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Momentum Transfer Cross Section for Electrons in Krypton Derived from Measurements of the Drift Velocity in H_2–Kr Mixtures

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Abstract

Measurements of electron drift velocities have been made in 0·4673% and 1·686% hydrogen–krypton mixtures at 293 K and values of E/N from 0·08 to 2·5 Td with an estimated uncertainty of $<\pm 0\cdot 7\%$. The data have been used in conjunction with the H_2 cross sections of England *et al.* (1988) to derive the momentum transfer cross section for krypton over the energy range 0·05 to 6·0 eV. The drift velocity data have also been used to test the Kr momentum transfer cross sections of Koizumi *et al.* (1986) and Hunter (personal communication 1988). The cross section of Koizumi *et al.* is clearly incompatible with the present measurements while the cross section of Hunter has been used to predict these measurements to within 1% to 3%.

1. Introduction

The analysis of electron transport coefficient data to obtain the momentum transfer collision cross section, σ_m, is a well established technique (Huxley and Crompton 1974). Recently, two such derivations of σ_m have been published for krypton. Koizumi *et al.* (1986) based their analysis on measurements of the ratio D_T/μ (where D_T is the transverse diffusion coefficient and μ the electron mobility, $\mu = v_{dr}/E$; v_{dr} is the drift velocity and E the electric field strength) for electrons in krypton as a function of E/N, where N is the gas number density. Hunter *et al.* (1987) and Hunter (personal communication 1988) analysed measurements of the drift velocity of electrons in krypton as a function of E/N. The analyses of each of these experiments yielded cross sections which differ by as much as 60%.

The present work, based on measurements of drift velocities in hydrogen–krypton mixtures, has enabled these two momentum transfer cross sections for krypton to be tested. The procedure used was to compare experimental drift velocities with values calculated using a set of hydrogen cross sections (England *et al.* 1988) and the Kr momentum transfer cross section in question. The analysis and the results obtained are discussed in Section 4.

A second aim was to carry out a new derivation of the krypton momentum transfer cross section using the present drift velocity data. The derivation is an iterative process with the trial krypton cross section used in the initial calculations being adjusted until the calculated and experimental drift velocity values agree to within the experimental uncertainty. This cross section is presented and compared with those obtained by Koizumi *et al.* and Hunter (personal communication 1988) in

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Section 5. The present cross section is also compared with the experimental cross sections of Frost and Phelps (1964) and Hoffman and Skarsgard (1969), and with the theoretically-derived cross sections of Sin Fai Lam (1982), Fon *et al.* (1984) and McEachran and Stauffer (1984 and personal communication 1988).

Modified effective range theory (MERT) (O'Malley 1963) was used to obtain a value for the scattering length for krypton from the present cross section. The results of a fit to the cross section using MERT are also presented in Section 5.

In the following section, the reasons for using data for hydrogen–krypton mixtures in the present analysis rather than those for pure krypton are discussed.

2. Use of Hydrogen–Krypton Mixtures

The use of hydrogen-krypton mixtures largely avoids a number of problems which occur in measurements with pure krypton. These problems are the low sensitivity of the drift velocity to the cross section in the vicinity of the minimum, the high sensitivity of all the transport coefficients to trace concentrations of molecular impurities, and large diffusion losses to boundaries. The primary cause of these problems is the combination of the very small value of the momentum transfer cross section at energies in the vicinity of the Ramsauer–Townsend minimum (approximately 0·5 eV) with the small value of the average energy lost per collision.

The low sensitivity of the drift velocity in pure krypton to the region of the minimum in the momentum transfer cross section can be explained by considering the expressions for the drift velocity:

$$v_{\mathrm{dr}} = -\frac{eE}{3N}\left(\frac{2}{m}\right)^{\frac{1}{2}} \int_0^\infty \frac{\epsilon}{\sigma_{\mathrm{m}}(\epsilon)}\frac{\mathrm{d}f}{\mathrm{d}\epsilon}\,\mathrm{d}\epsilon\,, \tag{1}$$

and the energy distribution function:

$$f(\epsilon) = A\exp\left\{-\int_0^\epsilon\left(\frac{ME^2e^2}{6mN^2\epsilon'\sigma_{\mathrm{m}}^2(\epsilon')}+kT\right)^{-1}\mathrm{d}\epsilon'\right\}, \tag{2}$$

for the case where only elastic collisions occur (Huxley and Crompton 1974). (Inelastic collision processes for krypton are not significant, since the first electronic excitation has a threshold energy of approximately 10 eV and at all values of E/N of interest in this discussion the fraction of electrons with energies greater than 9 eV is negligible.) In these equations, m and M are the electron and neutral particle masses, e is the electron charge, ϵ the energy, k is Boltzmann's constant, T is the gas temperature and A is a normalising constant. From equation (2), it can be shown that $\mathrm{d}f(\epsilon)/\mathrm{d}\epsilon$ becomes very small when $f(\epsilon)$ becomes small or when

$$\epsilon\sigma_{\mathrm{m}}^2(\epsilon) < \frac{ME^2e^2}{6mN^2kT}\,.$$

At energies around 0·5 eV, i.e. near the minimum of the cross section, the value of $\epsilon\sigma_{\mathrm{m}}^2$ satisfies this inequality except at small values of E/N. However, when E/N is small, $f(\epsilon)$ is also very small at 0·5 eV. Thus, for all values of E/N, $\mathrm{d}f(\epsilon)/\mathrm{d}\epsilon$ is small at energies in the vicinity of the minimum in σ_{m}. Consequently, the contribution to the integral in equation (1) from the integrand at energies in the vicinity of the minimum in σ_{m} is very small and this causes the drift velocity to be relatively insensitive to the value of σ_{m} near the minimum. In derivations of cross sections, this results in much higher uncertainties being placed on the cross section near the minimum compared with other parts of the energy range.

In contrast, measurements of D_T/μ in pure krypton are very sensitive to σ_m in the region of the minimum. In the expression for ND_T,

$$ND_T = \tfrac{1}{3}\left(\frac{2}{m}\right)^{\frac{1}{2}} \int_0^\infty \frac{\epsilon f(\epsilon)}{\sigma_m(\epsilon)}\,d\epsilon\,, \tag{3}$$

$df(\epsilon)/d\epsilon$ does not appear. Since the value of ϵ/σ_m is very large at the minimum of σ_m, the integral is highly sensitive to changes in σ_m in this region.

