfer cross section; although  $\sigma_{\text{mom}}$  does play a key role in determining these properties, in particular the transport coefficients, it changes in this instance by at most 10% due to the addition of so minute an amount of  $\text{H}_2$ . Rather, the changes in the transport properties arise

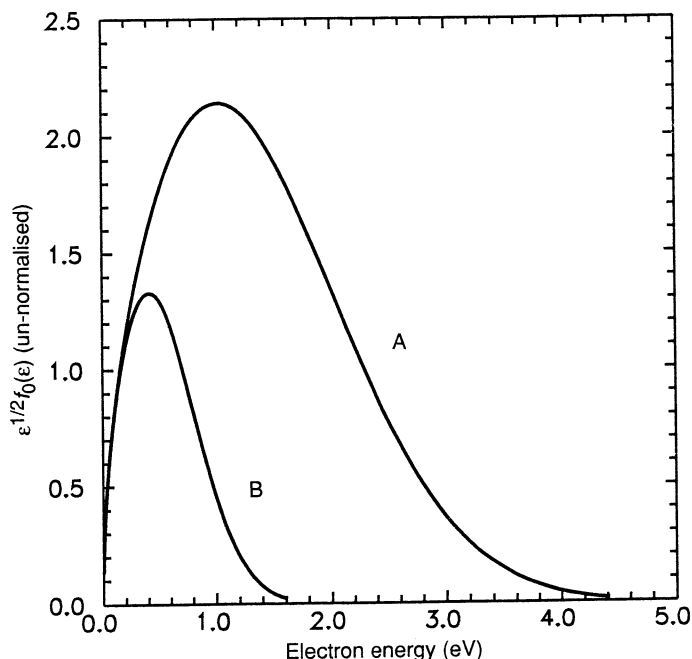


Fig. 1. Electron energy distribution functions in Ne (curve A) and in a mixture of 1.16%  $\text{H}_2$  in Ne (curve B).

from alterations to the exchange of energy between electrons and the gas due to rotational and vibrational excitation. So when calculating the drift velocity *for such a dilute mixture* the influence of  $\sigma_{\text{mom}}$  for H<sub>2</sub> is quite small compared to that of the inelastic cross sections. It follows that any errors in this cross section (which was derived from transport data in *pure* H<sub>2</sub>) do not induce corresponding errors in the inelastic cross sections derived from an analysis of the mixture data.

The second important point about this method is that it is, in effect, a *difference* method. [Petrović and Crompton (1987), in fact, treated the problem *explicitly* in this way.] One first takes measurements in a pure carrier gas (e.g. He, Ne, or Ar), then in a dilute mixture of H<sub>2</sub> with the gas, using the same apparatus under identical conditions. This procedure ensures that the major sources of systematic error (e.g. measurement of the pressure, the temperature, and the length of and voltage across the drift tube) are common to both sets of measurements. If, for example, the gas density  $N$ , as determined from the gas pressure and temperature, were in error, then the derived momentum transfer cross section for electron scattering from the carrier would reflect this fact. But since that cross section is used in the analysis of mixture data, which are themselves subject to the same systematic error, these errors cancel to first order.

These new mixture measurements also eliminate a concern about one of the experiments in the original determination of  $\sigma_{0 \rightarrow 1}^{(v)}$  by Crompton *et al.* (1969, 1970*a*). Those earlier analyses involved data for two transport coefficients: drift velocities, as measured in time-of-flight experiments, and the ratio of the transverse diffusion coefficient to the mobility, as measured in steady-state Townsend-Huxley experiments. The new studies, which do not incorporate the second measurement, do not involve the less-than-definitive interpretation of Townsend-Huxley experiments. Finally, the new measurements provide information about the vibrational cross section over a larger energy range, because one can now take data at higher swarm energies. In Section 3 we shall examine in detail one of the new data sets from the experiments of England *et al.* (1988) for a mixture of 1.16% H<sub>2</sub> in Ne.

## 2.2. New Theoretical Calculations

Complementing these experimental efforts were new theoretical studies based on a more accurate treatment of the vibrational dynamics and a more accurate, model-free treatment of the non-local exchange potential, which plays a crucial role in vibrational excitation.

In solving the continuum Schrödinger equation one must carefully and accurately allow for the effect of the nuclear motion on the scattering function (Morrison *et al.* 1984*a,b*). We now solve this equation using a body-frame vibrational close-coupling (BFVCC) theory (Morrison 1988 and references therein). This formulation includes the vibrational motion *fully* via an expansion of the scattering function in a (truncated) set of target vibrational states. It includes the rotational motion adiabatically, but we have demonstrated elsewhere (Morrison *et al.* 1984*a*) that this approximation to the rotational dynamics introduces errors of less than 2% in  $\sigma_{0 \rightarrow 1}^{(v)}$ . Moreover, it does not affect  $\sigma_{\text{tot}}$ , which is dominated by the elastic cross section below a few eV. We solve the coupled integrodifferential scattering equations via an implementation of the linear-algebraic method (Collins and

Schneider 1981; Schneider and Collins 1982, 1984) which allows for full vibrational coupling and an exact treatment of the non-local exchange potential (Trail 1992; Trail and Morrison 1993), and we enforce stringent convergence criteria which guarantee numerical precision of all scattering quantities to better than 2%.

The exchange potential appears in these coupled equations because the system wavefunction must be antisymmetric under pairwise electron interchange. Its presence makes their solution quite arduous: because exchange is non-local, the scattering equations are now integrodifferential in character, and their solution is computationally much more demanding than that of the differential equations which result if the potential is local. So in our earlier calculations, we approximated the effects of exchange with a local, energy-dependent model potential which has achieved great success for elastic and rotational excitation of a variety of electron-molecule systems (Morrison and Collins 1978, 1981). The successes of the free-electron-gas potential notwithstanding, its use in the present context seemed problematic, particularly in light of the acute sensitivity of vibrational cross sections to exchange.

In our new theoretical calculations we discarded this model and instead now treat the exchange potential more rigorously as a non-local operator. This operator acts along with the (local) static and polarisation potentials to couple components of the radial scattering function.

But exchange is only one of the three components of the interaction potential. We calculate the others, the static and correlation/polarisation terms, from a Hartree-Fock wavefunction for the ground electronic state of  $H_2$  (Morrison *et al.* 1984a). Our correlation/polarisation potential (Gibson and Morrison 1984; Morrison *et al.* 1987b), which represents long-range (adiabatic) polarisation of the  $H_2$  charge cloud and short-range bound-free correlation effects, is free of parameters but uses a non-penetrating approximation (Temkin 1957) in the near-target region.

### 2.3. Direct Comparison of Theoretical and Experimental Results

Buckman *et al.* (1990) have compared the new beam and theoretical cross sections and discussed the implications of this comparison for the current controversy. To some extent, the new experimental and theoretical results compound rather than resolve the problem. As shown in Fig. 2, the beam and theoretical  $v_0 = 0 \rightarrow v = 1$  cross sections agree extremely well from 1.0 eV (the lowest energy at which measurements were taken) to about 1.5 eV. Moreover, in this energy range these cross sections agree very well with those from earlier beam measurements by Ehrhardt *et al.* (1968) while at 1.5 eV and above there is good agreement with the results of Linder and Schmidt (1971). Below 1.5 eV, the swarm-derived cross section stands alone, differing by as much as 40% from the others.

Between 1.5 and 2.5 eV the beam and theoretical cross sections diverge; they converge again at higher energies. At 2.0 eV, the cross section of Brunger *et al.* lies roughly half-way between the theoretical and swarm-derived results, while at higher energies both sets of beam data tend to favour the latter. At and above 2.0 eV both the swarm and theoretical cross sections lie within (or at worst just outside) the  $\pm 20\%$  error bars of the cross section of Brunger *et al.* (1991).

On the other hand, the new vibrational cross section derived from mixture data essentially confirms the earlier values of Crompton *et al.* (1969, 1970*a*). This cross section, together with the rotational cross sections determined by England *et al.* (1988) from drift velocity data for two H<sub>2</sub>-Ne mixtures, fit three distinct sets of drift and diffusion data in para- and normal hydrogen, and three additional sets of drift velocity data in H<sub>2</sub>-rare gas mixtures (Haddad and Crompton 1980; Petrović and Crompton 1987).

