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New Experimental Techniques in the Study of Electron Swarms in Gases and their Impact on the Determination of Low Energy Electron Scattering Cross Sections

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Abstract

A new generation of experiments to study the transport of electron swarms in gases has been developed to enable transport coefficients in pure electric and crossed electric and magnetic fields to be measured with a precision and completeness not previously achieved. The basic concepts and strengths of these new techniques are presented in this paper. The application of the new techniques to the study of electron transport in hydrogen and the subsequent Boltzmann analysis of the newly measured transport coefficients has led to a more refined and detailed understanding of elastic and inelastic low energy electron scattering for this elementary system. The availability of a new set of cross sections for hydrogen has made possible a study of transport coefficients in mixtures of hydrogen with argon, krypton and xenon. We have checked the compatibility of the published elastic momentum transfer cross sections for the heavy noble gases with the present measurements and derived new and much more reliable cross sections. A precise knowledge of these elementary systems is of the greatest importance as the heavy noble gases can be used as powerful probes for deriving the low energy cross sections for more complex molecules from swarm experiments.

1. Swarm experiments and swarm derived cross sections – benefits and problems

The experimental study of transport phenomena of electrons in gases is not only of practical importance in view of the wide variety of technical and scientific applications involving electron discharge phenomena but is also a powerful tool for investigating the underlying microscopic processes, namely the interaction of low energy electrons with the atomic and molecular components of the gas. The importance of the method is enhanced by the fact that it provides information over an energy range from about 10 meV to several eV which is very difficult to access by other experimental techniques: Single scattering (crossed beam) experiments have been widely used to study the angular dependence of the scattering at fixed energies but are faced with a multitude of systematic problems if absolute values of integral cross sections at low energies are required. Using the most sophisticated techniques a lower energy limit of about 100 meV and a 20% uncertainty on the absolute cross sections would appear to be the present limit of these techniques. Total cross section experiments, measuring the attenuation of electrons of known energy in very dilute gases, furnish accurate information about the total collision strength but they are also confronted with escalating problems below 100 meV and moreover are unable to specify the contributions of different scattering channels.

But the swarm technique is also burdened with a formidable, critics may say even more substantial, intrinsic problem: The desired quantities (cross sections as a function of the electron energy) are related to the directly measurable data (transport coefficients as function of external fields, gas number density and temperature) through an energy distribution function which is usually non-Maxwellian and often complex in form. The microscopic properties have to be determined in a complicated and cumbersome unfolding procedure by seeking a self consistent set of cross sections which reproduce the experimental transport coefficients via a solution of an adequate formulation of the Maxwell–Boltzmann transport equation.† Nevertheless it is due to the pioneering work of Phelps [5] and especially the scrupulous and thorough achievements of Crompton, Elford and their co-workers [6] that the method has been widely accepted as competitive and complementary and has furnished more information on low energy electron scattering on atoms and molecules than any other experimental method. In the following it will be shown that for all the considerable progress made during the past 30 years the situation is still unsatisfactory and how the new experimental techniques developed in our laboratory during the past few years can be used to improve both the accuracy and reliability of this technique.

The strong demand for a sufficiently precise knowledge of low energy electron scattering from atoms and molecules comes essentially from two directions: from those involved modelling a variety of devices making use of electron transport phenomena in the most different ways (gas lasers, low temperture plasma discharges, gas filled particle detectors etc.) as well as from those whose interest is in a rigorous understanding of the electron atom/molecule scattering processes through quantum mechanical calculations. The latter group has made enormous progress through the application of supercomputers and parallel processors and reliable experimental data are imperative to test the applicability of different models and calculation schemes. On both fronts electron scattering cross sections for small molecules, especially hydrocarbons and their homologues, are of particular interest and for those molecules the experimental situation

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† The "adequate formulation" is a nontrivial and vexing problem outside the scope of this paper. A textbook introduction and historical overview can be found in Ref. [1], for a present state of the art discussion of the topic, especially in connection with the methods used throughout this paper, the reader is referred to the revealing papers of Robson and Ness [2–4] and the references therein.

is still extremely unsatisfactory. Uncertainties in the cross sections of up to 50% and greater are more the rule than the exception making both modelling of transport phenomena and testing theoretical approaches, highly questionable. A special difficulty for light hydrocarbons (and for homologues like CF_4 as well) arises from the combination of a strongly energy dependent elastic cross section (Ramsauer minimum) with the onset of inelastic channels (vibrational excitation). The combination results in severe ambiguity problems for swarm derived cross sections. Even for the best understood candidate, CH_4, the situation is astonishingly scanty [7]. If all the information available from transport coefficients in CH_4, measured with typical errors of standard swarm experiments [8], is considered it is easily possible to derive an infinite number of significantly different sets of elastic and inelastic cross sections (two of them are depicted in Figure 1 of Ref. [7]) which describe the entire set of transport coefficients within their typical limits of uncertainty. This is not only unsatisfactory in view of the proper understanding of e^-–CH_4 scattering, it is also highly undesirable in calculations of the behaviour of devices. The cross section variability mentioned above introduces uncertainties in the coefficients of electron transport in argon–CH_4 mixtures (the most popular type of gas for charged particle detectors) of up to 30%. The situation for other hydrocarbons is even worse. The pronounced sensitivity of argon–hydrocarbon mixtures (and krypton and xenon based mixtures as well) to the hydrocarbon cross sections provides a powerful method for solving the ambiguity problems and to determine the hydrocarbon cross sections with unprecedented accuracy [7]. But the question is now, are the cross sections of the heavy noble gases known precisely enough to be used as tools in such a probe of the molecular gases? Unfortunately the answer is "No". Thus any progress in the study of hydrocarbon cross sections has to start with a validation and improvement of the accuracy of the cross sections for heavy noble gases.

1.1. *The cross sections for noble gases*

The basic drawback of the swarm method, namely that energy dependent scattering cross sections have to be determined from a restricted number of measurable macroscopic transport parameters depending only very indirectly on the desired quantities, makes it evident that the technique has been most successful in cases where only one scattering process with moderate energy dependence is involved. Thus the momentum transfer cross section σ_m for elastic scattering of electrons from helium up to the threshold for electronic excitation was determined almost 30 years ago with an accuracy of a few percent [9] in extremely good agreement with other experimental techniques and theoretical calculations [10]. The situation for elastic scattering from neon is almost as satisfactory [11] but is essentially different for the heavy noble gases argon, krypton and xenon. The pronounced energy dependence of the elastic scattering cross section in these gases, varying over two orders of magnitude in the vicinity of the Ramsauer minimum, affects the simplicity and reliability of a swarm analysis in various ways. More accurate data of more transport coefficients over a wider range of experimental parameters are needed to achieve a reasonable level of accuracy and to reduce ambiguity problems. Unfortuantely the drift velocity, which is the coefficient which can be measured with the highest accuracy and is least prone to systematic errors of all transport coefficients, is almost *insensitive* to the structure and the strength of the cross section in the vicinity of the minimum [12] and the analysis usually relies on the accuracy of the arduous to measure diffusion coefficients. (In Ref. [7] we have proposed a method to avoid this difficulty which is applied in the analyses presented in Section 4 of this paper.) An additional complication arises from the extremely small mean energy loss per collision in these gases resulting not only in very broad swarms but also in a macroscopic "energy relaxation length" of a few centimetres at standard pressures. To avoid boundary problems very large drift cells are needed, the stratagem of pressurising the gas (which has been successfully followed in the case of argon by Milloy and Crompton [13]) is questionable for krypton and xenon since not very well understood density effects are suspected to affect the results, at least if high precision is required. Density effects, i.e. deviations from E/N scaling, have been observed experimentally in argon at very high densities [38]. Since they are expected to scale with the scattering length of the target atom [39] they might be of non-negligible influence in krypton and xenon even at moderate pressure. The elegant way to solve this problem is to use a few percent of a molecular gas as an additive to reduce the energy relaxation length by introducing "well known" inelastic processes [14]. This introduces another problem in the derivation of cross sections: the effect of the uncertainty in the molecular gas cross sections on the cross sections for the inert gas. The only well known additive which can be considered is molecular hydrogen, a gas which has been extensively studied for more than 30 years.

1.2. *The cross sections for hydrogen*

Hydrogen is not only the simplest molecule for quantum mechanical calculations, its properties are also in many ways advantageous for the determination of its electron scattering cross sections from swarm experiments. The elastic momentum transfer cross section exhibits an extremely weak energy dependence and the sparseness of its ro-vibrational excitation spectrum strongly limits the number of contributing inelastic channels. At room temperature only four transitions between rotational levels and two vibrational excitation processes contribute significantly to the inelastic energy loss and have to be determined in a Boltzmann analysis of transport coefficients if the analysis is limited to the region below where ionization is significant, i.e. <40 Td. Since the work of Frost and Phelps [5] and Crompton, Elford and McIntosh [15] the validity and accuracy of this analysis has been continually improved culminating in the paper of England *et al.* [16] in which a set of rotational, vibrational and elastic cross sections is presented which is capable of reproducing the complete assemblage of experimental transport data of that time for normal hydrogen (at 293 K and 77 K) and para-hydrogen (at 77 K) as well as in He–H_2 and Ne-H_2 mixtures within their stated limits of experimental uncertainty. Furthermore the data set seems to be in good agreement with crossed beam experiments and theoretical expectations with the exception of a stubborn and mysterious discrepancy in the strength of the vibrational v: $0 \rightarrow 1$ transition (see [17] and references therein for a detailed discussion of this topic). Thus electron

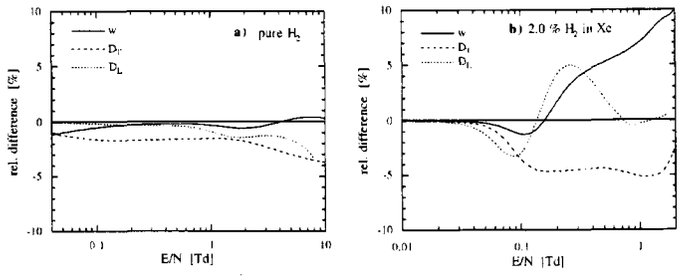

Fig. 1. Relative difference of the transport parameters in (a) pure hydrogen and (b) a H_2–Xe mixture calculated from two different sets of hydrogen cross sections.