Drift velocities in hydrogen–krypton mixtures show an enhanced sensitivity to the minimum in the krypton cross section compared with the drift velocities in pure krypton. The cause of this effect, however, may not be immediately obvious. As the proportion of hydrogen is increased, the aggregate momentum transfer cross section for the mixture, at energies near the minimum in σ_m for krypton, becomes dominated by σ_m for hydrogen. It might, therefore, be thought that the sensitivity of the drift velocity for the mixture to the krypton cross section near the minimum would decrease as the hydrogen concentration increases. However, by plotting calculated distribution functions, it can be shown that the magnitude of $df(\epsilon)/d\epsilon$ at the energy of the minimum in the cross section becomes larger as the hydrogen concentration increases. This factor increases the sensitivity of the drift velocity to the minimum of the krypton cross section. The net result of these two competing effects is that the drift velocity measurements in hydrogen–krypton mixtures with hydrogen concentrations of the order of 1% are more sensitive to the minimum of the krypton cross section than are those in pure krypton. The maximum sensitivity of the drift velocities in the mixture to the minimum in σ_m for krypton is still not as high as that of the D_T/μ values in pure krypton or hydrogen–krypton mixtures but, since drift velocities can in general be measured to a greater relative and absolute accuracy than values of D_T/μ, drift velocity measurements were used in the present analysis.

The relatively large values of D_L/μ (D_L is the longitudinal diffusion coefficient) for electrons in pure krypton cause large diffusion losses to boundaries and, hence, large errors in measured drift velocities (Elford 1972). Such effects can only be made insignificant by the use of high gas pressures. Hunter *et al.* (1987), for example, used pressures in excess of 300 kPa in their measurements of drift velocities in pure krypton.

The value of D_T/μ shows a rapid rise as E/N increases in the range of E/N where the transport coefficients are most sensitive to the minimum of the krypton cross section. This means that errors in the electric field due to contact potential differences can introduce large errors in the measured values of D_T/μ which decrease as the gas pressure is increased. Ogawa (personal communication 1988) has suggested that a significant variation with pressure found recently in the results of Koizumi *et al.* may be due to errors of this type and the published values may be in error by as much as 50% at the low values of E/N.

Measurements of transport coefficients in krypton are also highly sensitive to trace quantities of molecular impurities. The most common molecular impurities, as stated by the manufacturer, are nitrogen and hydrogen which both have rotational and vibrational excitation cross sections with thresholds at low energies. The presence of small levels of such impurities causes a significant increase in the energy lost by electrons and can produce large changes in the transport coefficients. In order to reduce the impurity levels, both Koizumi *et al.* and Hunter *et al.* installed purification systems. To demonstrate the magnitude of this problem, Hunter *et al.* investigated the data of Pack *et al.* (1962) for pure krypton and estimated that their published values for the drift velocity may be in error by as much as 20% due to the presence of 1 ppm of N_2 or another molecular impurity.

Rather than remove impurities, the approach using mixtures involves the deliberate introduction of an 'impurity', in this case hydrogen. By adding approximately 1% of hydrogen, the energy loss of the electrons becomes dominantly determined by rotational and vibrational excitation processes and hence any additional energy loss due to trace levels of other impurities is insignificant. The purity of the krypton gas is, therefore, no longer a critical factor and purification of the Matheson Research Grade gas is not required.

The large reduction in the diffusion coefficient caused by the addition of hydrogen greatly reduces the magnitude of errors caused by diffusion to boundaries discussed earlier in this section. It is therefore not necessary to use high gas pressures to reduce diffusion with a consequent significant saving in the cost of the gas.

The one disadvantage, however, in the use of hydrogen–krypton mixtures is the additional uncertainty introduced into the analysis by the uncertainty in the hydrogen cross sections. Because hydrogen is only present at a low concentration, the uncertainty in the calculated transport coefficients due to the uncertainty in σ_m for hydrogen is small. The hydrogen cross sections used in the present work have been been used to accurately predict drift velocities and D_T/μ values in para-hydrogen and normal hydrogen at 77 K and normal hydrogen at 293 K, as well as drift velocities in a H_2–He mixture and two H_2–Ne mixtures at 293 K (England *et al.* 1988). They are therefore believed to be the most reliable set of low-energy hydrogen cross sections available.

3. Measurements of Drift Velocities in H_2–Kr Mixtures

The electron drift velocities were measured using the Bradbury–Nielsen method and the apparatus and techniques described previously (Elford 1972; Huxley and Crompton 1974). The krypton gas was Matheson Research Grade, while the hydrogen gas was purified before use by passing it through a heated palladium osmosis thimble (Crompton and Elford 1962). All gas pressures were measured with an estimated uncertainty of $<\pm0 \cdot 1\%$ using a calibrated quartz spiral manometer (Texas Instruments Ltd). The gas temperatures were measured with an uncertainty of $<\pm0 \cdot 15$ K using internal copper–constantan thermocouples. The apparatus was immersed in a water bath for temperature stability and the measured temperatures were all within $\pm0 \cdot 5$ K of $292 \cdot 9$ K. This variation in temperature was found by calculation to produce changes in the drift velocities of less than $\pm0 \cdot 02\%$.

Before measurements were taken in hydrogen–krypton mixtures, some measurements were taken to test the accuracy of the apparatus and procedures used. Drift velocity measurements in hydrogen at a pressure of 40 kPa and at a number of values of E/N agreed with the results of Elford and Robertson (1973) to within $0 \cdot 2\%$.

Mixtures of hydrogen and krypton gases were made by volume sharing using a mixing vessel similar to that described by Haddad (1983). The uncertainty in mixture composition is estimated to be less than $\pm0 \cdot 2\%$. Hydrogen concentrations of 0·4673% and 1·686% were used for the measurements since these could be made using pressures corresponding to gauge calibration points thus avoiding interpolation errors. The concentrations were chosen so that errors due to diffusion were small and the sensitivity of the drift velocity to the minimum in the krypton cross section was close to its highest value as discussed in Section 2. The mixing vessel was immersed in a water bath to keep the temperature constant during the filling and volume sharing procedure. The gas mixture was allowed to mix by diffusion in the mixing vessel for at least one week before gas samples were taken. Drift velocity measurements made with gas samples after one and three weeks mixing time generally agreed to within ±0·05% indicating that a week for complete mixing was adequate.

