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The Momentum Transfer Cross Section for Electrons in Mercury Vapour from 0·1 to 5 eV

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Abstract

The momentum transfer cross section for electrons in mercury vapour has been derived over the energy range 0·1–5 eV from the drift velocity data of Elford (1980). The cross section has a resonance at 0·5 eV with a maximum value of 180 Å^2 ($1\cdot8\times10^{-18}$ m^2). It is shown that previous cross sections derived either from experimental data or obtained by *ab initio* calculations are incompatible with the drift velocity data.

1. Introduction

The derivation of the momentum transfer cross section σ_m for electrons in gases from measured electron transport coefficients is a well-established procedure and has been described in detail by Huxley and Crompton (1974). In the case of mercury vapour, three previous derivations have been made, namely those by McCutchen (1958), Rockwood (1973) and Nakamura and Lucas (1978). McCutchen and Nakamura and Lucas derived the cross section from drift velocity data only using their own experimental data while Rockwood used the drift velocity data of McCutchen in conjunction with electron transport data obtained by studies of mercury discharges using probes (Klarfeld 1938; Hayes and Wojaczek 1963; Ovcharenko and Chernyshev 1970).

One of the aims of making the measurements of electron drift velocities in mercury vapour described in the preceding paper (Elford 1980, present issue pp. 231–50; hereinafter referred to as Paper I) was to obtain data of improved accuracy for use in analyses to derive σ_m. However, there is a difficulty in using these data because the measured drift velocity v_{dr} at a given value of E/N (where E is the electric field strength and N the mercury number density) was found to increase linearly with N, an effect which has been postulated to be due to the presence of mercury dimers. This makes the analysis very complex since the drift velocity at a given value of E/N and gas temperature is determined by the scattering cross sections for both the monomer and the dimer. In the energy range covered by the data of Paper I the cross sections of significance are the momentum transfer, rotational and vibrational cross sections for the dimer plus the momentum transfer and electron excitation cross sections for the monomer. Since only one cross section can be derived uniquely from the analysis of a single set of drift velocity data, the momentum transfer cross section for the monomer can only be obtained by assuming values for the other cross sections. Unfortunately, none of the cross sections listed for the dimer are known. In order to derive σ_m for the monomer it was therefore necessary to extrapolate the drift velocity data to zero mercury vapour number density and thus obtain data for mercury vapour containing monomers only. The experimental drift velocity values referred to in the rest of this paper are these extrapolated values of Paper I.

In carrying out the analysis for the monomer it is necessary to assume values for the electronic excitation cross sections. As will be shown in Section 2 below, electronic excitation is a significant process only for values of E/N greater than about 2 Td; for lower values of E/N, the drift velocity is determined only by the momentum transfer cross section, E/N and the temperature.

All derivations of cross sections from electron transport coefficient data involve a consideration of the problem of uniqueness. In the present instance this problem is particularly severe because of the well-known broad resonance (Walker 1975) which occurs at low energies in σ_m. The lack of uniqueness caused by the rapid variation of σ_m with energy in the vicinity of the resonance is discussed in Section 2. The drift velocities calculated using the present theoretical cross sections are compared in Section 3 with the experimental drift velocities of Paper I.

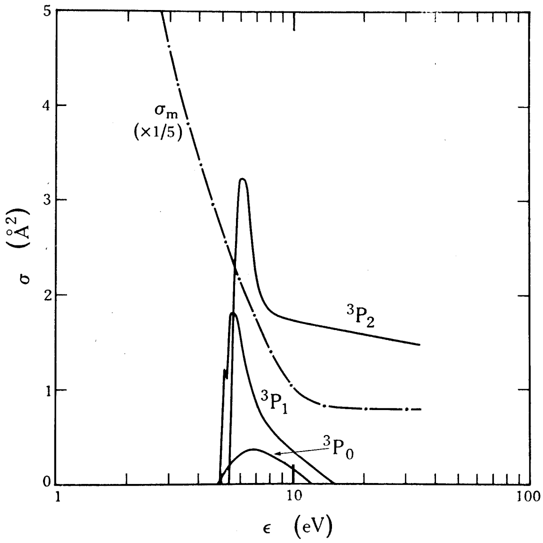

Fig. 1. Cross sections for the first three electronic transitions in mercury (from Rockwood 1973) as a function of electron energy ε. The momentum transfer cross section σ_m shown is that derived in the present work.