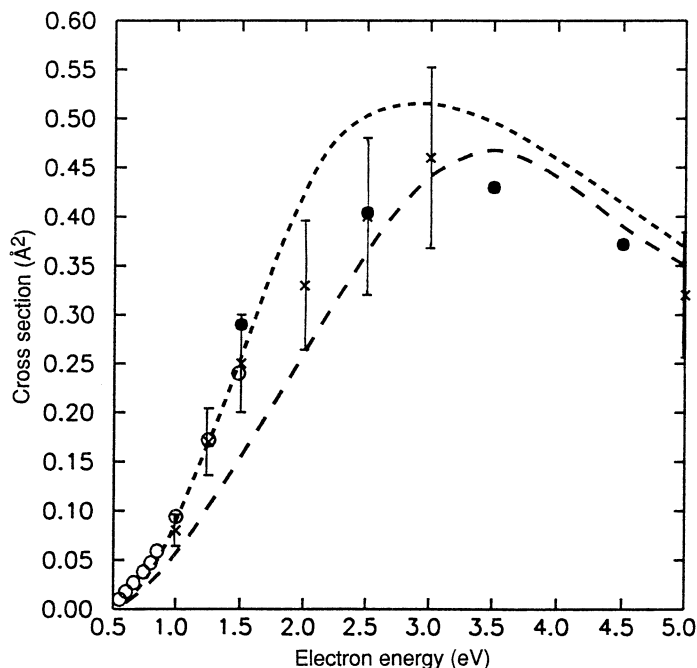


Fig. 2. Experimental and theoretical data for the  $v_0 = 0 \rightarrow v = 1$  excitation of H<sub>2</sub> by electron impact: × (with error bars), Brunger *et al.* (1991); ○, Ehrhardt *et al.* (1968); ●, Linder and Schmidt (1971); ---, England *et al.* (1988) (swarm-derived); -.- Trail (1992) (BFVCC theory). Interpolation of the data of Brunger *et al.* provided input for the transport calculations described in Section 3.3.

The direct comparison in Fig. 2 does not, therefore, illuminate the disagreement over  $\sigma_{0 \rightarrow 1}^{(v)}$  except to emphasise that it has not gone away. To gain insight into the remaining disagreements, both at low energies and in the interesting region below and above 1.5 eV, we have undertaken several studies based on transport analysis. These are the subject of the next section.

### 3. Transport Analysis of Experimental and Theoretical Cross Sections

The differences between the vibrational cross sections in Fig. 2 raise questions about their accuracy, particularly about the swarm result, which is significantly below both the theoretical and beam results for energies less than 2 eV. Furthermore, since all the experimental results lie below theory around 2.5 eV, one needs to know whether the experimental transport data from which the swarm cross section

is derived are sensitive to the vibrational cross sections in this energy range, and therefore whether the swarm results are truly in significant conflict with theory. But to date no one has systematically studied the sensitivity of the transport coefficients to the magnitude of this cross section. Unfortunately, one cannot simply tack error bars onto cross sections obtained from swarm experiments by matching calculated to measured transport coefficients. Indeed, quantifying the uncertainty in swarm-derived cross sections is conceptually quite different from determining error bars for cross sections measured directly in beam experiments.

Swarm data typically consist of two kinds of transport coefficients (Huxley and Crompton 1974; Morrison *et al.* 1987a): the drift velocity  $v_{\text{dr}}$  and the ratio of the transverse diffusion coefficient to mobility  $D_T/\mu$ , where the mobility is related to the drift velocity by  $\mu = v_{\text{dr}}/E$ . (Only the drift velocity is of concern in this paper.) One can certainly estimate the errors in these measured coefficients at various values of  $E/N$ , the fundamental independent variable in the experiments. But placing credible bounds on the resulting cross sections is much more difficult—especially for molecular gases, where the electron energy distribution and hence the transport coefficients are influenced, in general, by elastic and several inelastic processes. Using the new transport data for  $\text{H}_2$ -rare gas mixtures we can investigate two related questions:

- Question 1:** Over what energy range can one extract significant information about  $\sigma_{0 \rightarrow 1}^{(v)}$  from available transport data?
- Question 2:** At what energies does  $\sigma_{0 \rightarrow 1}^{(v)}$  most affect transport coefficients for a given  $E/N$ ?

Furthermore, we can examine quantitatively the compatibility of cross sections from theoretical calculations or other experiments with measured transport data. In particular, by artificially modifying selected cross sections in selected energy ranges, we can address a third question:

- Question 3:** Could one compensate for any differences between experimental transport data and values calculated using a particular  $\sigma_{0 \rightarrow 1}^{(v)}$  by making reasonable modifications to other cross sections that influence the electron energy distribution function, such as the rotational cross sections?

Study of this question sheds light on the *significance* of the differences in Fig. 2 between the swarm-derived  $\sigma_{0 \rightarrow 1}^{(v)}$  and those from other sources.

Beyond these questions is another which concerns the accuracy of the integral cross sections derived from the differential cross section (DCS) data. Because such data are necessarily restricted in their angular range, comparisons of theoretical results and those obtained from crossed-beam experiments are best made via differential rather than integral (total or momentum-transfer) cross section data; this approach avoids the additional errors which arise from extrapolation outside the range of measurement. On the other hand, swarm experiments yield only integral cross sections, so the only comparisons that can be made with them must be at this level. While this presents no problem when comparing *theoretical* and swarm-derived results, it unfortunately makes comparisons between beam and swarm results less than definitive.



Integral (grand total) cross sections obtained from time-of-flight absorption-cell experiments (Ferch *et al.* 1980; Jones 1985) and momentum-transfer cross sections derived from swarm experiments are intrinsically more accurate than those obtained by integrating DCS data, even were additional errors not introduced by extrapolation in that procedure.\* Neither of the former require normalisation, the essential advantage in this respect of both swarm and absorption-cell experiments being that the number density of the target gas can be accurately determined from measurements of the pressure and temperature of the static (or quasi-static) gas sample in the drift tube or absorption cell. Therefore it has been possible to determine  $\sigma_{\text{tot}}$  with uncertainties of less than 2 or 3% (Ferch *et al.* 1980; Jones 1985) while uncertainties of less than 2% have been achieved for the swarm-derived  $\sigma_{\text{mom}}$  for He and 5% for H<sub>2</sub>. At low energies (i.e. less than a few eV) this estimated uncertainty for H<sub>2</sub> is probably conservative.†

With these caveats, we compare theoretical and experimental total and momentum-transfer cross sections in Fig. 3. Over the whole energy range from 1.0 to 6.0 eV, the total e-H<sub>2</sub> cross sections of Brunger *et al.* (1991) are lower than the theoretical or time-of-flight results. Similarly, their momentum-transfer cross sections lie below theoretical and swarm-derived values. These observations pose a fourth and final question which we shall address:

**Question 4:** What are the implications for the controversy over vibrational excitation in hydrogen of these differences in  $\sigma_{\text{tot}}$  and  $\sigma_{\text{mom}}$ ?

### 3.1. The Energy Range of Significance for the Swarm-derived Vibrational Cross Section

Analysis of electron transport data at different values of  $E/N$  yields information about  $\sigma_{0 \rightarrow 1}^{(v)}$  over different energy ranges. To understand this, we need first to demonstrate the connection between the distribution function for electrons in the swarm,  $f(\epsilon)$ , and the transport coefficients (here only the drift velocity need concern us), and second, to show how the distribution function changes as  $E/N$  is varied.

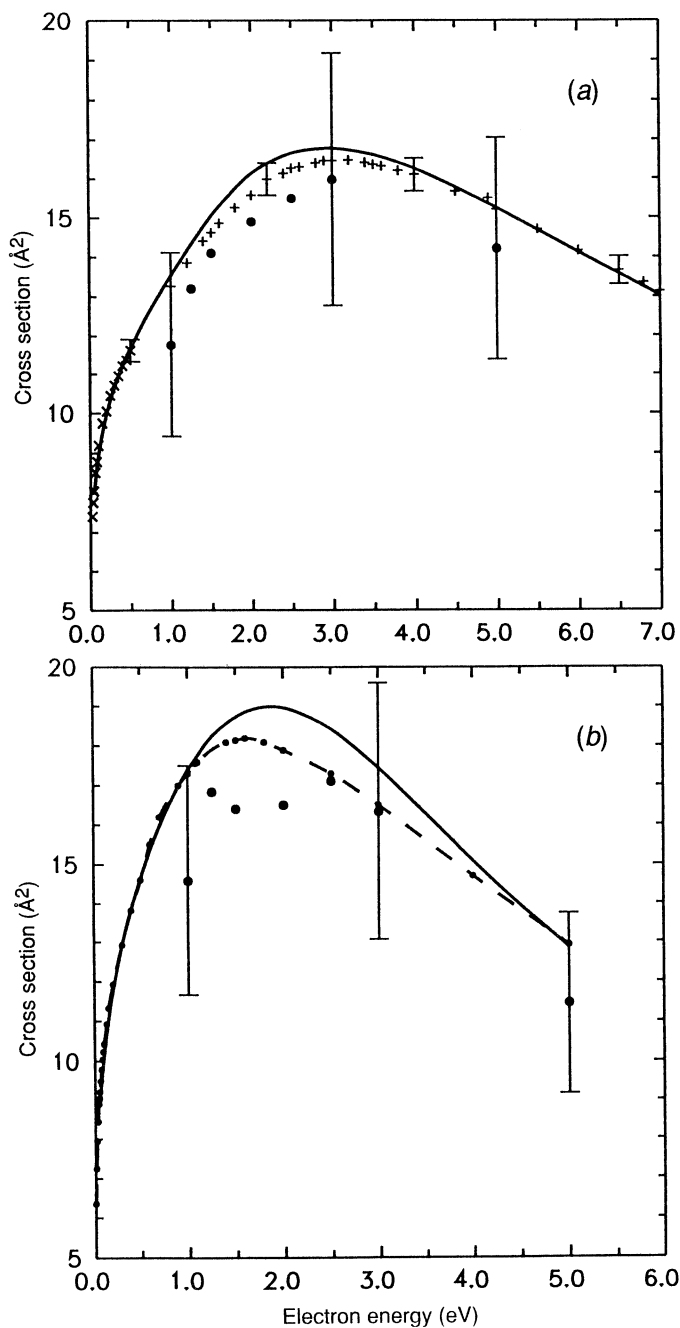
In the two-term approximation, the drift velocity is given by (Huxley and Crompton 1974)

$$v_{\text{dr}}(E/N) = -\frac{e}{3} \frac{E}{N} \left( \frac{2}{m} \right)^{1/2} \int_0^\infty \frac{\epsilon}{\sigma_{\text{mom}}(\epsilon)} \frac{d}{d\epsilon} f_0(\epsilon) d\epsilon, \quad (1)$$

where  $\sigma_{\text{mom}}$  is the aggregate (elastic and inelastic) momentum-transfer cross section and  $f_0(\epsilon)$  is the (symmetric) leading term in a Legendre expansion of the electron velocity distribution function, written in terms of the electron energy  $\epsilon$ . Thus  $v_{\text{dr}}$  depends directly on  $E/N$  and in a more complicated way on  $\sigma_{\text{mom}}$  and  $f(\epsilon)$  through the integral in equation (1). Note that the drift velocity does