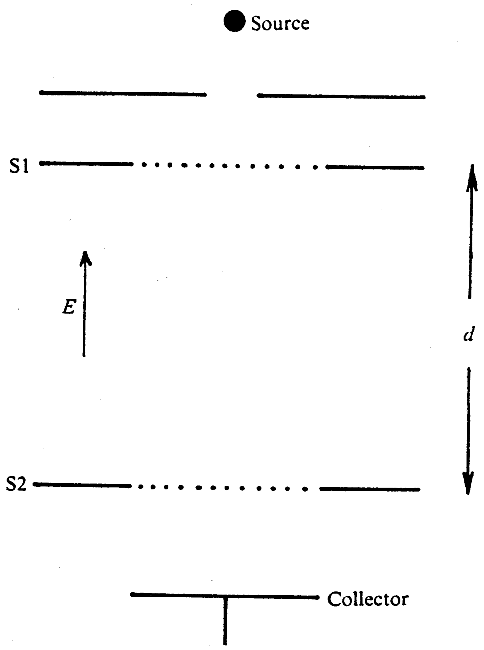

Fig. 1. Schematic diagram of the apparatus used in the present work to measure drift velocities. S1 and S2 are the two electrical shutters, d is the drift distance and E the electric field.

Apparatus used in the present experiment is shown schematically in Fig. 1. Each of the two shutters is a coplanar grid of wires with alternate wires connected. Sinusoidal potentials of equal amplitude but differing in phase by 180° are applied to each set of connected wires. Electrons are transmitted when the potential is close to zero and at higher potentials the shutters are opaque to electrons. The signals applied to both shutters are exactly in phase so that a group of electrons which traverses the distance between the shutters in an integral multiple of half periods will be transmitted to the collector. The current received by the collector when plotted against the frequency of the sinusoidal potential is called an arrival time spectrum and exhibits a series of equally spaced maxima and minima. The measured drift velocity is determined from the frequency of the maxima:

$$v_{dr}(\text{measured}) = 2f_n\, d/n,$$

where f_n is the frequency of the nth maximum and d is the distance between the two shutters.

In the present study, measurements of the frequency of the first peak often did not give the same measured drift velocity as measurements on higher peaks. Sometimes the second peak was also in error. Where such discrepancies existed, the arrival time spectra showed distortion of the lower order peaks. An arrival time spectrum with the most pronounced distortion (shoulders on the peaks) observed in this work is shown in Fig. 2 with another spectrum taken with a higher shutter voltage amplitude.

In an effort to explain this effect, the electron transmission characteristics of the electrical shutters were studied by applying a d.c. bias potential between the wires of one of the shutters and measuring the current transmitted as a function of the potential applied. The plot of current against potential is referred to as a cut-off curve. For most gases the transmitted current has been found to decrease monotonically as the potential is increased from zero (Elford 1972). However, using hydrogen–krypton mixtures, the current was found to have a maximum at a nonzero value of the bias voltage. Some examples of the cut-off curves obtained in the present work are shown in Fig. 3. The curves were found to be very similar for each of the two shutters and to be symmetrical about zero bias voltage. The maxima in transmission were found to occur at voltages as high as 7 V. The position of the maxima generally increased as the value of E/N was increased but did not change significantly when the pressure was varied from 5 to 33 kPa and E/N was held fixed.

This type of cut-off curve, called a butterfly curve, has previously been observed by Pack and Phelps (1961) for argon, by Robertson (1972, 1977) for neon and argon, and by Pribac (personal communication 1985) for helium, with maxima at bias voltages of <2 V (i.e. much lower than for the present hydrogen–krypton mixtures). Pack and Phelps and also Robertson attributed this effect to rapid changes in the cross sections with energy, but the presence of butterfly curves for helium where the cross section changes relatively slowly with energy suggests there may be another cause.

When the shutters are operated with sinusoidal potentials, these unusual transmission characteristics produce a bimodal electron pulse at the first shutter. The width of this pulse decreases with increasing frequency or signal amplitude of the potential. If diffusion is sufficiently large then such structure in the electron pulse is removed before the pulse reaches the second shutter. In the studies of Pack and Phelps and of Robertson, this is thought to have caused no abnormalities in the arrival time spectra. In contrast, the bimodal pulses are believed to be the cause of the distortion in the peaks and errors in the measured peak frequencies in the present work.

The following procedure was developed to avoid errors in the measured drift velocities. Firstly, all the measurements were taken using the highest shutter voltage amplitude that was available (47 V peak-to-peak) although tests showed that accurate values could still generally be taken with amplitudes as low as 35 V (p–p). No shutter voltage dependence was observed to within $\pm 0\cdot 05\%$, for a variation in shutter voltage from 35 to 47 V (p–p), indicating that there was negligible distortion of the electric field in the drift space.

Secondly, measurements were taken on peaks $n = 1$ to 7 for most values of E/N except where signal-to-noise ratios were too low to allow accurate measurements to be taken on the higher order peaks. It was found that, when there was distortion of the arrival time spectra, the first peak gave drift velocities which did not agree with the results obtained from higher order peaks. The measurements on the other peaks always gave drift velocities which agreed to within $\pm 0\cdot 05\%$. In the lower

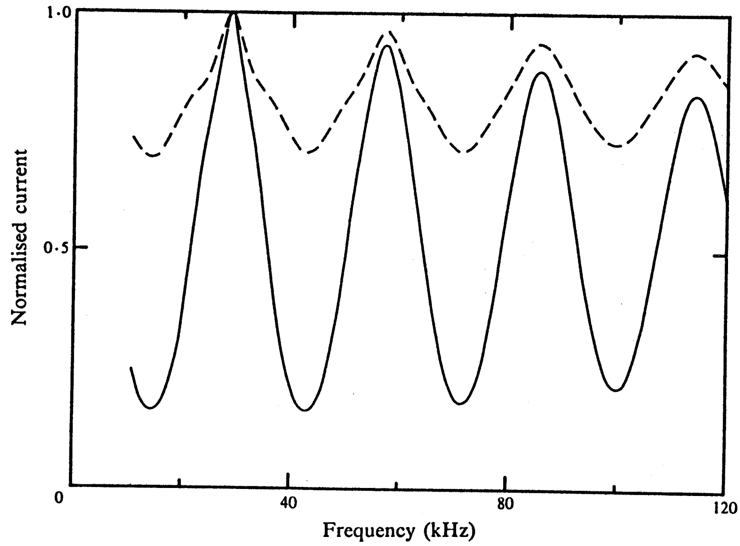

Fig. 2. Arrival time spectra obtained for a mixture of approximately 0·4% hydrogen in krypton at a pressure of 20 kPa and E/N value of 1·2 Td. The dashed curve was obtained using a shutter voltage of 30 V p–p and shows pronounced distortion of the first and second order peaks. The solid curve was obtained using 47 V p–p.