H_2 scattering at low energies is by far the best understood of all molecular systems making H_2 the best "moderator gas" for experiments in heavy noble gases. But the question of whether the understanding is good enough for our application remains. The severity of the problem is illustrated in Fig. 1 where two different sets of H_2 cross sections have been used to calculate transport coefficients in pure H_2 and a H_2–Xe mixture. Whereas in pure H_2 [Fig. 1(a)] the difference of both data sets causes changes in the transport coefficients which are barely outside the typical uncertainties for classical swarm experiments (w: 1%, D_T: 2%, D_L: 10%), the effect for a Xe–H_2 mixture [Fig. 1(b)] is of the order of 5–10% and thus of non-negligible influence on the validity of any xenon analysis based on H_2–Xe mixtures. Considering the importance of heavy noble gases as tools in solving the ambiguity problem in the determination of elastic and inelastic cross section of molecules, their dependence on a precise knowledge of the H_2 cross sections indicates the key role played by H_2 in low energy electron molecule scattering. The problem for us is therefore to investigate the validity of the "EEC–H_2" cross section-set [16] by the use of data with uncertainties which are well below the uncertainty limit of classical swarm experiments, a task which has been successfully solved using the new experimental techniques described in the following section.

2. New developments in experimental techniques

2.1. *The laser driven swarm source*

A common feature of the new type of swarm experiments that we have developed is the production of the electron swarm directly in the gas by means of a UV-laser pulse. In contrast to a previous experiment [18], in which single electrons were produced using a N_2-laser and a proportional counter used to detect electrons arriving at the anode plane, we are now producing swarms of 10^4 to 10^5 electrons within 3 ns using the focused pulse of a frequency quadrupled NdYAG laser. The pulse energy of about 0.3–1 mJ focused down to a beam diameter of several microns establishes a photon density high enough to produce the desired amount of ionization by two photon processes from trace concentrations of aromatic molecules in the gas [19]. Such trace concentrations at the ppb level are not only hard to avoid but have no significant influence on the transport properties to be investigated. (Their omnipresence can be estimated from the fact that a reduction of the gas pressure by seven orders of magnitude does not affect the ionization strength!) This laser driven swarm source offers a variety of advantages compared with the classical techniques used to produce the swarm in or at the cathode, either thermionic emission, by radioactive sources or by irradiating the anode material with UV light.

First of all the origin of the swarm is undisturbed by the presence of surfaces. Thus the cathode boundary problem in conventional experiments [1] is avoided. Just as important is the facility to vary the drift distance to the anode without changing the internal geometry of the drift tube. The transport coefficients can thus be derived from a set of measurements of the time development of the drifting swarm at distinct drift distances. As will be shown later, this reduces the unavoidable distortions of the swarm near the anode to second order effects which are negligibly small for the typical experimental conditions used in our experiments. The geometry of the laser driven swarm source can be adjusted to the requirements of the specific experiment by changing the parameters of the focusing optical system. In the case of the two apparatus to be discussed here, we used a very elongated, line shaped ionization region of about 1 cm in length with a waist of about 40 microns. This configuration provides a superb localization for the origin of the swarm in two dimensions but avoids extremely high charge densities and resulting space charge problems.

2.2. *The VD60 experiment*

The first experiment to be presented here is the long length drift tube VD60 designed to measure the complete set of conservative transport coefficients in pure electric fields (drift velocity and both diffusion coefficients) simultaneously and with very high accuracy. A schematic view of the experiment is shown in Fig. 2. An electric field is maintained uniform over a length of 60 cm by a set of flat, annular electrodes of 0.5 mm thickness and 6 mm spacing. The inner and outer diameters are 40 mm and 120 mm respectively. This electrode system is surrounded by a set of toroidal guard rings held at appropriate potentials to increase the break down voltage of the apparatus and to improve further the uniformity of the electric field. The line shaped electron swarm, produced by the laser driven swarm source described above, is detected time and space resolved after drifting a variable drift length of 0.5–58.0 cm. The detection system, shown in Fig. 3 in more detail, consists of a flat anode, segmented in seven strips oriented parallel to the ionization line and shielded against the drift region by a fine grid. Each of the seven anode strips is connected to a fast

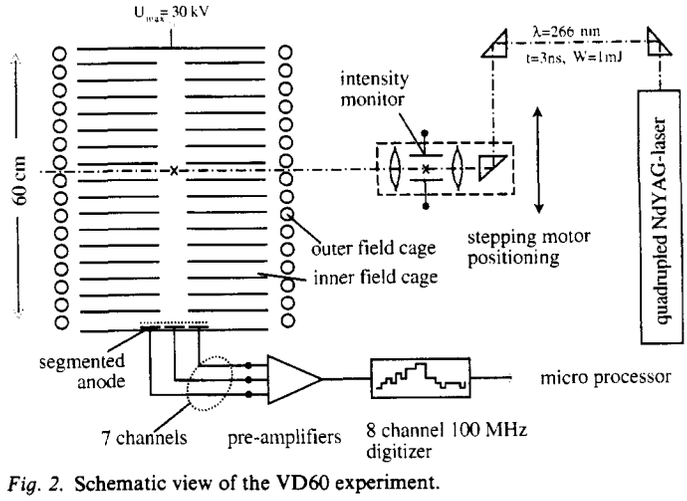

Fig. 2. Schematic view of the VD60 experiment.

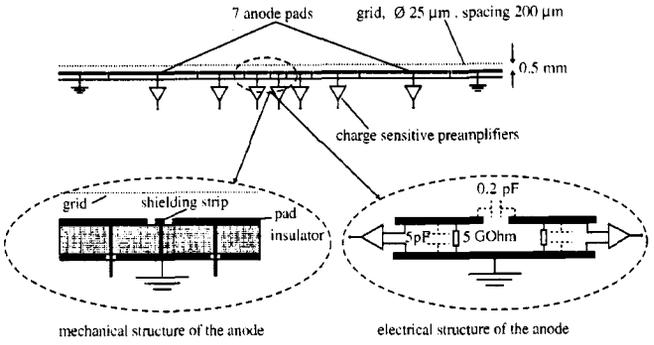

Fig. 3. Space and time resolving charge detection system of the VD60 drift tube.

charge sensitive preamplifier, the time dependent output signal being proportional to the total charge collected at that time. The decay time of the output signals (8 ms) is adjusted to be long compared with the time spread of the arriving charge (a few ns to several µs) and to be short compared with the time interval of successive laser shots (100 ms). To improve the signal to noise ratio the signals of typically 200 swarms are averaged, typical averaged signals measured at the seven anode strips for swarms arriving after 50 cm of drift are depicted in Fig. 4.

To obtain the mean time of arrival t_m and the longitudinal width σ_z of the swarm as well as the total charge collected at the individual strips q_i the measured signals are compared with the expected signal shape and t_m, σ_z and q_i obtained by χ^2 minimization. It should be noticed (Fig. 4), that the individual $t_{m,i}$ of the strips agree within their extremely small statistical errors of about 10^{-4} as do the individual variances $\sigma^2_{z,i}$ to within their statistical errors of about 10^{-2}. This indicates that there are no significant distortions of the swarm perpendicular to the direction of drift and that the degree of uniformity of the drift field is adequate. It can be shown, that for a fixed drift length h, the measured mean time t_m of the swarm is affected by boundary effects near the anode according to

$$t_m = \frac{h}{w} + \alpha_1\left(\frac{D_L}{w^2}\right) + \alpha_2\left(\frac{w}{h}\right)\left(\frac{D_L}{w^2}\right)^2 + \cdots \tag{1}$$

the unkown coefficients α_i depending on the treatment of the behaviour of the anode (totally absorbing, "transparent" etc.) and the definition of the mean time (maximum flux, mean value of total charge etc.). The most important point is, that the first order diffusional term is *independent* of the drift length h and thus cancels if measurements at different lengths are used to derive the drift velocity w. In a similar way it can be shown by numerical methods, that the measured variances σ^2 depend on the drift distance as

$$\sigma^2_{L,T} = 2D_{L,T}\frac{h}{w} + \beta_1\left(\frac{D_L}{w}\right)^2 + \cdots, \tag{2}$$

again the first order is independent of h and cancels if differencing is used to derive the $D_{L,T}$. If the anode is assumed to be totally absorbing and σ_i is defined by fitting a Gaussian distribution to the charge distribution β_1 is about $\frac{5}{2}$. Since the transport coefficients are derived free of first order corrections for diffusion, precise measurements can be performed even in cases where the ratio D_L/w is not particularly small and where classical swarm methods are prone to fail due to the insufficient knowledge of the necessary corrections for diffusion.