\* At energies greater than 0.5 eV, the threshold for the  $v_0 = 0 \rightarrow v = 1$  excitation,  $\sigma_{\text{tot}}$  includes contributions from vibrational excitations; however these amount to less than 3% for energies below 5 eV.

† At thermal energies, the electron energy distribution function is Maxwellian, and  $\sigma_{\text{mom}}$  alone determines the transport coefficients.



**Fig. 3.** Experimental and theoretical integrated e-H<sub>2</sub> cross sections. (a) Total cross section (showing typical error bars only for a few experimental points): x, Ferch *et al.* (1980); +, Jones (1985); •, Brunger *et al.* (1991); —, theory (Trail 1992). (The data of Jones are grand total cross sections and at higher energies therefore include small contributions from vibrational excitation.) (b) Momentum-transfer cross sections: •, Brunger *et al.* (1991); --- England *et al.* (1988) (swarm-derived); —, theory (Trail 1992).

not *explicitly* depend on the inelastic cross sections; their influence is indirect, through their effect on the distribution function  $f(\epsilon)$ .

One can compute the distribution function by solving the Boltzmann equation, using as input integral momentum-transfer and inelastic cross sections. In Fig. 4 we show this function at three values of  $E/N$  for electrons in a mixture of 1.16% H<sub>2</sub> in Ne, one of the two mixtures studied by England *et al.* (1988). As  $E/N$  increases, the energy range that contains the majority of the electrons in the swarm broadens and moves to higher energies. At the lowest value,  $E/N = 0.4$  Td, very few electrons in the swarm have energies greater than 1.5 eV; consequently we might expect the distribution function, and hence the drift velocity, to be little affected by the magnitude of the cross sections above this energy. At  $E/N = 0.8$  Td, a high proportion of electrons have energies above 1.5 eV, but very few above 3.5 eV. For this case, therefore, we would expect the drift velocity to be most affected by the magnitude of the cross sections from 1.5 to 3.5 eV, and to a lesser extent by its magnitude at lower energies. Finally, at  $E/N = 1.7$  Td, the highest value at which England *et al.* (1988) measured drift velocities, the distribution is sufficiently broad that the transport coefficients should exhibit some sensitivity to the cross sections at energies even above 4 eV, and considerable sensitivity to them near 3 eV. Fig. 4 also makes clear why one cannot define precisely the energy range over which swarm data provide significant information about these cross sections.

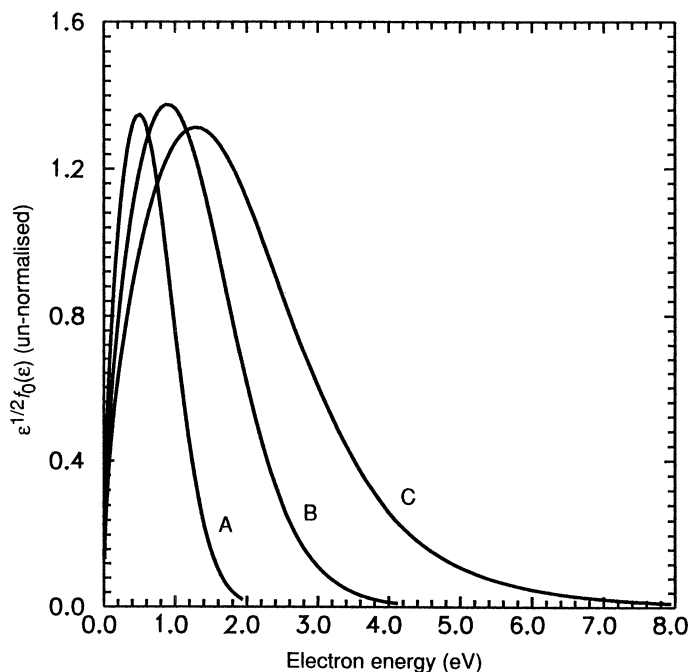


Fig. 4. Electron energy distribution functions in a mixture of 1.16% H<sub>2</sub> in Ne at  $E/N$  = (A) 0.4, (B) 0.8, and (C) 1.7 Td.

With this background we now consider the accuracy of vibrational cross sections derived from measured drift velocities. The tests we report here are similar to ones Crompton *et al.* (1970*b*) used to explore the range of validity of

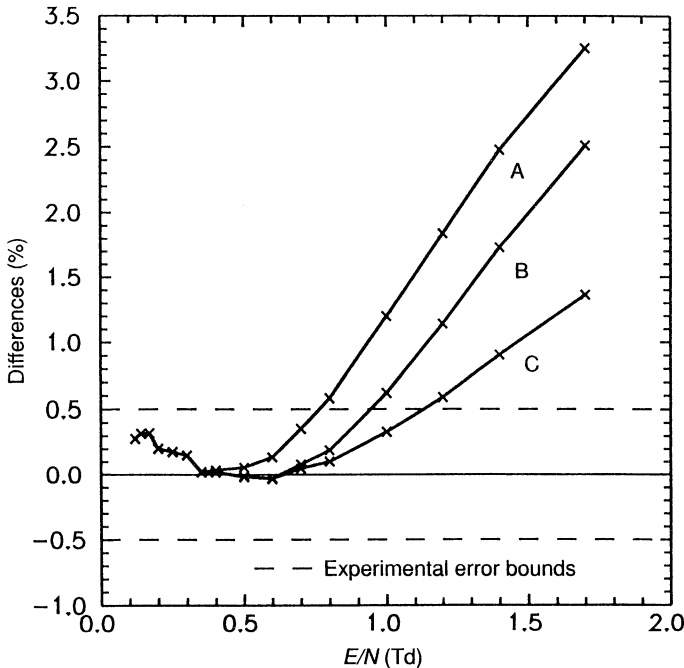
swarm-derived momentum transfer cross sections in monatomic gases. One way to determine the energy ranges where a given cross section most affects  $v_{\text{dr}}$  is to artificially alter that cross section over selected ranges and recompute the drift velocity. In the present instance, we increased  $\sigma_{0 \rightarrow 1}^{(v)}$  and  $\sigma_{0 \rightarrow 2}^{(v)}$  by 20% above a chosen minimum energy. In particular, we consider three such modifications:

- Case A:** We increase  $\sigma_{0 \rightarrow 1}^{(v)}$  linearly from its swarm-derived value at 1.8 eV to 20% above that value at 2.2 eV. At higher energies we increase this cross section by a constant factor of 20%. Finally, we apply the same modifications to  $\sigma_{0 \rightarrow 2}^{(v)}$  but with the transition occurring between 1.78 eV and 2.0 eV.
- Case B:** We increase  $\sigma_{0 \rightarrow 1}^{(v)}$  and  $\sigma_{0 \rightarrow 2}^{(v)}$  as in Case A with the transitions occurring between 2.6 and 3.0 eV.
- Case C:** We increase  $\sigma_{0 \rightarrow 1}^{(v)}$  and  $\sigma_{0 \rightarrow 2}^{(v)}$  as in Case A with the transitions occurring between 3.5 and 4.0 eV.

Case A exemplifies a class of modifications which produces a highly significant mismatch between calculated and measured drift velocities, while case C produces a much smaller but nevertheless significant mismatch. Case B is intermediate between these extremes.