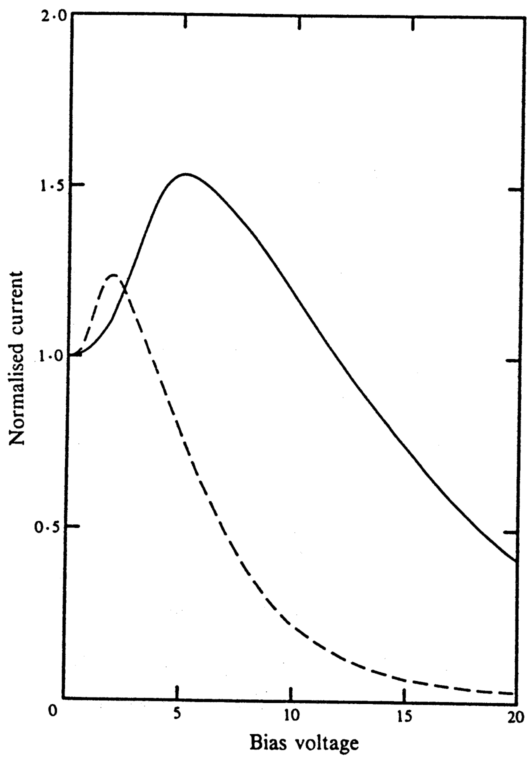

Fig. 3. Examples of cut-off curves showing peaks at nonzero values of the bias voltage. The curves were obtained using the 1·7% mixture of hydrogen in krypton at a pressure of 20 kPa and values of E/N of 0·2 Td (dashes) and 1·2 Td (solid).

range of values of E/N, no distortion in the first peak or errors in measured values were observed. This meant that measurements on the first three peaks were adequate in this range of E/N. A lower limit to the values of E/N which could be used for measurements at a given pressure was set by requiring measurements to be taken on at least three peaks (the signal current falls as n increases and generally also as E/N decreases).

Measurements of drift velocities were taken for the two gas mixtures of approximately 0·5% and 1·7% hydrogen. The range of values of E/N was from 0·08 to 2·5 Td (1 Td is 10^{-17} V cm^2) and five gas pressures between 10 and 33 kPa were used. The results for the 0·5% hydrogen mixture showed a small drift with time. This drift is believed to be caused by the out-gassing of hydrogen from the walls of the apparatus since the gas used in the apparatus immediately before these mixture measurements was hydrogen at a pressure of 40 kPa. Small corrections (all less than 1·0%) were made to the measured drift velocities by plotting the change with time and extrapolating to the time at which the gas was first admitted to the drift tube. The correction procedure was checked by repeating some measurements using fresh gas. The measurements taken with the older gas, to which corrections of about 0·9% had been made, agreed with the measurements taken with fresh gas to within ±0·05%, indicating that the correction procedure was reliable.

The measurements in the 1·7% hydrogen mixture were not affected by the out-gassing of hydrogen, the values changing by less than 0·05% in 100 hours. This is presumably because the rate of out-gassing had decreased by the time that measurements were made in this mixture, and also because the measurements at higher concentrations of hydrogen are less sensitive to small changes in the hydrogen concentration.

The measured drift velocities, after correction for hydrogen out-gassing, are shown in Table 1. These values have been obtained by averaging the results of three or more separate measurements. Due to diffusion of electrons to boundaries, the values shown in Table 1 are subject to errors which can be removed by extrapolation of the values measured at several pressures to infinite pressure (Elford 1972). For values of E/N where three or more pressures were used (i.e. 0·12 to 1·2 Td), the measured drift velocities were plotted as a function of the inverse of the pressure. The points lay about straight lines of best fit with a scatter generally less than ±0·05% and the values extrapolated to $1/p = 0$ were taken as the correct values for the drift velocities. There are, however, a number of values of E/N where drift velocities were measured at only two pressures and extrapolation to infinite pressure is not accurate due to the scatter. Extrapolation without more information is impossible in those cases where values were taken at only one pressure.

The additional information needed to carry out the extrapolation at values of E/N where measurements were obtained for less than three pressures was derived from the variation of the slope of the drift velocity versus pressure curves with E/N where the slope could be accurately determined, i.e. where results were taken at more than two pressures. When the slopes of the lines were plotted as a function of E/N for each mixture, they were found to fit the following relation:

$$\text{Slope} = a(E/N)^{-b}, \tag{4}$$

where the constants a and b are different for each mixture. The values of the

Table 1. Drift velocities (in units of 10^5 cm s^{-1}) of electrons in two mixtures of H_2-Kr at 292·9 K

E/N (Td)	Pressure (kPa) 10·33	13·43	19·62	26·85	33·05	Corrected for diffusion
			(*a*) 0·4673% H_2-Kr			
0.08				5.309	5.324	5.216
0.10				5.890	5.880	5.791
0.12			6.178	6.136	6.129	6.051
0.14		6.345	6.301	6.264	6.248	6.184
0.17		6.400	6.363	6.329	6.320	6.263
0.20		6.412	6.374	6.349	6.340	6.290
0.25	6.440	6.398	6.373	6.347	6.340	6.297
0.30	6.405	6.382	6.357	6.335	6.326	6.287
0.35	6.380	6.366	6.338	6.320	6.313	6.278
0.4	6.365	6.344	6.325	6.308	6.298	6.266
0.5	6.331	6.318	6.299	6.284	6.281	6.256
0.6	6.302	6.295	6.277	6.265	6.263	6.242
0.7	6.274	6.268	6.253	6.243	6.239	6.220
0.8	6.244	6.242	6.227	6.218	6.214	6.197
1.0	6.178	6.175	6.163	6.158		6.142
1.2	6.095	6.097	6.086			6.065
1.4	6.007	6.009				5.981
1.7	5.869	5.870				5.846
2.0	5.729					5.703
2.5	5.506					5.484
			(*b*) 1·686% H_2-Kr			
0.10				4.946	4.946	4.899
0.12			6.442	6.428	6.411	6.371
0.14		7.558	7.530	7.512	7.502	7.463
0.17		8.652	8.615	8.595	8.593	8.544
0.20		9.314	9.289	9.277	9.265	9.235
0.25		9.957	9.947	9.922	9.916	9.883
0.30		10.306	10.289	10.279	10.275	10.253
0.35		10.521	10.502	10.496	10.488	10.468
0.4		10.658	10.644	10.638	10.632	10.616
0.5	10.870	10.832	10.821	10.811	10.808	10.790
0.6	10.960	10.934	10.927	10.917	10.914	10.897
0.7	11.019	11.006	10.999	10.992	10.987	10.975
0.8	11.068	11.059	11.051	11.043	11.040	11.029
1.0	11.128	11.123	11.116	11.109		11.099
1.2	11.160	11.153	11.145			11.128
1.4	11.160	11.154				11.132
1.7	11.118	11.117				11.096
2.0	11.037					11.014
2.5	10.845					10.824