The intrinsic accuracy of the apparatus in measurements of the drift velocity is extremely high; the individual t_m can be measured to better than 1 part in 10^{-4} while the drift distances are known to about 100 µm. Thus the "drift velocity under given conditions" can be determined to better than 1 part in 10^{-4}. The systematic uncertainties of the desired transport parameter $w(E/N, T)$ is presently limited to about 1–2 × 10^{-3} due to uncertainties in E, N, and T.* Nevertheless this represents an improvement of about a factor of five compared with classical swarm techniques and enables the study of this transport coefficient to be undertaken on the desired sub-percent level of uncertainty. The uncertainty in the diffusion coefficient measurements is naturally about one order of magnitude worse and limited to about 1–2%, determined by the signal to noise ratio as well as systematic uncertainties. The main source of possible uncertainty is the space charge of the drifting swarm which effects the measured diffusion coefficients especially at small E/N values. It can be shown [20], that the expansion of the swarm due to space charge repulsion is proportional to the total charge of the swarm and exhibits the same time dependence as the diffusion, i.e. the width of the measured charge distribution increases with the drift distance h according to

$$\sigma^2_{L,T} = \frac{2h}{E}\left\{\frac{D_{L,T}}{\mu} + k_{L,T}\left(\frac{E}{N}\right)Q\right\}. \tag{3}$$

The function $k_{L,T}$ can be calculated theoretically up to an apparatus constant κ which has to be determined experimentally by comparing data sets measured with different swarm charge Q. Since κ can be easily determined to about 10% and the total repulsion effect does not exceed, even for small values of E/N, 10%, the systematic uncertainty due to space charge can be kept below 1%.

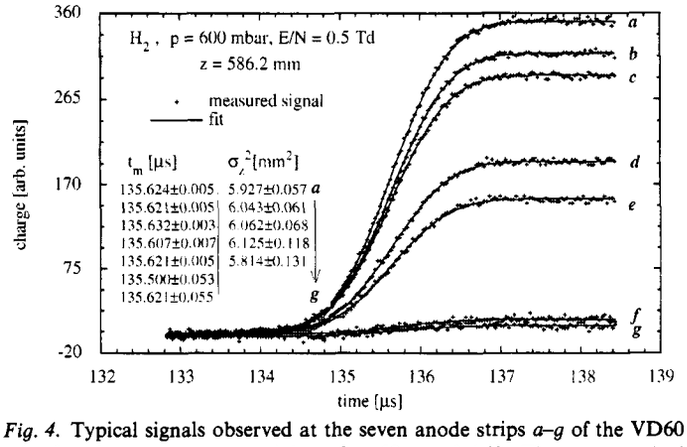

Fig. 4. Typical signals observed at the seven anode strips *a–g* of the VD60 tube for electron swarms arriving after 58 cm of drift. The mean arrival times t_m and the longitudinal and transverse widths (σ_z, σ_x) of the swarms are obtained by fitting expected and observed signal shapes.

* In the absence of ionization and attachment and in the limit of low gas density the electric field E and the number density of the gas N affect the electron transport only as the reduced electric field E/N thus leading to the "E/N scaling" of skilfully chosen transport coefficients. As common practice the "reduced electric field" is measured in Townsend, $1\,\text{Td} = 10^{-21}\,\text{V m}^2$. Following a suggestion of Kevin Ness we measure the reduced magnetic field B/N, governing the electron transport in the presence of both electric and magnetic fields, in Huxley, $1\,\text{Hx} = 10^{-27}\,\text{Tm}^3$.

The technique used in the VD60 drift tube provides the unique possibility of determining the drift velocity and both diffusion coefficients D_L/μ and D_T/μ* simultaneously from the same data set, with a level of systematic uncertainty which has for w and D_L/μ been considerably reduced compared to conventional techniques and is D_T/μ at least comparable with that obtained in the most elaborated specialized experiments. Since it is a pulsed experiment it can be successfully used also in cases where negative ions are present, conditions which are a major problem for steady stream techniques. The importance of the new technique to derive cross sections from transport coefficients will become evident in Section 3 of this paper.

2.3. *The $E \times B$ experiment*

The second experiment to be described here is dedicated to the measurement of electron transport coefficients in crossed electric and magnetic fields and furnishes important new information which can be used to enhance the reliability of swarm derived cross sections. A schematic view of the $E \times B$ experiment is shown in Fig. 5, a detailed discussion can be found in Ref. [21]. Again the laser driven swarm source is used to produce a line shaped electron cloud at variable drift distances from the anode. The experiment has been designed mainly to measure both components of the drift velocity in the $E \times B$ field, the directly measurable quantities are the velocity component parallel to the electric field w_z and the tangent of the magnetic deflection angle $\tan\alpha = w_x/w_z$. To determine these quantities the experiment can be run in two distinct modes with different orientations of the ionization line. In mode "I" (see Fig. 5) the line shaped swarm is oriented parallel to the magnetic field and $\tan\alpha$ determined from the charge distribution at the anode measured along the x-axis. The charge distribution is measured by means of 73 parallel anode strips (0.83 mm wide, 0.07 mm spacing) with each strip connected to one channel of a charge sensitive sample and hold analogue multiplexer (CAMEX [22]). The amplified charge Q, stored in this device, is then read out serially into a fast digitiser. By fitting a Gaussian distribution to the measured $Q(x)$ distribution the mean arrival position x_m is determined. Typical examples for two distinct drift distances are shown in Fig. 6. Values of x_m are obtained for typically 10–20 different drift distances h, in the range from 0.5 to 10 cm and the tangent of the deflection angle obtained from the slope of the linear x_m *vs.* h relationship. Again the use of the differencing method is essential if high accuracy is required. From the appropriate solution of the diffusion equation (eq. (8.57) in Ref. [1]) it can be calculated, that for the range of drift distances and $D_L/(hw)$ ratios used in our experiment, the expected $Q(x)$ distribution is almost perfectly Gaussian shaped (validating the function used in the fitting) and that the maximum of the distribution occurs at

$$x_m = \tan\alpha\left\{h - \varepsilon\frac{D_L}{w_z} + \cdots\right\}. \tag{4}$$

Again the first order diffusional corrections are independent of h and cancel due to the differencing method. The value of the constant ε depends on the exact treatment of the anode boundary condition. After a scrupulous calibration of the optical system [21] (the individual h are calibrated to about 30 μm) $\tan\alpha$ can now be measured with an intrinsic accuracy of 0.3% or 0.001 abs., whatever is greater. This level of accuracy can be achieved in gases with small D/w ratios, like H_2 at high values of E/N, for small values of E/N in gas mixtures as 2% H_2 in argon the accuracy is limited by the transverse spread of the swarm and increases up to about 1%.

With beam orientation "II" (Fig. 5) the experiment is used to measure the drift velocity component parallel to z using the "VD60 tube technique". The arrival time distribution of the charge collected at the grid shielded section "B" of the anode is used to determine t_m and σ_z by fitting to the expected signal shape. For $B/N = 0$, w_z can be measured with a systematic uncertainty of about 0.2% which is comparable to the uncertainty using the VD60 tube. For $B/N \neq 0$ an additional uncertainty of (0.3% × $\tan\alpha$) has to be added due to a possible calibration error in the angle between the directions of the incident UV beam and the electric field.

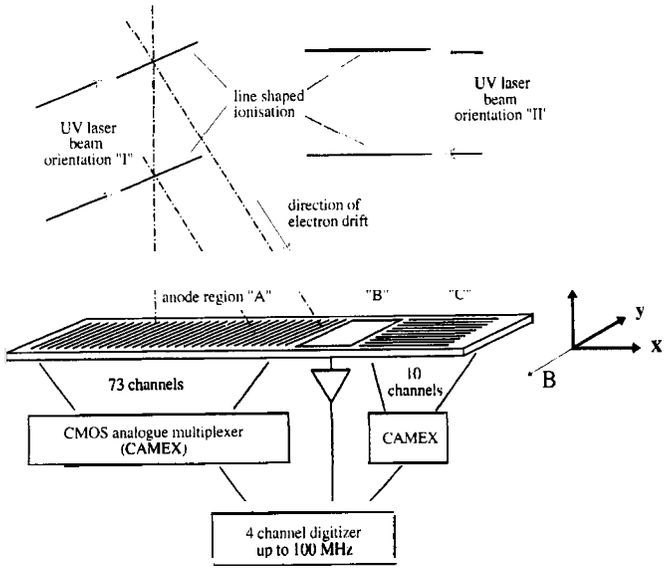

Fig. 5. Schematic view of the $E \times B$ experiment. The magnet as well as the electrode system producing the electric field have been omitted for the sake of clarity.

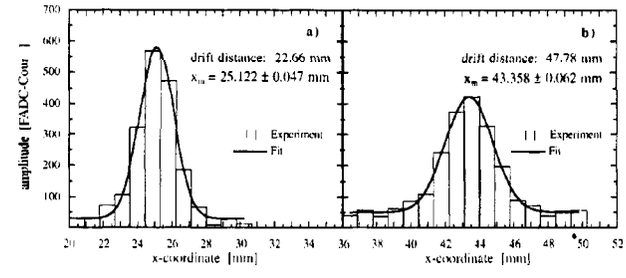

Fig. 6. Charge distribution of electron swarms ariving at the anode strips of the $E \times B$ experiment after (a) 2.3 cm and (b) 4.8 cm of drift in crossed electric and magnetic fields. The mean arrival co-ordinate x_m and the width σ_x of the distribution are obtained by fitting a Gaussian function.