2. Derivation of σ_m

The solution of the Boltzmann equation and the computer code used in the present work are those of Gibson (1970). The cross sections for electronic excitation of atomic mercury which were assumed in this analysis were those used by Rockwood (1973) and tabulated by Kieffer (1973). Initially all the processes included by Rockwood were incorporated in the present analysis but it was found that only the cross sections for the first three electronic excitation processes had a significant effect on the electron drift velocity at E/N values between 2 and 3 Td. These processes are

Table 1. Momentum transfer cross section for electrons in mercury vapour

Energy ε (eV)	Cross section σ_m (Å^2)	Energy ε (eV)	Cross section σ_m (Å^2)	Energy ε (eV)	Cross section σ_m (Å^2)
0·10	12	0·45	182	1·2	101
0·15	12·5	0·50	183	1·4	81
0·20	14·5	0·55	183	1·6	65
0·22	24	0·60	181·5	1·8	50
0·24	46·5	0·65	178	2·0	40
0·26	69	0·70	172	2·5	29
0·28	89	0·80	155	3·0	23
0·30	108	0·90	140	4·0	17
0·34	142	1·00	125	5·0	13
0·40	176				

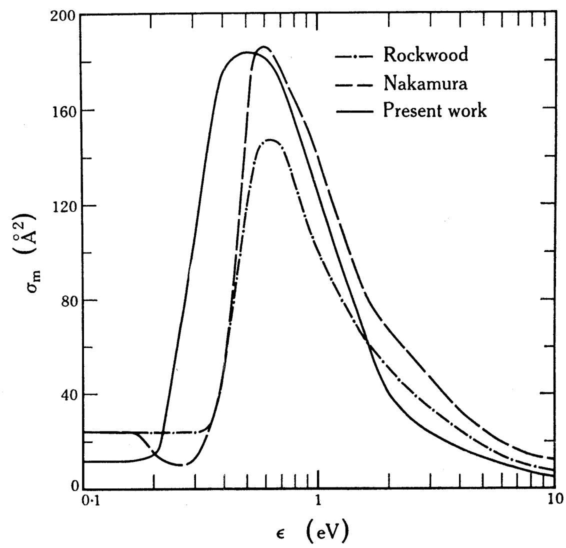

Fig. 2. Momentum transfer cross section σ_m for electrons in mercury vapour as a function of electron energy ε. The present results are compared with those of Rockwood (1973) and Nakamura and Lucas (1978).

the transitions from the $^1S_0$ ground state to the $^3P_0$, $^3P_1$ and $^3P_2$ states. The cross sections for these transitions are shown in Fig. 1. The sensitivity of the calculated drift velocities to the assumed electronic excitation cross sections was investigated by observing the change in the calculated values when these cross sections were set to zero. The calculated drift velocity was found to decrease by 0·4% at 2 Td and 20% at 3 Td. It was found to be unnecessary to include collisions of the second kind in the analysis.

The momentum transfer cross section of Rockwood (1973) was used as the first cross section in the fitting procedure and was subsequently modified until the predicted and experimental drift velocities were in good agreement over the whole E/N range (0·1–3 Td). The present derived σ_m (Table 1) is shown in Fig. 2. This cross section predicts the experimental drift velocities to within 1% for $0\cdot2 < E/N < 3$ Td and 2% at $E/N = 0\cdot1$ Td.