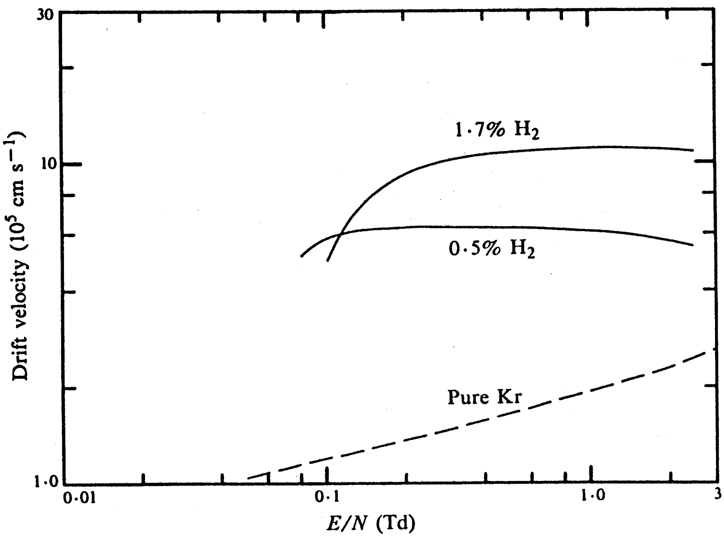

Fig. 4. Best estimate values for the electron drift velocities in hydrogen–krypton mixtures (solid). Also shown are the drift velocity values for pure krypton of Hunter *et al.* (1987) (dashes).

Table 2. Contributions to the absolute error

Source of error	Maximum effect on v_{dr} (%)
(a) Systematic errors	
Voltages between shutters	0.05
Temperature	0.10
Pressure	0.10
Drift distance	0.10
Mixture composition	0.15
Correction for drift with time	0.20
Diffusion correction	0.40
Total systematic	<0.55
(b) Random error	0.10
Total error	< ±0.7

constants and their standard errors, determined using a weighted least squares fit, are, for the 0·5% H_2–Kr mixture,

$$a = 0{\cdot}47 \pm 0{\cdot}02, \qquad b = 0{\cdot}79 \pm 0{\cdot}03,$$

and, for the $1\cdot7\%$ H_2–Kr mixture,

$$a = 0\cdot37\pm0\cdot01, \qquad b = 0\cdot59\pm0\cdot02.$$

It is difficult to give any physical interpretation of these results since the slopes are dependent upon many variables including apparatus-dependent variables. However, relation (4) was useful to predict slopes for values of E/N where results were available at less than three pressures. These slopes were then used to extrapolate to infinite pressure and thereby correct for the effects of diffusion at these values of E/N.

The best estimate value shown in Table 1 and in Fig. 4 are values obtained after corrections have been made to account for diffusion. The largest difference between the highest pressure result and the extrapolated value is 2% for the $0\cdot5\%$ H_2–Kr mixture. The differences for the $0\cdot5\%$ hydrogen–krypton mixture are approximately twice as large as those for the other mixture. Contributions to the total error in the best estimate drift velocities are shown in Table 2. An estimate of $<\pm0\cdot7\%$ was obtained for the total uncertainty by adding the systematic errors in quadrature and then adding the random error. Not all of the four or five figures of each entry in Table 1 are significant, but they have been included to avoid round-off errors in the subsequent analysis.

4. Tests of Momentum Transfer Cross Sections for Kr

Values of the drift velocities for mixtures of $0\cdot4673\%$ and $1\cdot686\%$ H_2–Kr were calculated using the hydrogen cross sections of England *et al.* (1988) and, in turn, the krypton momentum transfer cross sections of Koizumi *et al.* (1986) and Hunter (personal communication 1988). These calculations were performed using a computer code which solves the Boltzmann equation numerically using an expansion of the angular dependence of the velocity distribution function in spherical harmonics truncated to two terms (see for example Crompton *et al.* 1969). The validity of the truncation to two terms was checked over the full range of values of E/N by carrying out calculations using a multi-term code (Lin *et al.* 1979; Ness 1985). The differences between drift velocities calculated using two terms and using five terms in the expansion was less than $0\cdot1\%$. This was the case for both of the H_2–Kr mixtures and for pure Kr. Isotropic scattering was assumed in these calculations.

The input data for the calculations includes a tabulated set of cross sections at specified energies which subsequently require interpolation to match the mesh size in the calculation procedure. Normally, linear interpolation has been used. In the present calculations, it was found that, due to the high curvature of the cross section in the region of the Ramsauer–Townsend minimum, the Kr momentum transfer cross section needed to be specified at 200 energies between 0 and 6 eV before errors due to linear interpolation of the cross section became insignificant. On the other hand, when a quadratic interpolation routine was used, accurate results could be obtained using only 70 values. None of the calculations presented in this paper are subject to significant errors arising from interpolation. It was found, however, that the previously derived cross sections of Koizumi *et al.* and Hunter *et al.* were not given at an adequate number of points to allow accurate calculations when using linear or quadratic interpolation. Thus the cross sections had to be interpolated graphically in order to specify them at an adequate number of points to ensure the required accuracy of the subsequent quadratic interpolation.