* In swarm experiments the diffusion of the electrons is usually expressed as "diffusion coefficient/mobility" ratio D/μ. This is not only the directly measurable quantity, describing the spread of the swarm with increasing drift distance, but also scales with the reduced fields E/N and B/N.

The apparatus can be operated over a wide range of reduced electric and magnetic fields with deflection angles from zero up to 50° without significant loss of accuracy.

3. Application of the new techniques to hydrogen

As a first and crucial test of the new experimental techniques we investigated the hitherto most sophisticated set of low energy e^-–H_2 cross sections of England, Elford and Crompton [16] (to be called "EEC–H_2") on a sub-percent level of uncertainty in the hope of improving our understanding of electron scattering for this elementary system and to pin down the e^-–H_2 cross sections to the standards needed for the use of H_2 as well known additive in swarm experiments. Our experimental values of the drift velocity in pure H_2 at 298 K measured with both experiments, VD60 and $\boldsymbol{E} \times \boldsymbol{B}$ in $B = 0$ mode are compared with the calculated values based on "EEC–H_2" cross sections in Fig. 7(a). This graph illustrates several interesting points: The excellent agreement of the two independent experiments to within about 0.1% underlines the capabilities of the new experimental technique and supports our claim of an overall systematic uncertainty of better than 0.2% shown as short dashed lines around the theoretical expectation. It also illustrates the high quality of the previous H_2 swarm analyses and their underlying experimental data since the observed deviations barely exceed the typical schematic uncertainty limits of classical experimental techniques indicted by the two long dashed lines in Fig. 7(a). But finally Fig. 7(a) also shows the limits of the previous results and supports the demand for a refined e–H_2 cross section analysis based on the newly available high precision experimental data. As shown in Fig. 1 the uncertainties coming to light in Fig. 7(a) are severe for the determination of e^-–noble gas cross sections based on noble gas–hydrogen mixtures and would strictly limit their range of validity.

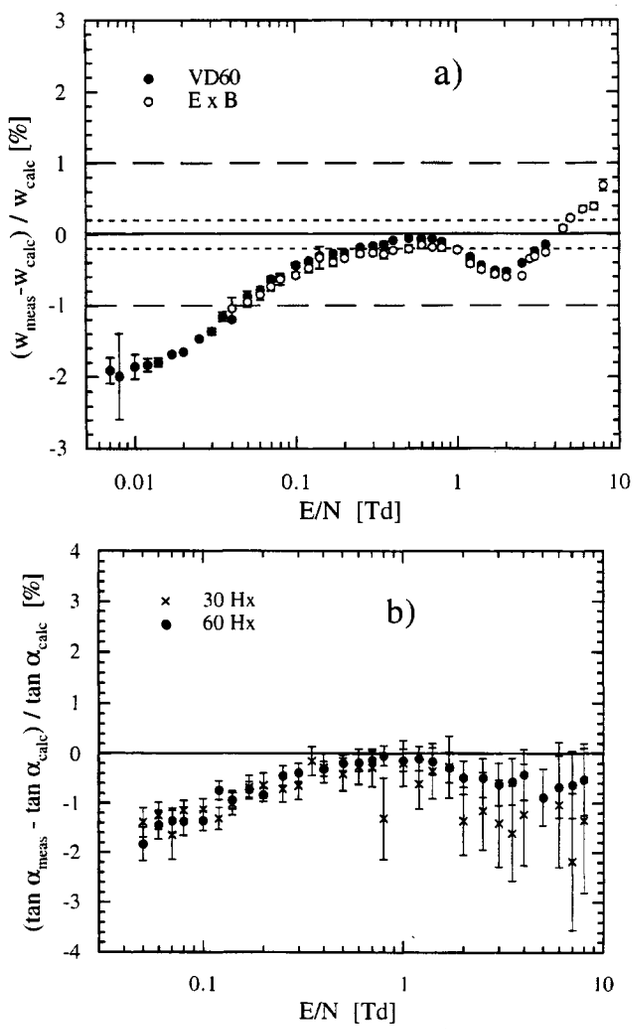

Fig. 7. (a) Relative difference of the calculated drift velocity in pure H_2 based on the cross sections of Ref. [16] and the experimental values obtained in the VD60 and $\boldsymbol{E} \times \boldsymbol{B}$ experiment. The short dashed lines indicate the overall systematic uncertainty of the two experiments whereas the long dashed lines stand for the accuracy limits of "classical" experimental techniques. (b) Relative difference of the calculated magnetic deflection angle for two values of B/N in pure H_2 based on the cross sections of Ref. [16] and the experimental values obtained in the $\boldsymbol{E} \times \boldsymbol{B}$ experiment.

To improve the significance of the observed deviations and to put further constraints to the envisaged H_2 analysis we examined the evidence of other transport coefficients; the only one which can be measured with comparable accuracy is the magnetic deflection angle $\tan\alpha$ since the uncertainty of the diffusion coefficients is limited to about 1–2% even using our new experimental techniques. A comparison of the experimental data for $\tan\alpha$ measured at two different reduced fields B/N with calculated values is shown in Fig. 7(b). The observed deviations from the EEC–H_2 based calculations are very similar (though not identical) to those observed in the drift velocity and almost independent of B/N. The latter point is important in view of the fact that the absolute values of $\tan\alpha$ at $B/N = 30$ Hx and $B/N = 60$ Hx differ by about a factor of two. Thus different parts of the apparatus are used to measure both data sets making systematic effects very unlikely as possible source of the observed deviations. Additionally we used the $\boldsymbol{E} \times \boldsymbol{B}$ apparatus to measure the drift velocity with $B/N \neq 0$; again very similar deviations from the calculated values have been observed with the extra information, that EEC–H_2 based calculations are unable to describe the observed B/N dependence of the drift velocity at small E/N. We therefore decided to determine a refined set of e^-–H_2 cross sections using our high precision data with the strong demand that all the above mentioned deviations should disappear simultaneously. Furthermore these refined cross sections should not be conflicting with the broad experimental data base of EEC–H_2, namely the drift velocity and transverse diffusion coefficients measured with classical methods in pure H_2 at room temperature and at 77 K as well as transport coefficients He–H_2 and Ne–H_2 mixtures.

3.1. *The technique of the Boltmann analysis*

As mentioned in the introduction, unfolding swarm data to derive the underlying scattering cross sections is a complicated and cumbersome procedure, especially for molecular gases where a set of inelastic cross sections and the elastic momentum transfer cross section have to be determined simultaneously. The classical way of finding a self consistent cross section set is by "trial and error by human interface", a method strongly dependent on the experience and patience of the investigator and subject to a certain degree of imponderableness. In the past a good deal of the criticism of swarm derived cross sections, especially of the range of validity and uniqueness, has concentrated on this point. To avoid these problems we decided to optimize our cross sections by χ^2-fitting of observed and calculated transport coef-

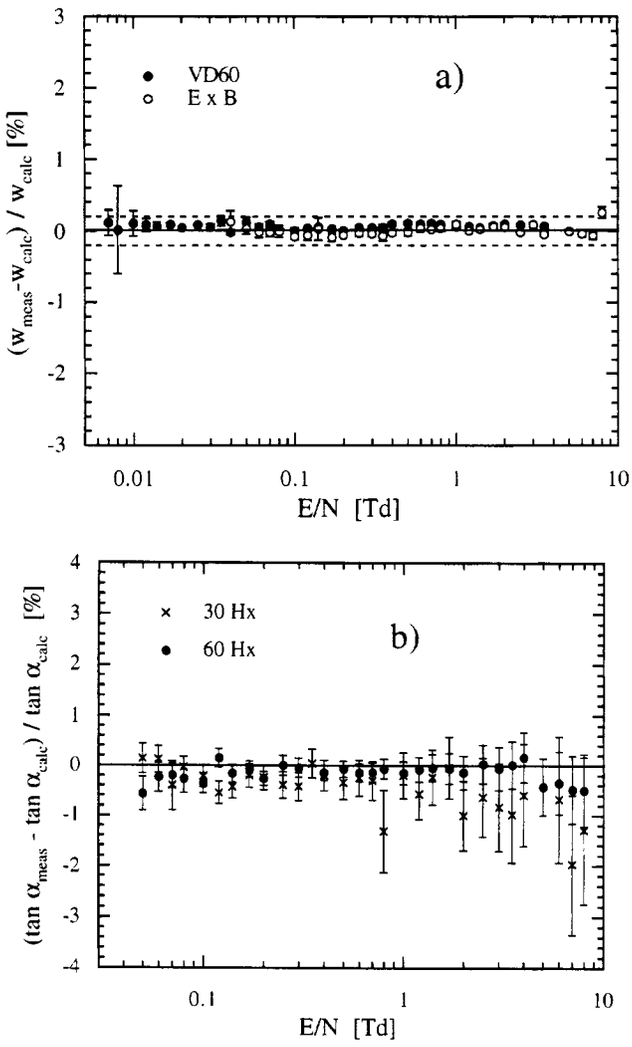

Fig. 8. Relative difference of the calculated and measured data for the drift velocity (a) and two magnetic deflection angles (b) after successful optimisation of the elastic and inelastic H_2 cross sections.