In order to find the sensitivity of the calculated drift velocity to changes in σ_m and hence the degree of uniqueness that can be achieved, various changes were made to the cross section over limited energy ranges and v_{dr} was re-calculated. It was found that a number of significantly different cross sections gave very similar calculated drift velocities, i.e. the derived cross section had a relatively low degree of uniqueness. To illustrate this uniqueness problem, Fig. 3 shows two cross sections (curves 1 and 2) which give calculated drift velocities at $E/N = 0 \cdot 1$ Td that agree to within 2%. These cross sections also give values of the drift velocity over the whole E/N range which lie within the estimated absolute errors of the experimental drift

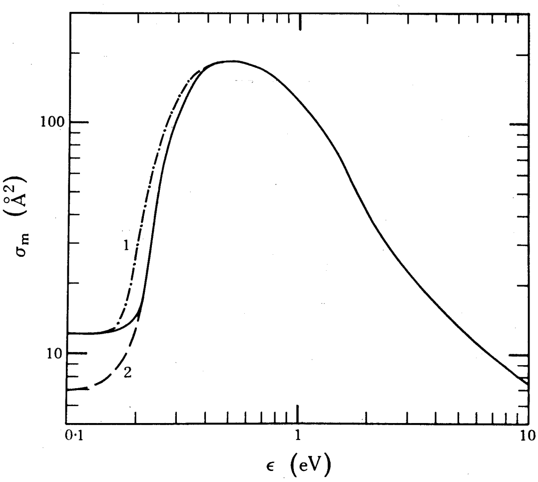

Fig. 3. Illustration of the problem of uniqueness. The full curve is the momentum transfer cross section as a function of electron energy which is the best fit to the drift velocity data of Paper I. The curves 1 and 2 give drift velocity values which agree to within 2% at $E/N = 0 \cdot 1$ Td and which fall within the error limits of the experimental data over the full E/N range.

velocity values. The full curve in Fig. 3 is the momentum transfer cross section which gives the best fit to the drift velocity data (Table 1 of Paper I). Because of this lack of uniqueness, no error limits are claimed for the present derived momentum transfer cross section.

By carrying out tests of the sensitivity of v_{dr} to changes in σ_m it has been concluded that σ_m can be derived over the energy range 0·1–5 eV using drift velocity data covering the E/N range 0·1–3 Td.

3. Discussion

The present momentum transfer cross section is compared with that of Rockwood (1973) and of Nakamura and Lucas (1978) in Fig. 2. The momentum transfer cross section of McCutchen (1958) has not been included as it was not based on a numerical solution of Boltzmann's equation. McCutchen used an approximate formula for the drift velocity and assumed that σ_m was independent of electron energy over the distribution of energies of the electrons at a given E/N value. In the case of mercury this assumption is clearly inadequate and leads to significant errors, as McCutchen himself pointed out. A discussion of early attempts to derive σ_m from electron swarm data using analyses similar to that used by McCutchen is given by Huxley and Crompton (1974).

The differences between the cross sections in Fig. 2 reflect the differences between the drift velocity data on which they are based, since the same solution of the Boltzmann equation was used in each case. The largest difference between the three sets of drift velocity data occurs at low E/N values (approximately 0·1–1·0 Td) and accounts for the large difference between the present derived σ_m curve and those of Rockwood (1973) and Nakamura and Lucas (1978). It should be noted that the cross section of Nakamura and Lucas has a minimum at 0·25 eV. It was not necessary to include a similar minimum in the present cross section to obtain an adequate fit to the drift velocity data.

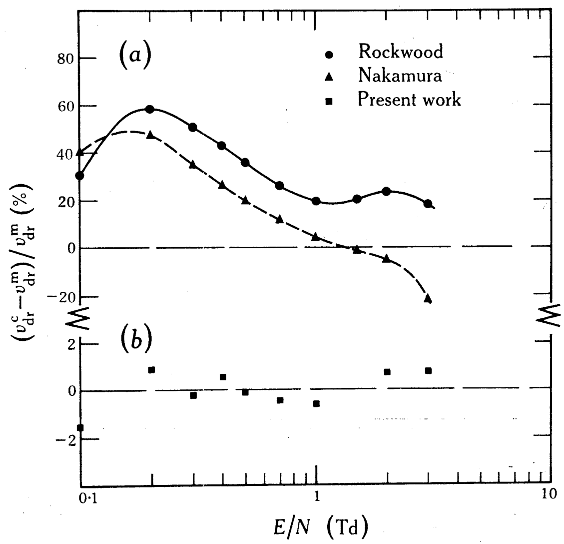

Fig. 4. Comparison of differences between the experimental drift velocity values (v^m_{dr}) of Paper I and those calculated (v^c_{dr}) using momentum transfer cross sections derived from electron swarm data, the differences being plotted as a function of E/N. The curves in (*a*) were derived from the cross sections of Rockwood (1973) and Nakamura and Lucas (1978), while the points in (*b*) show the fit achieved to the drift velocity data when the present σ_m curve is used.