To analyse these cases we computed the fractional difference between measured values of  $v_{\text{dr}}$  and those calculated using our two-term Boltzmann code (Gibson 1970), i.e.,

$$\text{percent difference} = \frac{v_{\text{dr}}^{(\text{calc})} - v_{\text{dr}}^{(\text{exp})}}{v_{\text{dr}}^{(\text{exp})}} \times 100. \quad (2)$$

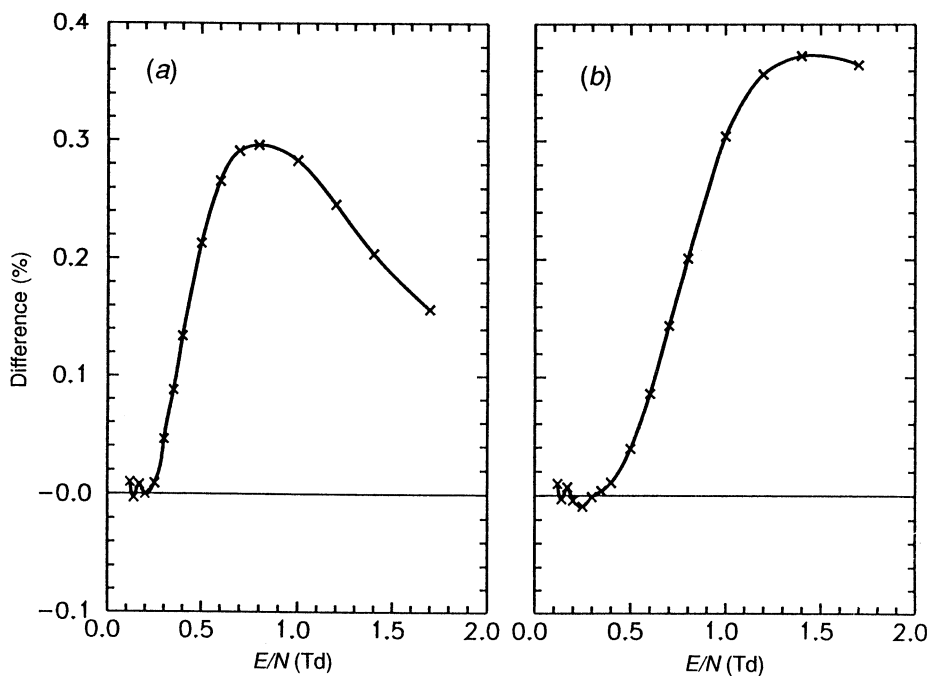


**Fig. 5.** Percent differences between calculated and measured drift velocities [see equation (2)] in a mixture of 1.16%  $\text{H}_2$  in Ne for the three cases discussed in Section 3.1.

In Fig. 5 we show these percent differences as functions of  $E/N$  for each of the three cases.

The results for case A highlight energies where the vibrational cross sections in Fig. 2 disagree most severely. Increasing  $\sigma_{0 \rightarrow 1}^{(v)}$  above 2 eV introduces errors in  $v_{dr}(E/N)$  which at the three highest values of  $E/N$  are 4 to 6 times experimental error, showing that  $v_{dr}$  is quite sensitive to the magnitude of this cross section at these energies. Case C extends this inquiry to higher energies. Now only at the three highest values of  $E/N$  do the calculated  $v_{dr}$  disagree with measured coefficients by more than experimental error. Still, the drift velocity is demonstrably sensitive to  $\sigma_{0 \rightarrow 1}^{(v)}$  even above 3.5 eV. Finally, in case B, which is intermediate between cases A and C, we find as expected that calculated drift velocities at the four highest values of  $E/N$  are near or beyond the limits of experimental error. The calculated  $v_{dr}$  at  $E/N = 1.7$  Td, for example, lies above the measured value by more than 3.5 times the experimental uncertainty.

Together, these tests place 'error bars' of a sort on the determination of  $\sigma_{0 \rightarrow 1}^{(v)}$  from measured drift velocities. Specifically, they show that analysis of this transport coefficient, measured to state-of-the-art precision, can determine this vibrational cross section to significantly better than 20% from threshold to between 3 and 4 eV. Clearly, then, one can extract significant information about  $\sigma_{0 \rightarrow 1}^{(v)}$  at energies up to a few eV, and the differences between the swarm result and those from beam experiments and theory up to 3 or 4 eV cannot be ignored.



**Fig. 6.** Percent differences between calculated drift velocities in a mixture of 1.16% H<sub>2</sub> in Ne using the cross section set of England *et al.* (1988) and the modified sets described in Section 3.2. (a) When perturbations are applied to the vibrational cross sections between 1.4 and 1.6 eV, the drift velocities are maximally affected around  $E/N = 0.8$  Td. (b) When the perturbations are moved to the range 2.0 to 2.4 eV, the maximally affected range shifts to about  $E/N = 1.5$  Td.

### 3.2 Correlating the Energy Dependence of $\sigma_{0 \rightarrow 1}^{(v)}$ with the $E/N$ Dependence of $v_{dr}$

Having demonstrated the sensitivity of  $v_{dr}$  to the vibrational cross section, we now refine this study in order to determine quantitatively the values of  $E/N$  at which this transport coefficient is most *sensitive* to the magnitude of  $\sigma_{0 \rightarrow 1}^{(v)}$  within specific energy ranges. The indirect character of the determination of cross sections via transport analysis precludes a precise correlation of electron energy with maximum sensitivity because differences in  $\sigma_{0 \rightarrow 1}^{(v)}$  influence the energy distribution function  $f(\epsilon)$ , and hence the transport coefficients, in complicated ways. Nevertheless, we can obtain insight into the matter using a procedure akin to that of Section 3.1.

In particular, we use the  $\sigma_{0 \rightarrow 1}^{(v)}$  and  $\sigma_{0 \rightarrow 2}^{(v)}$  cross sections of England *et al.* (1988) modified within a small energy range to calculate ‘perturbed’ drift velocities which we then compare to drift velocities calculated with unmodified cross sections. By using *calculated* rather than measured drift velocities as a standard we reduce the effect of ‘noise’ (scatter), inherent in the experimental data, which would otherwise mask the effect of such small perturbations to the cross sections.

Figure 6 shows percent differences calculated as in equation (2) for two such studies. In Fig. 6*a* we increased  $\sigma_{0 \rightarrow 1}^{(v)}$  and  $\sigma_{0 \rightarrow 2}^{(v)}$  by 10% between 1.4 and 1.6 eV, and in Fig. 6*b* by the same amount between 2.0 and 2.4 eV. Fig. 6*a* shows that we can use the resulting percent difference to identify  $0.7 \leq E/N \leq 0.9$  Td as the range of  $E/N$  where  $v_{dr}$  is *maximally sensitive* to alterations in these cross sections from 1.4 to 1.6 eV. Similarly,  $1.2 \leq E/N \leq 1.7$  Td is the region of maximum sensitivity for energies from 2.0 to 2.4 eV.

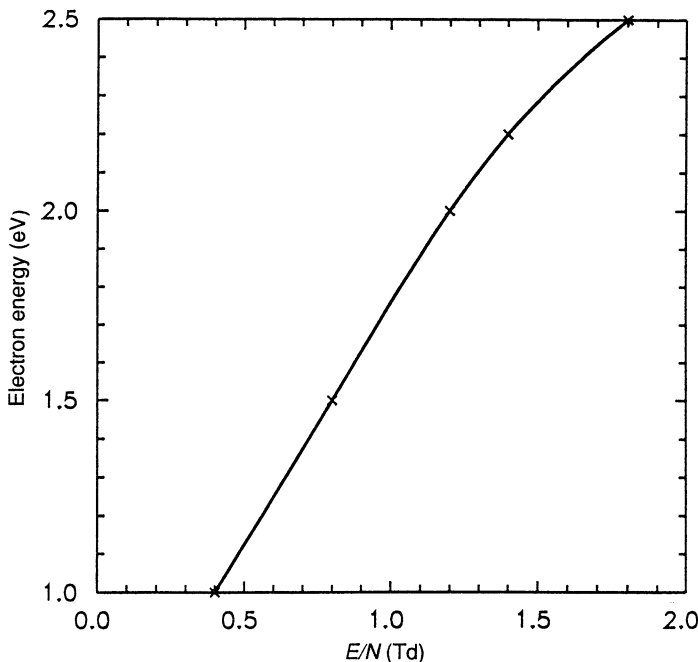


Fig. 7. Correlation between the value of  $E/N$  at which the drift velocity is most sensitive to perturbations of the vibrational cross sections and the mid-point of the energy range of the perturbations.

From several such studies at energies between 1.0 and 2.5 eV we construct in Fig. 7 a correlation of the maximum sensitivity of  $v_{dr}$  and the mid-point of the energy range of the perturbation of the vibrational cross sections. The relationship between modifications to a cross section and changes in the calculated drift velocity are complex when the modifications are large. Still, this figure indicates which part of the cross section most influences  $v_{dr}$  at a given  $E/N$ , and therefore where one should modify this cross section to optimise a fit to the measured coefficients.

Together, the results of the analyses shown in Figs 4–7 support several conclusions. First, as anticipated from the distribution functions  $f(\epsilon)$  in Fig. 4, at higher values of  $E/N$  the distribution of electrons in the swarm makes possible the determination of  $\sigma_{0 \rightarrow 1}^{(v)}$  to within 20% or better at energies as high as 3 eV. This statement rests first on the fact that although the stated uncertainty in  $v_{dr}$  from the mixture experiments is  $\pm 0.5\%$ , the *relative* accuracy of these values is much higher, as is evident in the smooth variation of the difference between calculated and experimental quantities with  $E/N$ . It also rests on the requirement that the swarm-derived cross sections  $\sigma_{0 \rightarrow 1}^{(v)}$  and  $\sigma_{0 \rightarrow 2}^{(v)}$  vary smoothly with energy and qualitatively resemble the theoretical cross section curves.