ficients using standard mathematical optimization algorithms. Our Boltzmann analysis is based on the moment theory of Robson and Ness [2, 3] to solve the transport equation in any order of the spherical harmonic expansion of the distribution function, a powerful method which has been extended to the case of crossed electric and magnetic fields by K. F. Ness recently [4]. A detailed description of this important progress in swarm theory can be found in a different paper of this volume. Despite the advantage of the moment theory of not needing iterative procedures to solve the transport equation, the calculation of the interaction matrices to the required accuracy needs considerable computer time. Thus we decided to use the well known modified Levenberg Marquard optimisation scheme which offers the fastest convergence for problems with many correlated parameters. One of the fundamental problems in the automation of the Boltmann analysis was to find a proper set of variables to be optimized. Since usually no analytic form of the cross sections is known (with the exception of elastic scattering from noble gases at low energies, where a MERT parameterization can be used [23]), they are given by a set of energy/cross section pairs in tabulated form. For one cross section typically about 30–100 data points in the range of energy $0.01\,\text{eV} < \varepsilon < 10\,\text{eV}$ are used. In the case of H_2, where 12 cross sections are involved in this energy range, about 400 data pairs have to be determined. It is obvious, that subsequent data points of the same cross section are highly correlated, thus it is unreasonable to use them as individual free parameters. A fixed parameterization of the cross section on the other hand would put too many constraints on the analysis not only producing unphysical results but also possibly obscuring the true χ^2-minimum. As a solution of this problem we used a set of parmeterized "modification" functions acting on the cross section data set, a method of combining the advantages of the tabulated cross sections with a limited number of fitting parameters. The required flexibility of the fitting procedure is retained by the subsequent use of a variety of different modification functions spanning the range of polynomials and power laws to multiple Gaussians and combinations of these. The skill and "good nose" of the scientist is involved to advance the procedure through the proper choice of the sequence of modification functions to be used.

After the successful determination of the χ^2-minimum the range of validity of the derived cross sections as a function of the electron energy was checked by applying localized modification functions to explore the steepness of the χ^2-minimum. For the error bounds on the cross sections shown below, a Gaussian modification centred at energy ε and with a width of 0.2 ε has been used and an increase of the reduced χ^2/f (χ^2 divided by the number of data points minus fitted parameters) by 1 has been required to determine the range of validity of the cross section at the energy ε.

3.2. *New Boltzmann analysis of e–H_2 scattering cross sections*

In Table I we have summarized the cross sections for e^-–H_2 scattering contributing in the energy range $0.01 < \varepsilon < 3\,\text{eV}$ covered in this analysis. This set of cross sections, which is identical to the one used in the EEC–H_2 analysis, fulfills the two basic requirements for a Boltzmann analysis: to be comprehensive and minimal. No significant process has been neglected and the introduction of indistinguishable and highly correlated candidates has been avoided. The latter point is mainly related to the problem of the rotational splitting of the vibrational transitions. Whereas the transitions v: $0 \rightarrow 1$ with no additional change of the rotational quantum number ($\Delta j = 0$) have almost identical thresholds (and thus energy losses of the colliding electron) independent of the initial rotational state of the molecule, this is not the case for transitions with accompanying $\Delta j = 2$. Due to the large rotational constant of H_2 the threshold energies of the processes with significant populations at room temperature differ from 0.442 eV for the rotationally superelastic v, j: $0,3 \rightarrow 1,1$ transition to 0.609 eV for v, j: $0,4 \rightarrow 1,6$. Whereas at the time of the Swarm Seminar we were convinced, that it is necessary and advisable to include these processes individually, we now came to the conclusion that this would violate the requirement of minimality. Since the threshold energies are so close and the shape of the cross sections are expected to be very similar, their strengths cannot be fitted individually without introducing too much arbitrariness in the analysis. The individual cross sections derived in this way would be highly correlated and thus more or less meaningless. We therefore decided to use, as was done in the "EEC" analysis, a single "combined" v:

$0 \rightarrow 1$, $\Delta j = 2$ cross section keeping in mind that this should be called an effective cross section which could be temperature dependent if the contributions starting from different initial states are very unlike. At room temperature the dominant contribution is v, j: $0,1 \rightarrow 1,3$ (66%) and the average energy loss is 0.568 eV.

For our Boltzmann analysis we used the drift velocity with no magnetic field $w(0)$ and the deflection angle at $B/N = 60$ Hx, tan α (60 Hx), as transport parameters to be fitted since these are the experimental data with the smallest uncertainies. Other data, such as tan α(30 Hx), $w(B/N)$ and the diffusion coefficients were used to check the validity of the results obtained. Finally we succeeded in finding a set of cross sections as functions of energy which fitted *all* the newly measured transport parameters, with and without magnetic fields, to within their tight limits of uncertainty. A comparison of measured and calculated values is shown in Fig. 8. The χ^2/f for the fitted parameters has been reduced from 75 for $w(0)$ and 10 for tan α(60 Hx) based on EEC-H_2 (see Fig. 7) to now 0.55 and 0.60 respectively. Furthermore the non-fitted parameter tan α(30 Hx) as well as the B/N dependence of w are reproduced to within their limits of accuracy. Figure 9 shows a comparison of the experimental values for the transverse and longitudinal D/μ ratios, as measured with the VD60 apparatus, with the calculated values based on EEC–H_2 and the newly derived cross sections. Whereas the longitudinal diffusion is almost insensitive to the differences of the two cross section sets, D_T/μ slightly favors the new values with an improvement of χ^2/f from 1.53 to 0.62. The comparatively "large" uncertainties of the diffusion coefficients of 1–2% strictly limits their applicability in a Boltzmann analysis when very high accuracy is required.

From a consideration of the ground state populations, the cross sections of Table I have very different effects on the calculation of transport parameters and on their expected ranges of validity when obtained from a Boltzmann analysis. The restriction of our new experimental data to E/N values less than 10 Td introduces a certain weakness in the analysis of electron energies >1 eV which can only be slightly reduced by including transport data at higher values of E/N measured in classical experiments [24] with their typical uncertainties. This deficiency of the swarm analysis in the energy range above 1 eV is particularly annoying in view of the long standing and obstinate discrepancy between theoretical, crossed beam and swarm derived values of the v: $0 \rightarrow 1$ cross section which cast a shadow on the reliability of the various methods. (See [17, 25 and 26] for an overview of this topic.) To overcome our insensitivity in that energy regime we used the transport coefficient data in a mixture of 2% H_2 in argon up to $E/N = 1.7$ Td, extending the sensitive energy range to about 3 eV. As in pure H_2 we used the drift velocity with no magnetic field and the deflection angle as fitted parameters. The method offers the benefit of an increased sensitivity to inelastic cross sections in the energy regime mentioned above compared with pure H_2 or He–H_2 mixtures with the minor drawback, that the elastic momentum transfer cross section σ_m of argon is not known precisely enough to be used that way without caution. Using the most reliable data available for σ_m(Ar) [27] we were not able to find a set of H_2 cross sections which gave satisfactory agreement between calculated and measured transport coefficients in *both* pure H_2 and the Ar–H_2 mixture. Thus we felt compelled to fit the inelastic H_2 cross sections *and* σ_m(Ar) simultaneously. This procedure is in fact less dubious than it might seem to be: first of all it did not introduce changes to the already well converged H_2 cross sections outside their expected accuracy limits but significantly improved these in the above mentioned energy range. Additionally, only a minor modification of the excellent σ_m(Ar) of Ref. [27] was needed to improve the quality of the combined fit considerably. Fitting both elastic and inelastic cross sections for the Ar–H_2 mixture simultaneously is in fact exactly the same as has to be done for any pure molecular gas, with the strong constraint of the inelastic cross sections being identical to those of the pure H_2 gas. The final results of our fitting procedure and sensitivity analysis are shown in the following figures.

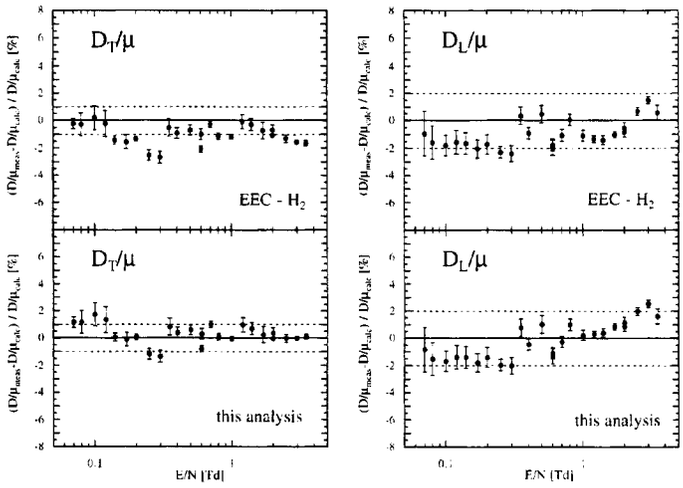

Fig. 9. Comparison of the experimental values for longitudinal and transverse diffusion in pure H_2 obtained in the VD60 apparatus with calculations based on the cross sections of Ref. [16] (top line) and the newly derived data set (bottom line). The dashed lines indicate the systematic uncertainty limits of our experiment whereas the individual bars are the pure statistical errors.