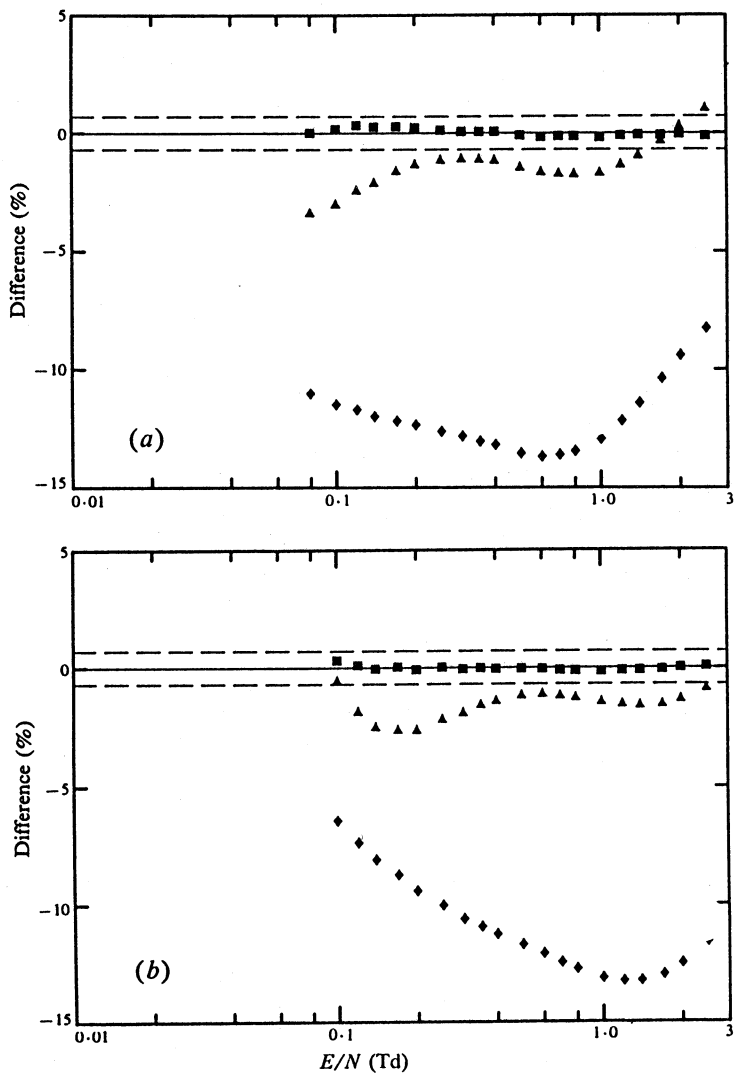

Fig. 5. Differences between calculated and experimental drift velocities, Difference = $\{v_{dr}(calc) - v_{dr}(exp)\}/v_{dr}(exp)$, using the krypton momentum transfer cross sections of Koizumi *et al.* (1986) (diamonds), Hunter (personal communication 1988) (triangles), and the present work (squares) for (*a*) 0·4673% and (*b*) 1·686% H_2–Kr mixtures. The dashed lines indicate the uncertainty of ±0·7% in the experimental results.

Hunter (personal communication 1988) found that it was necessary to include a krypton electronic excitation cross section for calculations of the drift velocities for pure krypton. The process with the lowest threshold has a threshold energy of 9·91 eV and only becomes significant at his highest values of E/N. This cross section was, however, not included in the present calculations of drift velocities in either of the H_2–Kr mixtures since the number of electrons with energies higher than 9·9 eV is insignificant at all the values of E/N used.

The differences of the calculated values from the experimental values for mixtures of 0·4673% and 1·686% H_2–Kr are shown in Figs 5*a* and 5*b* respectively. The

Table 3. Present krypton momentum transfer cross section

Energy (eV)	Cross section (Å²)	Energy (eV)	Cross section (Å²)	Energy (eV)	Cross section (Å²)
0.0	41.5	0.44	0.1643	0.96	0.589
0.02	22.3	0.46	0.1591	1.0	0.677
0.04	16.2	0.48	0.1563	1.1	0.890
0.06	12.35	0.50	0.1550	1.2	1.113
0.08	9.65	0.52	0.1552	1.3	1.340
0.10	7.64	0.54	0.1558	1.4	1.570
0.12	6.09	0.56	0.1571	1.5	1.802
0.14	4.868	0.58	0.1593	1.6	2.036
0.16	3.890	0.60	0.1627	1.7	2.274
0.18	3.099	0.62	0.1683	1.8	2.520
0.20	2.455	0.64	0.1761	1.9	2.772
0.22	1.932	0.66	0.1865	2.0	3.040
0.24	1.505	0.68	0.2000	2.2	3.59
0.26	1.159	0.70	0.2166	2.5	4.49
0.28	0.8812	0.72	0.2361	2.7	5.16
0.30	0.6615	0.74	0.2572	3.0	6.24
0.32	0.4916	0.76	0.2816	3.3	7.42
0.34	0.3648	0.78	0.3068	3.6	8.71
0.36	0.2724	0.80	0.3333	4.0	10.44
0.38	0.2233	0.84	0.3898	4.5	12.69
0.40	0.1924	0.88	0.449	5.0	14.6
0.42	0.1743	0.92	0.517	6.0	17.7

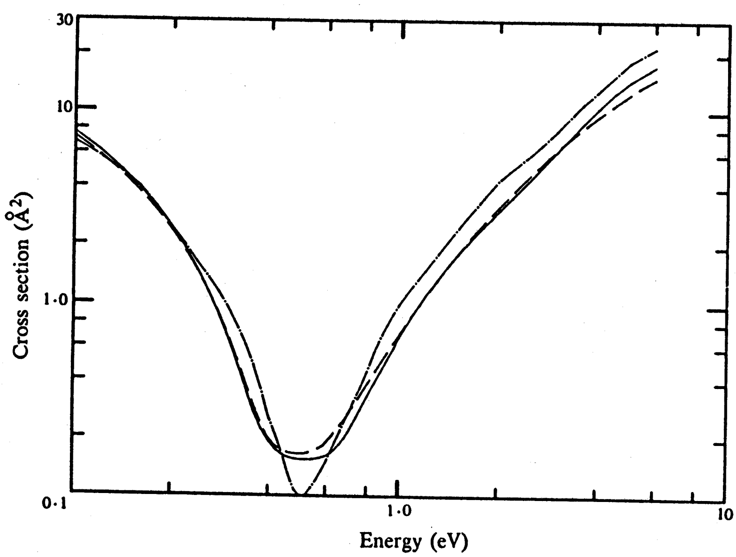

Fig. 6. Kr momentum transfer cross sections of Koizumi *et al.* (1986) (dash–dots), Hunter (personal communication 1988) (dashes), and the present work (solid).

differences of as much as 13%, or almost twenty times the experimental uncertainty, obtained using the cross section of Koizumi *et al.* are too large to be explained by errors in the hydrogen cross sections. The cross section of Hunter predicts drift velocities which are much closer to the present values (differences less than from 1% to 3%), but these differences are also outside the experimental error limits. Errors in the hydrogen cross sections used in the present work seem unlikely to be large enough to produce differences of this size.