The second conclusion implicit in Figs 4–7 is that the experimental data for this mixture of 1.16% H<sub>2</sub> in Ne are most sensitive to the vibrational cross sections in the range of greatest divergence between the cross sections shown in Fig. 2. As  $E/N$  increases from 0.4 to 1.7 Td, the most probable energy of the electrons in the swarm increases from 0.5 to about 1.5 eV (see Fig. 4), while the energy of electrons that most strongly influence the drift velocity (through vibrational excitation) increases from about 1.0 to 2.5 eV. Moreover, we note that at  $E/N = 1.7$  Td a high proportion of electrons have energies greater than 3.0 eV. It is therefore not surprising that  $v_{dr}$  remains sensitive to the magnitude of  $\sigma_{0 \rightarrow 1}^{(v)}$  at energies above this value.

### 3.3 The Significance of Differences between Swarm-derived, Beam, and Theoretical Cross Sections

We can now assess the significance of the differences between the vibrational cross sections shown in Fig. 2 in relation to the transport data from which the swarm cross section was derived. We can do so definitively for the theoretical cross sections because the BFVCC calculations produce a complete set of pure rotational and ro-vibrational cross sections. Using this set we can calculate drift velocities and compare them unambiguously to measured values. Unfortunately, so straightforward a comparison is not possible for cross sections derived from relative angular distributions measured in beam experiments. To calculate drift velocities from the  $\sigma_{0 \rightarrow 1}^{(v)}$  of Brunger *et al.* (1991) we must interpolate their results (at the seven energies reported) to produce a cross section from threshold to 5.0 eV. Moreover, since beam experiments cannot resolve rotational excitations, we must determine the branching ratios required for this analysis, i.e. the ro-vibrational breakdown of the  $v_0 = 0 \rightarrow v = 1$  cross section, from the theoretical results, and we must assume a set of pure rotational cross sections. With these caveats in mind, we can come to some meaningful conclusions about the differences in Fig. 2.

In Fig. 8 we compare measured and calculated drift velocities for three sets of cross sections: those determined by England *et al.* (1988) from their analysis of transport data (curve A), those calculated from BFVCC theory (curve B), and those derived by Brunger *et al.* (1991) from measured angular distributions (curve C). At first glance, curve A seems to indicate flawless consistency between swarm-derived cross sections and measured values of  $v_{dr}$ . But in terms of our earlier discussion, the smooth increase of the percent difference between 0.8 and 1.7 Td is significant, even though it exceeds experimental uncertainty only at the largest value of  $E/N$ , and there by very little. Although this variation could have been eliminated had England *et al.* chosen to fit only their data for the  $H_2$ -Ne mixture, it should be noted that in fact they determined these cross sections by fitting their own data and *nine* other sets of transport data (including  $D_T/\mu$ ) for para-hydrogen, normal hydrogen, and mixtures of  $H_2$  with He, Ne, and Ar.

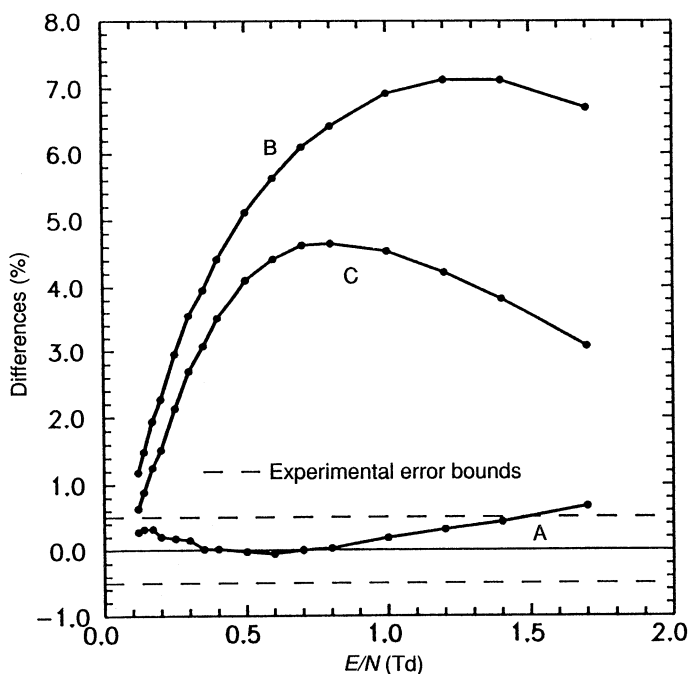


Fig. 8. Percent differences between measured and calculated drift velocities in a mixture of 1.16%  $H_2$  in Ne for the cross section set of England *et al.* (curve A), for cross sections calculated using BFVCC theory (curve B), and for a set based on those of England *et al.* with the vibrational cross sections replaced by those derived by Brunger *et al.* from their measured angular distributions (curve C).

Curve B in Fig. 8 shows that when we substitute theoretical pure rotational and ro-vibrational cross sections for the swarm-derived values, the resulting drift velocities exceed 10 times experimental error over a large range of  $E/N$ .<sup>\*</sup> This indicates either incompatibility of theory and experiment or an invalid assumption in the theory used to analyse the swarm experiments.

<sup>\*</sup> Because of the small fraction of  $H_2$  (1.16%) in the mixture and the close agreement between the swarm-derived and theoretical momentum-transfer cross sections, we need not replace this cross section with its theoretical counterpart.



Finally, curve C shows that a similar serious disagreement arises when we replace the swarm-derived cross sections by the results of Brunger *et al.* (1991). We have used the theoretical ratios of the pure vibrational ( $\sigma_{00 \rightarrow 10}^{(rv)}$ ) to ro-vibrational ( $\sigma_{00 \rightarrow 12}^{(rv)}$ ) cross sections to separate the latter vibrational cross sections into ro-vibrational components. Overall, the difference between calculated and measured drift velocities is smaller than in case B, particularly at values of  $E/N$  above 0.8 Td. This reflects the smaller difference between the beam- and swarm-derived cross sections between 2 and 3 eV, and the compensating effect of the crossover above 3.0 eV (see Fig. 2). Still, for  $E/N$  between 0.3 and 1.7 Td, this difference exceeds 5 times experimental uncertainty, and at its maximum reaches 9 times the quoted error.

Two other features of this comparison are significant. First, although the theoretical and beam cross sections are in excellent agreement from threshold to 1.5 eV, the differences between calculated and experimental drift velocities of curve B, which is based on the theoretical cross sections, exceed those of curve C, which is based on the beam cross section, even at the lowest values of  $E/N$ . This reflects the influence of  $\sigma_{0 \rightarrow 1}^{(v)}$  over a range of energies on  $v_{dr}$  at a given value of  $E/N$ , which underscores why it is difficult to specify a precise uncertainty on the swarm-derived cross sections at any particular energy.

Similarly, the energy dependence of  $\sigma_{0 \rightarrow 1}^{(v)}$  clearly influences the percent differences in Fig. 8 at higher values of  $E/N$ . The beam cross section above 3 eV which we used to calculate  $v_{dr}$  for this comparison is at best a reasonable guess in that it passes through the values reported by Brunger *et al.* at 3 and 5 eV. Still, the comparison at  $E/N = 1.7$  Td, for example, illustrates that  $\sigma_{0 \rightarrow 1}^{(v)}$  above 3.5 eV, which is only about 10% below the swarm-derived value, cannot compensate fully for the more substantial differences at lower energies.

One might reasonably ask how the comparison in curve C is affected by the particular pure rotational cross sections used in calculating  $v_{dr}$ . That is, one could use either theoretical BFVCC cross sections or those derived from transport analysis. As shown in Fig. 9, the rotational cross section that best fits measured transport data agrees very well with the theoretical curve from threshold up to 1 eV, but at higher energies diverges from it by about 10%. For H<sub>2</sub>, however, the influence of rotations is relatively small: since the rotational and vibrational energy spacings differ by about a factor of 10, replacing the swarm-derived rotational cross sections with theoretical values changes the difference curves in Fig. 8 by less than 2%. Moreover, since the theoretical cross section is larger than the swarm-derived cross section between 0.5 and 2.0 eV, where rotation is a more significant energy-loss process than at higher energies, this replacement increases rather than decreases the differences.

Another exigent question concerns the lack of uniqueness of swarm-derived inelastic cross sections. As noted earlier, in mixtures, electron scattering from H<sub>2</sub> influences  $v_{dr}$  almost entirely through energy exchange in rotational and vibrational collisions, rather than through momentum transfer. So any set of cross sections derived from drift velocity data is to some extent not unique. One could, for example, compensate for adjustments to a vibrational cross section largely (though not exactly) by appropriately modifying the rotational cross sections, although the required modifications may be drastic. This feature of transport analysis raises yet another question: could the differences between

swarm-derived vibrational cross sections and the others in Fig. 2 be due to errors in the *rotational* cross section?