3.2.1. *Rotational excitation.* As expected from the ground state population at room temperature, our analysis exhibits the highest sensitivity for the j: $1 \rightarrow 3$ transition which is the dominant energy loss process below the vibrational threshold. This cross section can be determined with an uncertainty of about 5% from threshold up to 0.5 eV and about 10% up to 1 eV. As shown in Fig. 10(a) the result of the fitting procedure is in perfect agreement with the theoretical values of Morrison *et al.* [25], the previous swarm derived result [16] lying just outside our limits of reliability. Similarly good agreement with the theoretical values is obtained for the j: $0 \rightarrow 2$ transition but with much wider error limits (except for the regime below the j: $1 \rightarrow 3$ threshold) and the deviation from the EEC result [16] is of only minor significance. In Fig. 10(b) we show the values of the j: $2 \rightarrow 4$ and j: $3 \rightarrow 5$ cross sections used in the fit for sake of completeness. Due to their small ground state populations the sensitivity limits are very faint but the derived cross sections seem to be reasonable.

3.2.2. *Vibrational excitation.* Above about 0.7 eV the vibrational excitation process v: $0 \rightarrow 1$ is the dominant energy loss process in H_2 and the Boltzmann analysis becomes particularly sensitive to the strength of this transition. As mentioned earlier, the analysis is complicated by

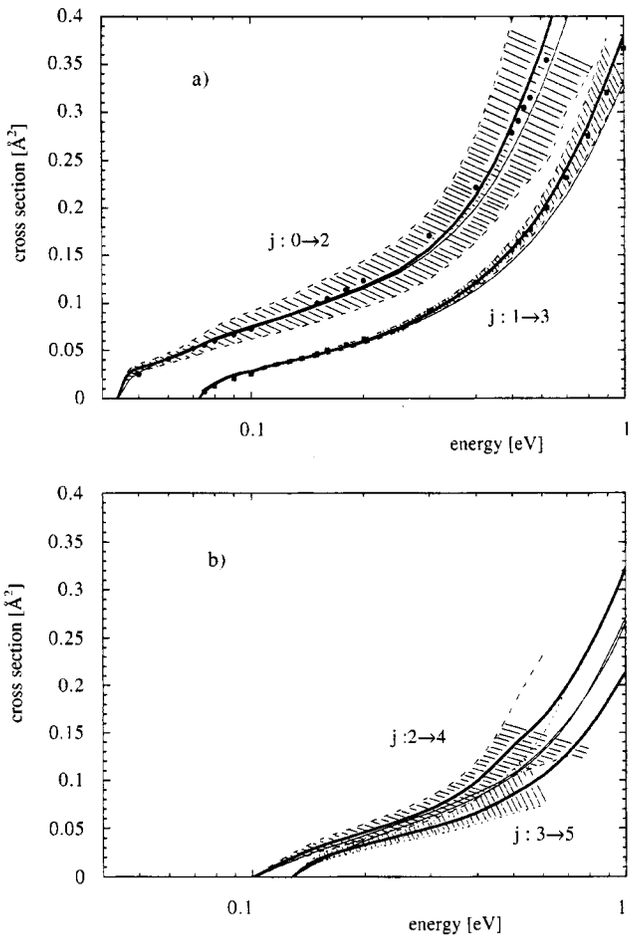

Fig. 10. Cross sections for rotational excitation of H_2 by electron impact obtained in this analysis (thick line) compared with the results of a previous swarm analysis [16] (thin line) and the most rigorous theoretical calculations [25] (dots). The hatched areas indicate the limits of accuracy in this analysis for a *local* variation of the cross section. An overall "shift" would give much more restricted bounds. (a) j: 0 → 2 and j: 1 → 3. (b) j: 2 → 4 and j: 3 → 5.

the rotational splitting of the process, only the strength of the rotationally summed v: 0 → 1 transition can be determined with resonable accuracy. Nevertheless we retained in our analysis two separate cross sections for $\Delta j = 0$ and $\Delta j = 2$ transitions considering the rather different mean energy losses of both processes (see Table I). A comparison of the rotationally summed v: 0 → 1 cross section with the previous swarm result, crossed beam and theoretical data is shown in Fig. 11. Above 0.6 eV our cross section is considerably higher than the EEC result [16] almost bisecting the

Table I. *Inelastic processes in H_2 contributing in the energy range 0.01 < ε < 3 eV and included in this analysis with their thermal population of the ground state at 298 K*

Process		$\varepsilon_{thr.}$ (eV)	q_{pop} (298 K)
rot:	0 → 2	0.0439	12.9%
	1 → 3	0.0727	65.9%
	2 → 4	0.1008	11.8%
	3 → 5	0.1280	9.0%
	4 → 6	0.1538	0.4%
vib:	0 → 1, $\Delta j = 0$	0.5159	100%
	0 → 1, $\Delta j = 2$	0.442 ... 0.609	100%
	0 → 2, $\sum \Delta j$	1.003	100%
	0 → 3, $\sum \Delta j$	1.461	100%

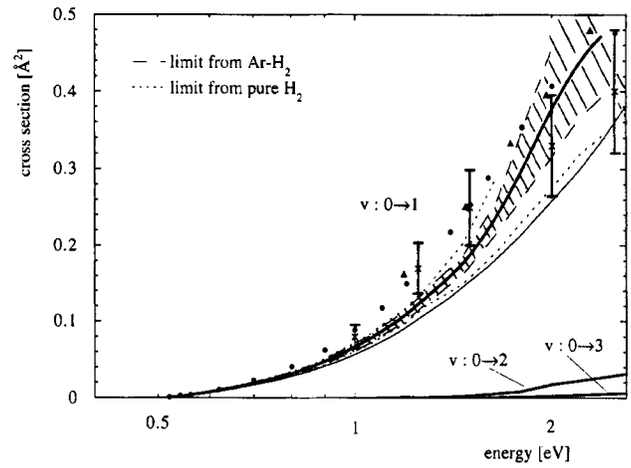

Fig. 11. Rotationally summed cross section for vibrational excitation of H_2 as obtained in this analysis (thick line) and compared with the result of a previous swarm analysis [16] (thin line), crossed beam experiments (Brunger *et al.* [28] (crosses with error bars) and Ehrhardt *et al.* [29] (triangles without error bars) and the most rigorous theoretical calculation [25] (dots without error bars). The hatched area indicates the uncertainty limits in this analysis for a *local* variation of the cross section. The cross sections for the transitions v: 0 → 2 and v: 0 → 3 used in the analysis are shown for completeness and are of negligible influence in this energy range.

discrepancy between the swarm derived cross section and the theoretical calculations of Ref. [25]. Although this seems to diminish the Great Hydrogen Controversy [17] a good deal, the Controversy is in fact reinforced by the narrow band of uncertainty we are able to specify for the cross section up to about 1.8 eV. In the region of energy 0.7 eV to 1.6 eV the theoretical values are well outside the range of possibility for compatibility with our analysis. In view of the fact that the cross sections obtained in a Boltzmann analysis are to some extent correlated, we carefully examined the possibility, that the observed deficiency of the v: 0 → 1 cross section might be due to an overestimation of other inelastic processes. If the v: 0 → 1 transition is fixed at its *theoretical* value and the fitting procedure repeated for the other inelastic and elastic cross sections, *all* other inelastic channels drop to zero above 0.7 eV, a completely unphysical behaviour, but even in this extreme case no satisfactory agreement of calculated and measured transport coefficients is obtained ($\chi^2/f = 11$). The situation is even worse in the case of the Ar–H_2 mixture due to their higher sensitivity in the energy range. The χ^2/f value does not fall short of a few hundred in this case whereas the converged value with the cross sections shown above is 2.3. Thus we have to conclude that the theoretical values for the v: 0 → 1 transition of Ref. [25] are incompatible with the swarm derived cross section by many standard deviations even if completely unphysical assumptions for other inelastic channels are considered.

From Fig. 11 it should be noted that there is no significant discrepancy of our swarm derived result with the most recent crossed beam data from Brunger *et al.* [28] if their error estimates, representing the present state of the art in this energy regime, are correct. (χ^2/f is 0.95 based on the uncertainty of the crossed beam data alone.) Regarding the early results of Erhardt *et al.* [29], one has to keep in mind that the principal motivation of this experiment was to study the angular and energy dependence of the cross section and that absolute values were obtained by extrapolating the angular range to 0 and 2π and normalizing to a total elastic cross section. Notwithstanding their support for

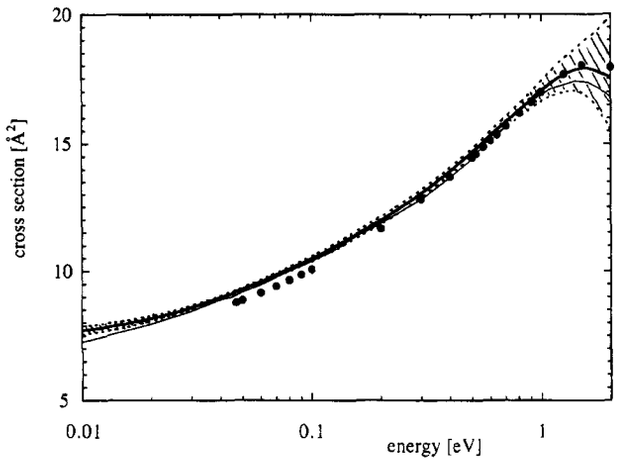

Fig. 12. Elastic momentum transfer cross section of H_2 as obtained in this analysis (thick line) compared with the result of a previous swarm analysis [16] (thin line) and the most rigorous theoretical calculations [25] (dots). The hatched area indicate the limits of accuracy in this analysis for a *local* variation of the cross section.

the theoretical values it seems to be hard to specify the systematic uncertainty of their cross section in view of the limits of the more recent crossed beam experiment [28] which was undertaken with the specific aim of determining the absolute value of the cross section in this energy regime.