Since neither of these two Kr cross sections appeared adequate, a new cross section was derived.

5. The Present Kr Momentum Transfer Cross Section

A cross section was derived which gave drift velocities using the hydrogen cross sections of England *et al.* (1988) that were the best fit to the present drift velocity measurements in the hydrogen–krypton mixtures. The differences between values calculated using this cross section and the experimental drift velocities are shown in Fig. 5. The present cross section is listed in Table 3 and shown in Fig. 6. An assessment of the uncertainty in the fitted cross section is particularly difficult due to the presence of a Ramsauer–Townsend minimum (see for example the discussion for argon in Milloy *et al.* 1977). Although the present data for hydrogen–krypton mixtures are more sensitive to the region of the minimum than the data for pure krypton (Section 2), nevertheless the sensitivity is still low. The depth of the minimum can be varied significantly and a fit still obtained to the data to within the stated error limits by varying the cross section on either side. Hunter has quoted error limits on his derived cross section of ±20% in the region of the minimum and ±5% elsewhere. From experience in carrying out a large number of fits it is considered that similar error limits apply to the present cross section.

Fig. 6 shows the cross sections of Koizumi *et al.* and Hunter in comparison with the present cross section. For energies above approximately 0·3 eV, the cross section of Koizumi *et al.* differs considerably from both the Hunter and the present cross section, whereas the differences between the present cross section and that of Hunter are less than ±5% except in a small range of energies about 0·7 eV where the differences are as large as 23%.

The present krypton cross section predicts values of D_T/μ which are as much as 57% higher than the experimental values of Koizumi *et al.* The Kr cross section of Hunter gives similar differences. It is thought that the values of Koizumi *et al.* may be in error due to the effects discussed in Section 2. The present cross section has also been used to calculate drift velocities in pure krypton. The values obtained agree with the experimental values of Hunter *et al.* to within ±2% for E/N from 0·04 to 1·0 Td, but outside this E/N range the predicted values are lower than the experimental values by as much as 6%.

Comparisons with other experimental cross sections are shown in Fig. 7. The cross section of Frost and Phelps (1964) was derived from measurements of drift velocities in pure krypton, while Hoffmann and Skarsgard (1969) used measurements of microwave conductivity ratios. Hunter *et al.* (1987) have suggested that the drift velocity measurements used by Frost and Phelps are in error due to the presence of impurities (Section 2). The differences of the present cross section from that of Hoffmann and Skarsgard are not understood. Fig. 8 shows the momentum transfer

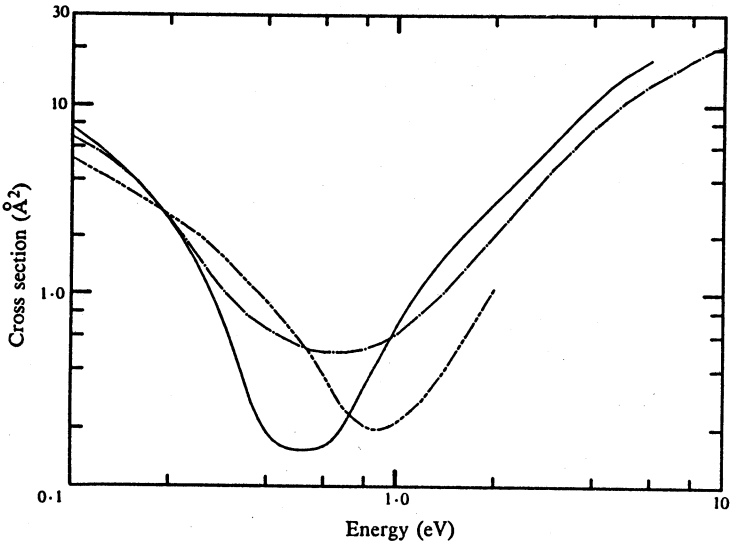

Fig. 7. Kr momentum transfer cross sections of the present work (solid), Frost and Phelps (1964) (dash–dots), and Hoffmann and Skarsgard (1969) (dashes).

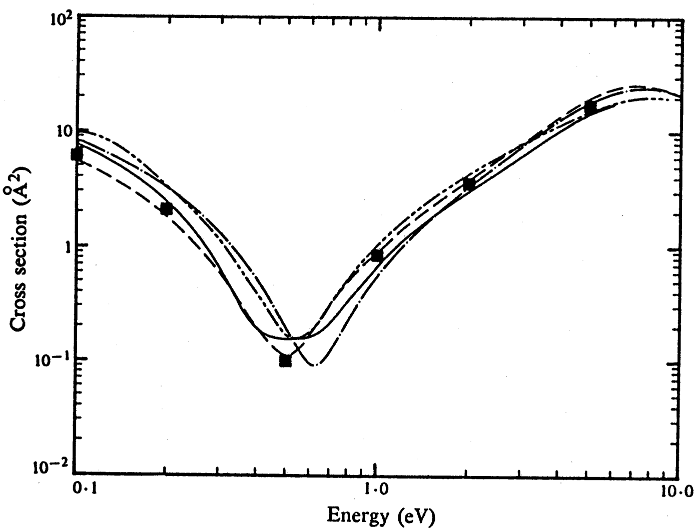

Fig. 8. Kr momentum transfer cross section of the present work (solid), Sin Fai Lam (1982) (squares), Fon *et al.* (1984) (dash–dashes), and McEachran and Stauffer (1984 and personal communication 1988) (dashes and dash–dots respectively).

cross sections derived theoretically by Sin Fai Lam (1982), Fon *et al.* (1984) and McEachran and Stauffer (1984 and personal communication 1988). The cross sections apart from that of McEachran and Stauffer (1988) have minima at 0·5 eV, but all differ considerably from the present cross section over the entire energy range. The cross section of Sin Fai Lam, derived from a relativistic calculation, and the cross section of McEachran and Stauffer (1984), a polarised orbital calculation, agree well although the latter is not a relativistic calculation. Recently, McEachran and Stauffer (1988) carried out a full relativistic calculation and obtained a cross section with a very different energy for the minimum in the cross section. The cross section of Fon *et al.* is an R-matrix calculation.