For the theoretical cross sections, we can answer this question unequivocally without undertaking time-consuming repeated solution of the Boltzmann equation to find the set of rotational cross sections that best matches the transport data. Since the theoretical  $\sigma_{0 \rightarrow 1}^{(v)}$  is *larger* than the swarm result, we would have to *reduce* the rotational cross sections to maintain the same energy losses due to inelastic scattering. Curve A of Fig. 10 shows percent differences of measured drift velocities with values calculated with the most extreme such modification: zero rotational cross sections.

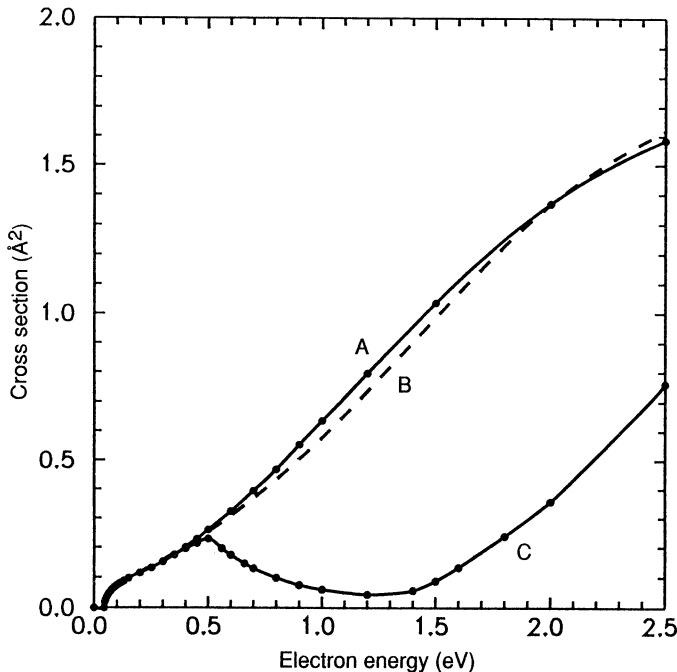


Fig. 9. Rotational excitation cross sections ( $j_0 = 0 \rightarrow j = 2$ ) from BFVCC theory (curve A), from the analysis of swarm data by England *et al.* (1988) (curve B), and from a modified set of rotational cross sections that gives reasonable agreement between calculated and measured drift velocities (for the  $\text{H}_2$ -Ne mixture) when determined using the interpolated vibrational cross sections of Brunger *et al.* (curve C; see Section 3.3).

We see that for  $0.7 \leq E/N \leq 1.5 \text{ Td}$  the resulting drift velocities are *larger* than the experimental values. But since inelastic scattering reduces the average energy of the swarm and hence the collision frequency of the electrons in it, such collisions can only increase  $v_{\text{dr}}$ . We conclude that if the experimental data are as accurate as claimed and if the Boltzmann analysis is correct, then the energy losses predicted by the theoretical vibrational cross section are too large, even in the hypothetical limiting case that no additional loss occurs due to rotational excitation.

Eliminating this energy-loss process from calculations of  $v_{\text{dr}}$  based on (interpolated) beam vibrational cross section produces curve B of Fig. 10.

These drift velocities never exceed the experimental values, so in this case one can find compensating rotational cross sections that yield agreement to first order. But since the calculated and experimental drift velocities approach one another at certain values of  $E/N$ , the modified rotational cross sections must be quite small. Curve C in Fig. 9 shows the  $\sigma_{0 \rightarrow 2}^{(r)}$  from a modified set that gives calculated drift velocities within  $\pm 1\%$  of the experimental data for the mixture. Although one might be able to obtain by further modifications an even better fit, this cross section is indicative and conforms to what one would expect from general physical arguments. Obviously, at energies above 0.5 eV, it in no way resembles either the theoretical or swarm-derived rotational cross section.\*

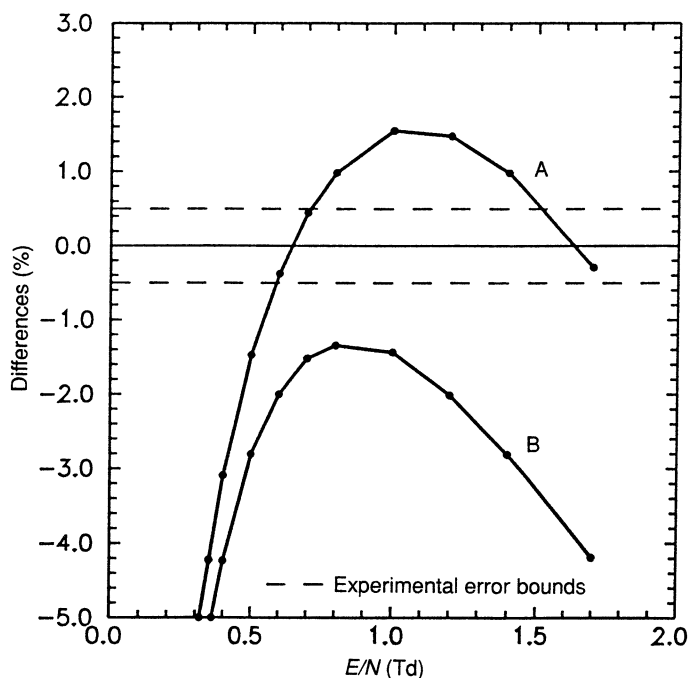


Fig. 10. Percent differences between drift velocities measured in the H<sub>2</sub>-Ne mixture and those calculated using *zero* rotational cross sections along with the BFVCC theory cross sections (curve A), and the interpolated vibrational cross sections of Brunger *et al.* (curve B).

#### 4. Remarks on the Total and Momentum-transfer e-H<sub>2</sub> Cross Sections

The problems involved in converting raw angular distributions from a crossed-beam experiment to *absolute* DCS are well known (see, for example, Trajmar *et al.* 1984). One can normalise the angular distribution in various ways. Brunger *et al.* (1991) chose the relative flow technique, using as a benchmark Nesbet's theoretical e-He DCS (Nesbet 1979). One can usefully check the normalisation—and, indeed, the DCS themselves—by comparing the total and momentum-transfer

\* Development of a rotational cross section for use with a vibrational cross section that conforms to the *lower bounds* of the beam-derived data would require less drastic modifications. But the 20% difference between beam- and swarm-derived vibrational cross sections at 1.5 eV would result in rotational cross sections that differ substantially from the theoretical values.

cross sections calculated by numerically integrating the (normalised) experimental DCS against results from time-of-flight experiments and transport analysis of swarm data.

Each of these latter experiments yields integral cross sections that are intrinsically more accurate than those based on relative angular distributions from beam experiments. At moderately low energies, the total cross section for systems such as e-He and e-H<sub>2</sub> vary slowly with energy, so their measurement in time-of-flight experiments suffers mainly from uncertainty in the target number density in the flight tube. State-of-the-art techniques for the mTorr region can reduce these uncertainties to between 1 and 2% (Ferch *et al.* 1980; Jones 1985; Buckman and Lohmann 1986). Thus Jones (1985) claims an uncertainty of  $\pm 2.5\%$  in his total e-H<sub>2</sub> cross sections between 1 and 4 eV. The slow variation of  $\sigma_{\text{mom}}$  with energy also contributes to the confidence that can be claimed for this cross section as derived from an analysis of transport data, and at energies up to 1 or 2 eV the  $\pm 5\%$  uncertainty limits that have been placed on it are likely to be conservative. This view is strengthened by the agreement between theory and experiment in this energy range (Morrison *et al.* 1987a).

A second uncertainty that arises when one compares integral cross sections derived from DCS data and those from time-of-flight and swarm experiments is the need to extrapolate the angular distributions from the experimental limits (typically 20° to 130°) to 0° and 180°. Thus Brunger *et al.* (1990, 1991) estimate the error in their vibrationally elastic differential cross sections to be  $\pm 8\%$ , a combination of systematic and random error as well as uncertainties due to normalisation, but conservatively estimate the error in  $\sigma_{\text{tot}}$  to be  $\pm 20\%$ , the major additional contributor being extrapolation to small and large angles.

Using a new technique based on known physical properties of the *S* matrix (Trail and Morrison 1991; Morrison *et al.* 1993) we have virtually eliminated this additional uncertainty. This method for extrapolation of normalised angular distributions to small and large angles entails fitting measured data to an equation that incorporates physical constraints so as to reduce to less than 1% additional error (in all cases studied so far) and eliminate some of the ‘noise’ typically found in experimental distributions. Conceptually, this method resembles the ‘phase shift analysis’ that has been used to circumvent the extrapolation problem for electron-atom scattering (Taylor 1972; Bransden 1976; Williams 1979; Steph *et al.* 1979; Allen 1986; Allen and McCarthy 1987).

Electron-atom phase-shift analysis is based on the usual expression for the elastic differential cross section for scattering from a spherically symmetric local potential, written in terms of partial-wave phase shifts  $\delta_\ell(k)$ . The analysis detaches these phase shifts from their usual physical significance, using them instead as parameters in a numerical fit to the measured DCS. With the fitted phase shifts one can easily calculate integral (total and momentum transfer) cross sections via well-known formulae (Joachain 1975).