Our conclusion on the present state of the v: $0 \rightarrow 1$ cross section in hydrogen is therefore, that there is still a non-trivial discrepancy between the theoretical and swarm derived values of at most 28% in the energy range 0.7 eV to 1.6 eV which is in all probability out of the range of possible hidden problems in the swarm experimental method. Crossed beam data, though overall slightly favouring the theoretical result, are unable to give strong evidence for where one has to look for the "improbable".

3.3.3. *Elastic momentum transfer.* In Fig. 12 we show our result for the elastic momentum transfer cross section of H_2 which is very close to the previous result of Ref. [16] except at electron energies below 0.04 eV. The uncertainties extracted from our analysis are $\leqslant 1\%$ for energies between 0.03 and 0.6 eV increasing to about 5% at 1.6 eV. The result of the theoretical calculation of Morrison *et al.* [25] is in very good agreement with the swarm derived values with a slight but significant tendency to be too small for electron energies below 0.1 eV.

We believe that the analysis presented in this section has consolidated our knowledge of the low energy e^-–H_2 cross sections to such an extent, that it should now be possible to study H_2–noble gas mixtures without strong limitations on the validity of the noble gas cross sections from this cause.

4. Application of the new techniques to H_2–noble gas mixtures

After the successful reanalysis of the low energy e^-–H_2 cross sections we applied our new experimental techniques to H_2–noble gas mixtures, especially to mixtures with argon, krypton and xenon. The goal of this study was to examine the reliability of the available elastic e^-–noble gas cross sections or rather to derive new and more accurate data sets. Since a comprehensive discussion of this study would exceed the scope of this paper, only a brief overview of the results obtained to date will be given. An extensive discussion of the topic including newly measured data for diffusion coefficients and a rigorous sensitivity analysis as well as a comparison with crossed beam and total cross section data and theoretical calculations will be given in a forthcoming publication.

Besides the higher accuracy of the new experimental techniques it is the use of the magnetic deflection angle as an additional transport parameter in the Boltzmann analysis fitting that enables considerable progress in this field of research, a fact we have already demonstrated in Ref. [17]. The marked insensitivity of the drift velocity to the momentum transfer cross section in the vicinity of the Ramsauer minimum [12] causes an enormous ambiguity problem if only drift velocity data are used in the analysis. Amongst the other transport coefficients which can be used in the analysis, such as the diffusion coefficients and the magnetic parameters, $\tan \alpha$ is the most favourable choice since it combines a high sensitivity to the cross sections with lower error limits on the experimental values.

In the case of elastic scattering from noble gases the momentum transfer cross section at low energies can favourably be parameterized in a modified effective range theory (MERT) scheme [23], a proven method which we have adopted throughout our analysis. For "higher energies" the cross section is given as a polynomial with the additional flexiblity of changing the point and method of the crossover from MERT to the polynomial expansion.

4.1. *Argon–H_2*

As mentioned in the previous section, we used a mixture of 2% H_2 in argon to enhance the reliability of our newly derived H_2 cross sections and, simultaneously, to derive an improved momentum transfer cross section for argon. In the top line of Fig. 13 the experimental values of our fitted parameters $w(0)$ and $\tan \alpha$ are compared with calculated values based on the most reliable cross sections for H_2 [16] and argon [27] so far. The observed deviations of up to 3%, which are well outside our experimental limits, demand an improvement to be made to the above mentioned data sets. After optimising the cross sections for both gases we obtained the results shown in the bottom line of Fig. 13,

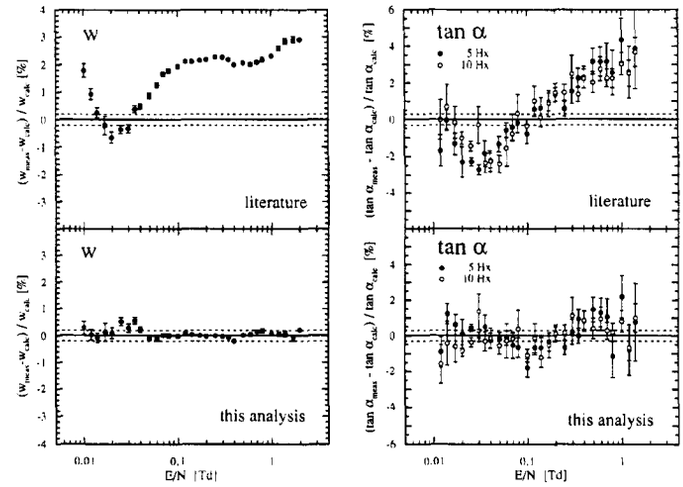

Fig. 13. Comparison of experimental values for the drift velocity w with no magnetic field and the magnetic deflection angles at two values of B/N in a mixture of 2% H_2 in argon with calculated values based on the cross sections of Ref. [16] (H_2) and [27] (Ar) (top line) and the new values of this analysis (bottom line). The dashed lines indicate our systematic uncertainty limits whereas the individual bars correspond to statistical errors.

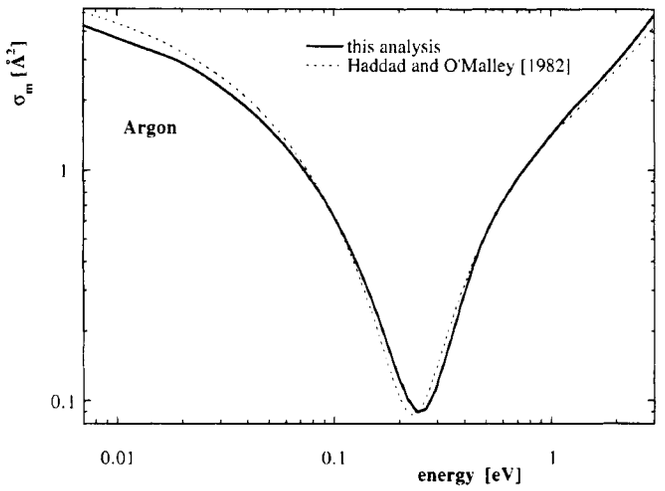

Fig. 14. Elastic momentum transfer cross section of argon derived in this analysis (solid line) and from a previous swarm study [27] (dashed line).

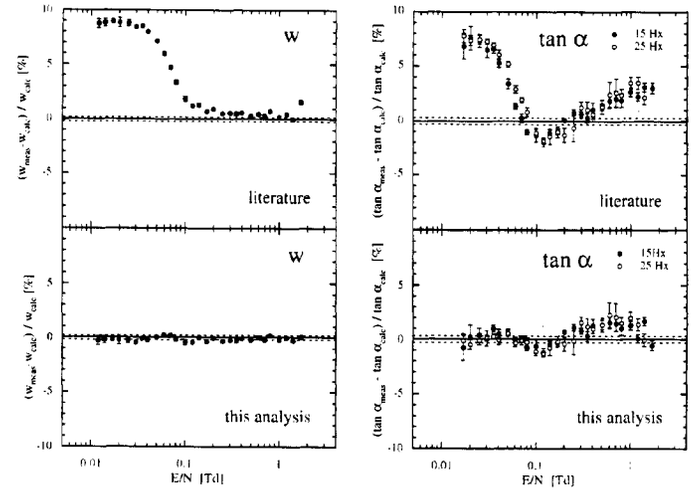

Fig. 15. Comparison of experimental values for the drift velocity w with no magnetic field and the magnetic deflection angles at two values of B/N in a mixture of 1.686% H_2 in krypton with calculated values based on the cross sections of Refs [16] (H_2) and [33] (Kr) (top line) and the new values of this analysis (bottom line). The dashed lines indicate our systematic uncertainty limits whereas the individual bars correspond to statistical errors.

now based on the newly derived H_2 cross sections shown in Section 3 and the elastic momentum transfer cross section for argon given in Fig. 14. It agrees in shape and magnitude quite well with the previous result of Haddad and O'Malley [27] (based mainly on the high pressure D_T/μ experiment in pure argon by Milloy and Crompton [13]), but requires lower values in the limit of small electron energies and there is a slight shift of the position of the Ramsauer minimum. As mentioned above, a detailed discussion of this result together with a thorough analysis of its significance will be given in a forthcoming publication.