The present results were extended to zero energy to obtain a value for the scattering length A, for electron–krypton scattering using modified effective-range theory (MERT). This theory involves the expansion of the scattering phase shifts using the dipole polarisability α and four parameters A, A_1, D and F, which can be determined by fitting to cross sections. In the present study, a MERT fit to the derived cross section was carried out in the energy range from 0·08 to 0·35 eV to obtain values of the parameters with $\alpha = 16{\cdot}736 a_0^3$ (Miller and Bederson 1977), where a_0 is the Bohr radius. It was found that for energies above 0·35 eV MERT could not be used to accurately fit the present cross section, in agreement with the conclusions of Buckman and Lohmann (1987). Table 4 shows the parameters used in the present work and those obtained in a number of previous studies, including those based on measurements of the total cross section (Jost *et al.* 1983; Buckman and Lohmann 1987) and differential cross sections (Weyhreter *et al.* 1988). The parameters from the four most recent studies are in reasonable agreement and any discrepancies may be due to the use of a slightly different value of the dipole polarisability (Buckman and Lohmann used $\alpha = 16{\cdot}8 a_0^3$).

Table 4. MERT parameters obtained by fitting to cross sections

An asterisk indicates that the parameters are those derived by Buckman and Lohmann (1987) using $\alpha = 16{\cdot}8 a_0^3$. In the present work a value of $\alpha = 16{\cdot}736 a_0^3$ was used

	Energy range	A/a_0	Parameter A_1/a_0^3	D/a_0^3	F/a_0^4
Frost & Phelps (1964)*	0·01–0·5	3·32	13·38	154·14	−72·92
Jost *et al.* (1983)*	0·3–0·5	−2·43	11·15	210·21	−469·8
Buckman & Lohmann (1987)	0·175–0·5	−3·19	12·12	184·75	−300·8
Hunter (1988)	?–0·4	−3·36	12·50	178·8	−288·3
Weyhreter *et al.* (1988)	0·05–0·3	−3·536	12·31	161·5	−148·4
Present	0·08–0·35	−3·43	12·47	178·6	−291·2

6. Conclusions

Measurements of electron drift velocities have been made in two H_2–Kr mixtures at 293 K. The values have been used together with the hydrogen cross sections of England *et al.* (1988) to test the values for the krypton momentum transfer cross section of Koizumi *et al.* (1986) and Hunter (personal communication 1988). It was found that the values of Koizumi *et al.* were incompatible with the present results. The cross section values of Hunter, however, give differences from the present measurements which are less than from 1% to 3%. A cross section was derived which gave drift velocities which agreed with the present experimental values to within ±0·3%. The shape of this cross section in the vicinity of the Ramsauer–Townsend minimum is flatter than might be suggested by an examination of the available theoretical cross sections or predicted by MERT. The possibility of some error in the cross section arising from an inadequate treatment of anisotropic scattering in the application of the transport theory is being investigated. The differences between the values of this cross section and the values of Hunter *et al.* are less than ±5% except at energies close to the Ramsauer–Townsend minimum. A value of $-3{\cdot}43 a_0$ was obtained for the scattering length using a MERT fit to the present cross section. This value is in good agreement with the values of Frost and Phelps (1964), Buckman and Lohmann (1987), Hunter (1988) and Weyhreter *et al.* (1988).

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References

Buckman, S. J., and Lohmann, B. (1987). *J. Phys.* B **20**, 5807.
Crompton, R. W., and Elford, M. T. (1962). *J. Scient. Instrum.* **39**, 480.
Crompton, R. W., Gibson, D. K., and McIntosh, A. I. (1969). *Aust. J. Phys.* **22**, 715.
Elford, M. T. (1972). *In* 'Case Studies in Atomic and Collision Physics' (Eds E. W. McDaniel and M. R. C. McDowell), Vol. 2, Ch. 2 (North-Holland: Amsterdam).
Elford, M. T., and Robertson, A. G. (1973). *Aust. J. Phys.* **26**, 685.
England, J. P., Elford, M. T., and Crompton, R. W. (1988). *Aust. J. Phys.* **41**, 573.
Fon, W. C., Berrington, K. A., and Hibbert, A. (1984). *J. Phys.* B **17**, 3279.
Frost, L. S., and Phelps, A. V. (1964). *Phys. Rev.* **136**, A1538.
Haddad, G. N. (1983). *Aust. J. Phys.* **36**, 297.
Hoffmann, C. R., and Skarsgard, H. M. (1969). *Phys. Rev.* **178**, 168.
Hunter, S. R., Carter, J. G., and Christophorou, L. G. (1987). Fifth Int. Swarm Sem. Proc., Birmingham, p. 5.
Huxley, L. G. H., and Crompton, R. W. (1974). 'The Diffusion and Drift of Electrons in Gases' (Wiley–Interscience: New York).
Jost, K., Bisling, P. G. F., Eschen, F., Felsmann, M., and Walther, L. (1983). Proc. 13th Int. Conf. on the Physics of Electronic and Atomic Collisions, Berlin (Eds J. Eichler *et al.*), p. 91 (North-Holland: Amsterdam).
Koizumi, T., Shirakawa, E., and Ogawa, I. (1986). *J. Phys.* B **19**, 2331.
Lin, S. L., Robson, R. E., and Mason, L. (1979). *J. Chem. Phys.* **71**, 3483.
McEachran, R. P., and Stauffer, A. D. (1984). *J. Phys.* B **17**, 2507.
Miller, T. M., and Bederson, B. (1977). *In* 'Advances in Atomic and Molecular Physics', Vol. 13 (Eds D. R. Bates and B. Bederson), p. 1 (Academic: New York).
Milloy, H. B., Crompton, R. W., Rees, J. A., and Robertson, A. G. (1977). *Aust. J. Phys.* **30**, 61.
Ness, K. F. (1985). Ph.D. Thesis, James Cook Univ., Queensland.
O'Malley, T. F. (1963). *Phys. Rev.* **130**, 1020.
Pack, J. L., and Phelps, A. V. (1961). *Phys. Rev.* **121**, 798.
Pack, J. L., Voshall, R. E., and Phelps, A. V. (1962). *Phys. Rev.* **127**, 2084.
Robertson, A. G. (1972). *J. Phys.* B **5**, 648.
Robertson, A. G. (1977). *Aust. J. Phys.* **30**, 39.
Sin Fai Lam, L. T. (1982). *J. Phys.* B **15**, 119.
Weyhreter, M., Barzick, B., Mann, A., and Linder, F. (1988). *Z. Phys.* D **7**, 333.

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