But this method is not applicable to electron-molecule scattering, because its underlying assumptions do not hold. Most important, electron-molecule potentials are not spherically symmetric, so partial-wave phase shifts cannot even be defined for these systems. Morrison *et al.* (1993) treat the molecule as properly non-spherical, using a non-linear least-squares fitting algorithm (Press *et al.* 1986) and incorporating known aspects of the collision physics to minimise the

number of parameters. Since the experiments of interest measure total, elastic, or vibrational DCS, the method need not deal explicitly with rotational dynamics and so is formulated in the body frame (BF), using the fixed-nuclear-orientation (FNO) approximation (Lane 1980; Morrison 1988).

For an elastic collision  $\mathbf{k}_0 \rightarrow k_0 \hat{\mathbf{k}}$ , the BF-FNO amplitude for scattering into a (lab-frame) scattering angle  $\theta = \hat{\mathbf{k}} \cdot \hat{\mathbf{k}}_0$  can be written in terms of the elements of the corresponding  $T$ -matrices  $T^{\Lambda\eta}$  as (Morrison 1988 and references therein)

$$f(\theta) = \frac{2\pi}{k_0} \sum_{\Lambda} \sum_{\ell\ell_0} i^{\ell_0-\ell+1} Y_{\ell}^{\Lambda}(\hat{\mathbf{k}}) T_{\ell\ell_0}^{\Lambda} Y_{\ell_0}^{\Lambda*}(\hat{\mathbf{k}}_0), \quad (3)$$

where  $\Lambda$  is the projection of the electron's orbital angular momentum on the internuclear axis and  $\eta$  is the parity. Using Wigner rotation matrices (Rose 1957) one can transform this expression into the lab frame and derive for the total DCS the expression

$$\left. \frac{d\sigma}{d\Omega} \right|_{\text{tot}} = \frac{1}{4k_0^2} \sum_L \sum_{\Lambda\ell\ell_0} \sum_{\bar{\Lambda}\bar{\ell}\bar{\ell}_0} d_L(\bar{\ell}\bar{\ell}\ell_0\bar{\ell}_0; \Lambda\bar{\Lambda}) T_{\ell\ell_0}^{\Lambda} T_{\bar{\ell}\bar{\ell}_0}^{\bar{\Lambda}*} P_L(\cos\theta), \quad (4)$$

where the coefficient  $d_L$  is a simple product of numerical factors and Clebsch-Gordan coefficients.

It would be impractical to use the  $T$ -matrix elements in (4) as fitting parameters. But one can develop a variant of this equation suitable for least-squares fitting with a minimum number of parameters by decoupling the partial waves and then unitarising the corresponding (approximate)  $S$ -matrix. To this end we introduce 'phase parameters'  $\delta_{\ell}^{\Lambda\eta}$  defined as

$$\delta_{\ell}^{\Lambda\eta} \equiv \sin^{-1} \left( \frac{1}{2} \text{Im } T_{\ell\ell}^{\Lambda} \right) \quad (5)$$

and approximate the (vibrationally elastic) differential cross section by

$$\left. \frac{d\sigma}{d\Omega} \right|_{\text{tot}} = \frac{1}{k_0^2} \sum_L \left[ \sum_{\Lambda\ell} \sum_{\bar{\Lambda}\bar{\ell}} d_L(\bar{\ell}\bar{\ell}\ell\bar{\ell}; \Lambda\bar{\Lambda}) \sin \delta_{\ell}^{\Lambda} \sin \delta_{\bar{\ell}}^{\bar{\Lambda}} \cos(\delta_{\ell}^{\Lambda} - \delta_{\bar{\ell}}^{\bar{\Lambda}}) \right] P_L(\cos\theta). \quad (6)$$

Unlike (4), this expression is ideally suited to fitting experimental data. Finally, one uses the phase parameters resulting from such a fit to calculate the integral (total and momentum-transfer) cross sections.

In applications to recently measured e-H<sub>2</sub> and e-N<sub>2</sub> DCS, Morrison *et al.* (1992) found that while several phase parameters are required to converge the DCS, only a very few need be *fitting* parameters. That is, most of the high-order (large- $\ell$ ) parameters  $\delta_{\ell}^{\Lambda}$  are given to very high accuracy by the first Born approximation (Feldt and Morrison 1982; Morrison *et al.* 1984a) because of the influence of a strong centrifugal barrier at low energies, and so only a few low-order parameters need be varied in the fit. For example, to fit the elastic DCS of Brunger *et al.* (1991) at 2.0 eV, only *three* of the 10 required phase parameters must be left 'free' (to be determined by the least-squares fit):

$$\underbrace{\delta_0^{\Sigma_g}, \delta_1^{\Sigma_u}, \delta_1^{\Pi_u}}_{\text{free parameters}} \quad \underbrace{\delta_2^{\Sigma_g}, \delta_2^{\Pi_g}, \delta_3^{\Sigma_u}, \delta_3^{\Pi_g}, \delta_4^{\Sigma_g}, \delta_4^{\Pi_g}, \delta_5^{\Sigma_u}}_{\text{first Born approximation}}. \quad (7)$$

Convergence of the integral total cross sections (in  $\text{\AA}^2$ ) with the number of free parameters  $N_f$ , is clean:

$$\underbrace{\sigma_{\text{tot}} = 15.07}_{N_f=1} \rightarrow \underbrace{\sigma_{\text{tot}} = 16.07}_{N_f=2} \rightarrow \underbrace{\sigma_{\text{tot}} = 14.64}_{N_f=3} \rightarrow \underbrace{\sigma_{\text{tot}} = 14.69}_{N_f=4}. \quad (8)$$

In Table 1 we compare  $\sigma_{\text{tot}}$  from application of this technique to the (normalised) angular distributions of Brunger *et al.* (1991) at 1.0 and 2.0 eV. Because this procedure introduces negligible additional error, we believe that these integral cross sections suffer essentially only the error of  $\pm 8\%$  quoted for those distributions. We also compare cross sections measured in time-of-flight experiments by Jones (1985) and calculated by Trail (1992).

**Table 1.** Vibrationally elastic total cross sections from beam experiments (Brunger *et al.* 1991), time-of-flight experiments (Jones 1985), and theoretical calculations (Trail 1992)

Energy (eV)	Beam DCS <sup>A</sup> ( $\text{\AA}^2$ )	Fitted DCS <sup>B</sup> ( $\text{\AA}^2$ )	Theory ( $\text{\AA}^2$ )	Time-of-flight ( $\text{\AA}^2$ )	Time-of-flight (adjusted) <sup>C</sup> ( $\text{\AA}^2$ )
1.0	11.68	11.71	13.39	13.21	13.1
2.0	14.56	14.64	15.78	15.59	15.26

<sup>A</sup> As quoted in Table 3 of Brunger *et al.* (1991), these integral cross sections were calculated from extrapolations (based on the shape of the theoretical DCS) from the measured angular region  $[20^\circ, 130^\circ]$  to  $0^\circ$  and  $180^\circ$ , followed by numerical integration.

<sup>B</sup> These integral cross sections were determined by Morrison *et al.* (1993) by fitting the vibrationally elastic measured angular distributions of Brunger *et al.* (1991) to eliminate extrapolation error.

<sup>C</sup> For purposes of this comparison we have subtracted the  $0 \rightarrow 1$  vibrational cross sections of Brunger *et al.* (1991) from Jones's grand total cross sections to obtain these 'adjusted' results.

Using the same phase parameters, we compute the momentum-transfer cross sections in Table 2. But in comparing these results to swarm-derived values, one must consider that the sources of error in swarm experiments are somewhat different from those in beam experiments. Because the gas pressures in drift and diffusion experiments range from a few torr to several atmospheres, errors in measuring this pressure contribute little to the overall uncertainty in the transport coefficients. Although this uncertainty is magnified in the unfolding of cross sections by solution of the Boltzmann equation, Crompton *et al.* (1970*b*) have claimed an overall uncertainty of  $\pm 2\%$  in the most favourable case, elastic e-He scattering, and  $\pm 5\%$  for the e-H<sub>2</sub> momentum-transfer cross section (Crompton *et al.* 1969).

In Table 2 we compare  $\sigma_{\text{mom}}$  as calculated by Morrison *et al.* (1993) from the normalised angular distributions of Brunger *et al.* (1991) to the swarm-derived values of Crompton *et al.* (1970*b*) and theoretical cross sections of Trail (1992). The theoretical and fitted cross sections correspond to vibrationally elastic scattering. By contrast, the cross sections reported in Table 3 of Brunger *et al.* and the swarm-derived cross sections also include contributions from vibrational excitations. So we have subtracted from these results the contributions from (theoretical) inelastic vibrational cross sections, leaving the results shown in parentheses underneath the reported data. These *vibrationally elastic* cross sections can meaningfully be compared to the others in this table.

These comparisons suggest several conclusions. On theoretical grounds we believe one can reduce virtually to zero the additional uncertainty of 12% which Brunger *et al.* (1990, 1991) attributed to their extrapolation when assessing the error bounds for their total and momentum-transfer cross sections. We note that for both cross sections at 1.0 and 2.0 eV, the differences between the integral cross sections reported by Brunger *et al.* (1991) and those obtained by the fitting procedure of Morrison *et al.* (1993) are less than 2%. The resulting reduction of experimental error bars increases the significance of comparisons with other integral cross sections.