4.2. *Krypton–H_2*

In the case of krypton we are confronted with the situation that five different swarm analyses of the momentum transfer cross section leading to considerably different results have been published since 1986 [30, 31, 14, 32, 33]. Two of them are based on drift velocity [31] and transverse diffusion [30] data in pure krypton whereas the others rely on H_2–Kr mixtures. These might be affected by additional uncertainties introduced by the use of less precise H_2 cross sections in the analysis. Already in Ref [7] we have shown that none of the above mentioned krypton cross sections is able to reproduce our measurements in a H_2–Kr mixture with typical deviations of 5–10%. The most recent analysis of Brennan and Ness [33] is based on both, w [14] and D_T/μ [34], in a H_2–Kr mixture to avoid the insensitivity problem of the drift velocity to the cross section minimum and is expected to give the most reliable result. If we compare our new experimental data with calculations (Fig. 15, top line) based on this cross section, together with EEC–H_2 as used in the analysis of Ref. [33], we see that the drift velocity values above 0.1 Td are reproduced quite well, reflecting the fact that data in this E/N range have been available from previous experiments [14] and were used in the analysis of Ref. [33]. For lower fields, where no experimental data existed so far, deviations of up to 9% in both, the drift velocity and the deflection angle are found. In fact, the deviations are due to uncertainties in both, the krypton and the hydrogen cross sections. When we tried to analyse our H_2–Kr data on the basis of the EEC–H_2 cross section set, the fit was able to find *any* krypton cross section in the frame of the above mentioned parameterization (MERT + polynomial = 15 free parameters). No χ^2/f below 200 could be achieved whatever was chosen as the transition point from MERT to the polynomial region. In contrast to this the convergence is quite fast if the new H_2 data set of Section 3 is used and a final χ^2/f of 2.7 can be achieved. The accompanying deviations after the fit are shown in the bottom line of Fig. 15. Since it is unlikely that the true krypton cross section is very far from being parameterizable in the way mentioned above, we take this as a strong indication of the superiority of the new H_2 cross sections derived here. The result of our krypton analysis is shown in Fig. 16 together with the previous swarm derived cross sections since 1986. As in the case of argon, we derive a smaller momentum transfer cross section at low energies than most of the previous results. At energies below the cross section minimum there is astonishingly good agreement with the cross sections of Koizumi *et al.* [30] derived from D_T/μ measurements in pure krypton gas. In the vicinity of the minimum our cross section agrees with Ref. [33] within their stated limit of uncertainty. The energy at which the minimum occurs has now been determined to be 0.51 eV,

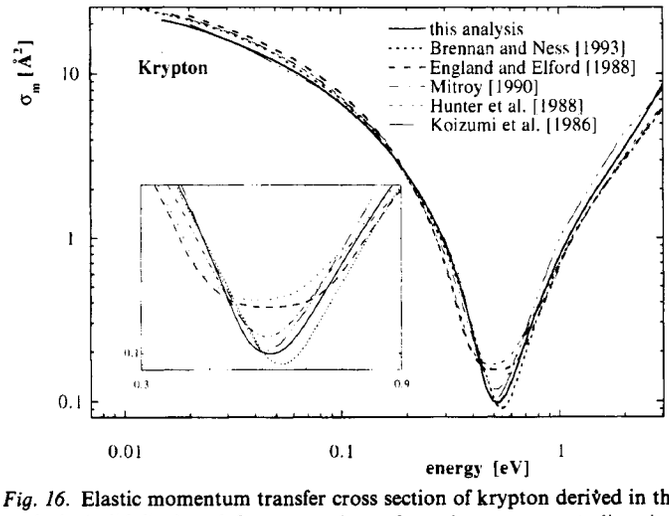

Fig. 16. Elastic momentum transfer cross section of krypton derived in this analysis (solid line) and from a variety of previous swarm studies since 1986: Koizumi *et al.* [30] (long dot dashed) and Hunter *et al.* [31] (thin dashed) from transport coefficients in pure krypton; England and Elford [14] (thick long dashed), Mitroy [32] (dot dashed) and Brennan and Ness [33] (thick dashed) from transport coefficients in H_2–krypton mixtures.

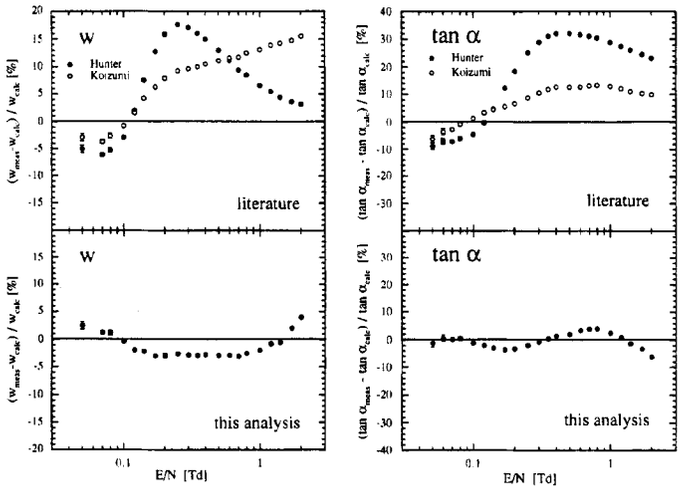

Fig. 17. Comparison of experimental values for the drift velocity w with no magnetic field and the magnetic deflection angles at $B/N = 40\,\mathrm{Hx}$ in a mixture of 2% H_2 in xenon with calculated values based on the cross sections of Koizumi *et al.* [30] and Hunter *et al.* [31] (top line) and the new values of this analysis (bottom line).

the cross section having a minimal value of almost exactly 0.1 Å^2. Looking in close detail at Fig. 15 we find some evidence for a systematic imperfection in the agreement between calculated and measured deflection angles which exhibits some similarities to those observed in the fitted H_2–Ar data (Fig. 13). This indicates that a small uncertainty is still present in the hydrogen cross sections which is amplified by the much higher sensitivity of the heavy noble gas mixtures compared with the pure molecular gas, a feature which can be of great advantage in the study of inelastic cross sections for more complex molecules [7].

4.3. *Xe–H_2*

The published momentum transfer cross sections of xenon are without exception derived from swarm experiments in pure xenon. As in the case of krypton, Hunter *et al.* [31] used drift velocity data whereas Koizumi and co-workers rely on their measurements of D_T/μ [30]. A more recent analysis of Nakamura using drift velocity and D_L/μ data [35] comes, at least for small electron energies, very close to Ref. [31] and is not discussed separately since no cross sections in tabulated form have been available to us. Recently Elford *et al.* have measured the drift velocity and D_T/μ in a

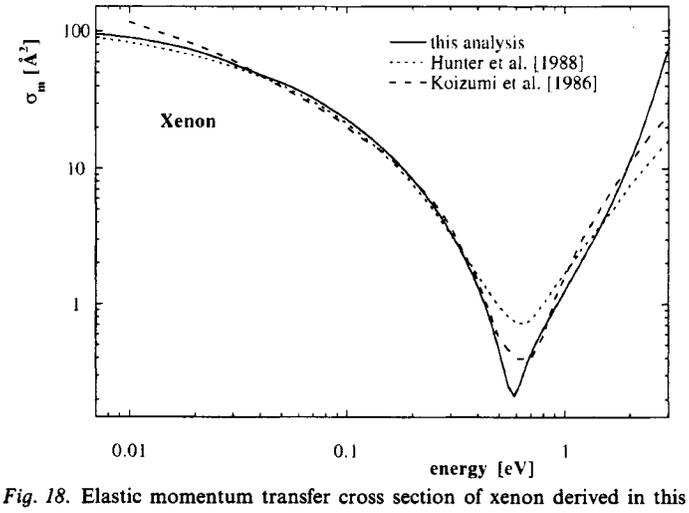

Fig. 18. Elastic momentum transfer cross section of xenon derived in this analysis (solid line) and from two previous swarm studies: Koizumi *et al.* [30] (long dashed) and Hunter *et al.* [31] (short dashed).

H_2–Xe mixture, their analysis [36] has shown that none of the above mentioned xenon cross sections is able to reproduce the experimental values when used in combination with the EEC–H_2 data set. A similar result can be seen from Fig. 17 (top line) where we compared our experimental values with calculations based on the xenon cross sections of Refs [30, 31] and observed extremely strong deviations of up to 30%. As in the case of krypton we found that our fitting procedure was unable to find a solution for the xenon momentum transfer cross section in the frame of MERT + polynomial parameterization when the EEC–H_2 data set was used. Using our new cross section set a much better convergence was observed, but no satisfactory agreement could still be obtained. The remaining deviations shown in Fig. 17 (bottom line) still reflect a very poor χ^2/f of about 70 which seems to be the final value in the frame of the above mentioned parameterization. This might reflect the fact that this parameterization is not flexible enough to find the "true" xenon momentum transfer cross section (in the case of e^-–Xe scattering relativistic effects are of great importance [37] and might make the MERT parameterization invalid). More likely the deviations are due to the extraordinary sensitivity of the xenon mixture to the fine structure of the inelastic H_2 cross sections in the vicinity of the vibrational thresholds. The reason becomes obvious from Fig. 18 which shows the two xenon cross sections from Refs [30, 31] together with our present results. The very pronounced and sharp Ramsauer minimum coincides exactly with the onset of the H_2 vibrational channels introducing a very high sensitivity to those processes. When we changed the vibrational cross sections at threshold by amounts which produced completely negligible changes in the transport coefficients for both pure H_2 and the Ar–H_2 mixture and which are also well within our stated uncertainty limits of Section 3, we observed significant alterations of the transport parameters in the H_2–Xe mixture. The use of this sensitivity for further refinement of the inelastic H_2 cross sections is a delicate procedure and under study.

Finally we would like to comment, that it is a common feature of all Boltzmann analyses shown here that it is *no problem at all* to find noble gas cross sections which reproduce the drift velocity or the deflection angle *separately*, but which give very poor agreement with the non-fitted parameter. It is only the combination of both transport coefficients "causing the problems" and thus offering the opportunity of obtaining far more reliable results.

5. Summary and outlook

The new experimental techniques presented in Section 2 have now demonstrated their ability of considerably improving the reliability of the cross sections for some of the most fundamental systems, hydrogen and heavy noble gases. This is of special importance in view of experiments to derive electron scattering cross sections for more complex moleules from Boltzmann analyses, where experimental data from molecular gas–heavy noble gas mixtures are of particular interest in disentangling the contributions of the various inelastic channels. A solid data base of well understood gases together with the efficiency of the new experimental techniques stand a good chance of success in consolidating the "paramount importance" [26] of swarm experiments in the study of electron scattering at very low

energies and providing reliable results for a wide range of molecular species.

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