**Table 2.** Elastic momentum transfer cross sections for e-H<sub>2</sub> scattering from beam experiments (Brunger *et al.* 1991), from transport analysis of swarm data, and from theoretical calculations (Trail 1992)

Energy (eV)	DCS <sup>A</sup> (Å <sup>2</sup> )	DCS <sup>B</sup> (Å <sup>2</sup> )	Theory (Å <sup>2</sup> )	Swarm (Å <sup>2</sup> )
1.0	14.59 (14.49)	14.57	17.36	17.3 (17.2)
2.0	16.51 (16.10)	16.50	18.79	17.89 (17.48)

<sup>A</sup> As in Table 1, these results from Table 3 of Brunger *et al.* (1991) were calculated from extrapolations (based on the shape of the theoretical DCS). They do include contributions from vibrational excitation.

<sup>B</sup> As in Table 1, these *vibrationally elastic* integral cross sections were determined by Morrison *et al.* (1993) by fitting the vibrationally elastic angular distributions of Brunger *et al.* (1991).

In this context, we find that the theoretical and time-of-flight total cross sections agree to well within the quoted experimental uncertainty of the latter,  $\pm 2.5\%$ . At 1 eV, however, the total cross section from the beam experiment lies about 10% below the others. At 2 eV the agreement is much better, about 4%. In any case, these differences are well within the uncertainties quoted by the respective authors.

Turning now to the momentum-transfer cross sections of Table 2 we find that the theoretical and swarm-derived values agree at both energies to just outside the quoted uncertainty of 5%. But the values calculated from the normalised angular distributions show larger differences than those for  $\sigma_{\text{tot}}$ : they lie 16% below the theoretical and swarm-derived cross sections at 1 eV, and 11 and 7% below at 2 eV. While these differences do fall within the combined uncertainties placed on these data by the authors, those at 1 eV are now on the limit or outside the combined uncertainties when the revised error limits for the cross sections of Brunger *et al.* (1991) are used.

From these comparisons we draw two conclusions. First, the integral cross sections derived from the angular distributions of Brunger *et al.* (1991) are consistently lower than the BFVCC theoretical, time-of-flight, and swarm-derived values. Therefore the normalisation factor used by Brunger *et al.* is probably too low at both energies, with the largest error at 1 eV. Second, the differences between the theoretical and swarm momentum-transfer cross sections and values determined from the measured angular distributions suggest that the beam experiments may be recording insufficient scattering in the backward direction.

## 5. Summary and Conclusions

Our earlier paper (Morrison *et al.* 1987*b*) focused on energies below 1.5 eV. At that time the swarm-derived vibrational cross section, which disagreed with both theory and the then-available results from beam experiments, was based solely on an analysis of transport data in pure hydrogen. The new results from crossed-beam experiments and from the analysis of new swarm experiments in H<sub>2</sub>-He and H<sub>2</sub>-Ne mixtures, which are summarised in Section 2, confirm that disagreement. But they also provide new evidence which, when subjected to the analysis in Section 3, makes it more difficult to reach conclusions as definitive as those obtained in earlier discussions of this conundrum (Buckman *et al.* 1990). For, while the new beam experiments gave vibrational cross sections in excellent agreement with those from theory up to 1.5 eV, the integral cross sections derived from these DCS data are closer to the swarm-derived results at higher energies, and both lie below the theoretical cross section at energies around 2.5 eV. These new results therefore pose the question: can we give the same weight to the cross section derived from the swarm experiments in mixtures above 1.5 eV as was given to the earlier swarm results below that energy, and, if so, to what energy can useful comparisons be made with the swarm results?

To answer this question we have quantitatively correlated energy ranges of the vibrational cross section with values of  $E/N$  at which drift velocities in the mixture are most sensitive to changes in the cross section within these ranges (see Fig. 7). We have also determined the sensitivity of the drift velocities to changes in the cross section above specified energies (see Fig. 5). Taken together, the results of these tests probably provide as much information as possible about 'error bars' for the swarm-derived cross section—in the absence of results from some kind of numerical optimisation algorithm technique such as that proposed by Morgan (1991).

The most important conclusion revealed by our analysis is that a critical assessment of the beam-derived, theoretical, and swarm-derived cross sections should not be restricted to energies below 1.5 eV, but should be extended to at least 3.0 eV. Although that assessment muddies rather than clarifies the disagreement apparent in Fig. 2, one can state without qualification that the set of theoretical cross sections is incompatible with the swarm data from mixtures, using currently accepted transport theory, and that the same seems to be true of the integral cross sections derived from the DCS data (see Fig. 8).

Because of the intransigence of this problem, it seemed worthwhile to further compare the *vibrationally elastic* total cross sections from theory and both types of experiment, as we have done in Section 4. In making such comparisons one can derive significant additional information from time-of-flight absorption-cell experiments.

One problem in making such comparisons (as well as those for vibrational cross sections) is the additional uncertainty (12%) which was assigned to the integral cross sections derived from the DCS data due to extrapolation to small and large angles (Brunger *et al.* 1991). The analysis in Section 4 shows that we can reduce this uncertainty to a negligible level (less than 1%) using a physically motivated fitting procedure (see also Morrison *et al.* 1993). This brings the disagreement between variously determined total and momentum-transfer cross sections (see Fig. 3) near or beyond the combined uncertainties of the measurements.



Finally, Tables 1 and 2 show that below 2 eV both the total and momentum-transfer cross sections derived from the DCS data are systematically lower than theory and the other experimental data. This suggests the possibility of an error in normalisation, although errors in the shapes of the DCS curves could also account for some of these differences. However, if there were an error in normalisation, correcting for it would *increase* the difference between the beam and swarm results for vibrational excitation in this energy range. We have not extended this analysis to higher energies in this paper because of the increasing uncertainties in the vibrationally elastic total and momentum-transfer cross sections derived from the absorption-cell and swarm experiments, respectively, due to the subtraction of contributions from the inelastic processes, and because the questions raised by such comparisons are somewhat secondary to the main issues discussed here.

Prospects for future work on this problem are limited. On the theory front, our new implementation of an essentially exact treatment of exchange and inclusion of full vibrational dynamics in the solution of the scattering equations removed two major assumptions from our prior calculations but did not, alas, qualitatively change the cross sections. We have exhaustively checked these calculations using several distinct computer codes (some of which entail different numerical algorithms) and in all calculations have ensured that the resulting scattering quantities are numerically accurate to 2% or better.

There would therefore appear to remain one source of potential uncertainty: our (parameter-free) approximate treatment of short-range bound-free correlation effects in our polarisation potential (Gibson and Morrison 1984). This potential treats correctly all intermediate- and long-range polarisation effects (in the region outside the target charge cloud) and so is approximate only in the near-target region. But a recent examination of the role of the static, exchange, and polarisation interactions for vibrational excitation of H<sub>2</sub> (Trail 1992) has shown that polarisation, although important for vibrational excitation, is not sufficiently important to resolve the experimental/theoretical discord in Fig. 2 (Morrison and Trail 1993). In fact, *even were our polarisation model completely incorrect*, replacing it (with, say, an accurate non-local optical potential) could not correct the 60% maximum discrepancy between theoretical and swarm-derived values for  $\sigma_{0 \rightarrow 1}^{(v)}$ . We consider so massive an error due to our treatment of polarisation highly unlikely: in fact, comparisons of various scattering quantities (at fixed internuclear geometries) with such optical-potential results as are available in the literature (Morrison *et al.* 1987a) suggest that our model potential is considerably more accurate than one might infer from this discrepancy.

On the beam front, the experiments of Brunger *et al.* (1991) are at the cutting edge of accuracy and minimum measurement energy. The non-spherical fitting procedure of Morrison *et al.* (1993) can eliminate essentially all error in integrated cross sections due to extrapolation and normalisation, and it is possible that the forthcoming extension of this procedure to inelastic scattering will clarify the situation for  $\sigma_{0 \rightarrow 1}^{(v)}$ . But it is unlikely that near-future technological advances will enable significantly more accurate measurements of relative angular distributions at these or lower energies.

Finally, it is worth emphasising that our conclusions concerning the vibrational controversy hinge on the quoted accuracy of the measured drift velocities for H<sub>2</sub>-rare gas mixtures, and on the viability of the Boltzmann analysis for rotational

and vibrational excitation of  $H_2$ . The possibility of experimental error larger than the quoted uncertainty can never be ruled out, but a significant increase in this uncertainty is unlikely, because the same apparatus and techniques were used for the mixture measurements as for earlier measurements on He and other monatomic gases for which there is no disagreement with theory. An additional potential source of experimental error is the preparation of the mixtures. But this, too, is unlikely, for the results from the  $H_2$ -rare gas mixture measurements support those analyses of transport data in pure  $H_2$ . We are therefore left with the possibility of an error or inconsistency in the analysis of swarm data in *molecular* gases, noting, however, that no such problems appear in the analysis for *atomic* gases. This possibility must be considered along with the other possible explanations of the persistent discrepancy discussed in this paper, no matter how remote they may seem.

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