It is instructive to determine the compatability of various derived cross sections with experimental data by calculating drift velocities using these cross sections and comparing them with experimental values. Fig. 4 shows the results of such a comparison using the cross sections of Rockwood (1973) and of Nakamura and Lucas (1978) and the experimental drift velocities of Paper I. As can be seen from Fig. 4*a*, the cross section of Rockwood results in drift velocities up to 60% higher than the experimental values while that of Nakamura and Lucas gives values up to 50% higher. In both cases this difference is much larger than the estimated absolute error of the drift velocity data. The points in Fig. 4*b* show the comparison when the present cross section is used and indicate no more than the goodness of fit achieved.

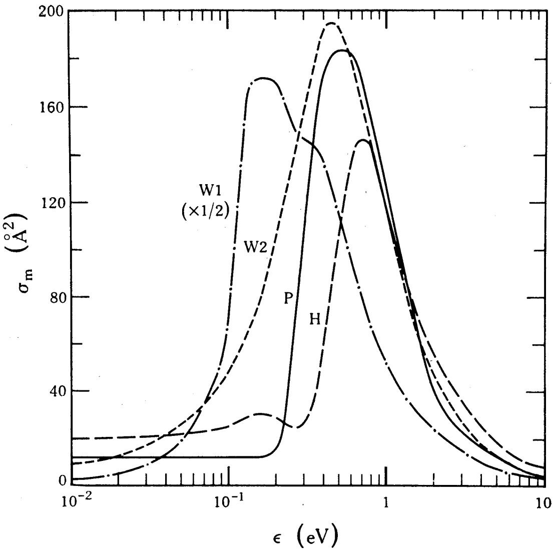

Fig. 5. Comparison between calculated momentum transfer cross sections for electrons in mercury as a function of electron energy: W1, W2, *ab initio* calculations by Walker (1975, personal communication); H, phase shift analysis by Hutt (1975); P, present result derived from the drift velocity data of Paper I.

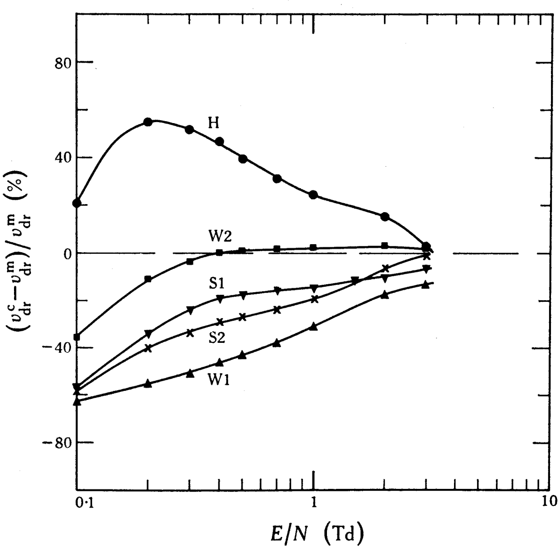

Fig. 6. Comparison of differences between the experimental drift velocity values (v_{dr}^m) of Paper I and those calculated (v_{dr}^c) using momentum transfer cross sections obtained in *ab initio* calculations: W1, W2, Walker (1975, personal communication); H, Hutt (1975); S1, S2, Sin Fai Lam (1980) for his Pauli approximation and second-order Dirac potential models respectively.

Several *ab initio* calculations for electron scattering from mercury have been made by Walker (1969, 1970, 1975). In his 1969 calculation he included relativistic and exchange effects but not polarization. In 1970 he extended the calculation by including a polarization contribution to the interaction potential and used the method of polarized orbitals. In the third calculation in 1975, the same physical approximations were used as in the 1970 calculation but different methods of calculation

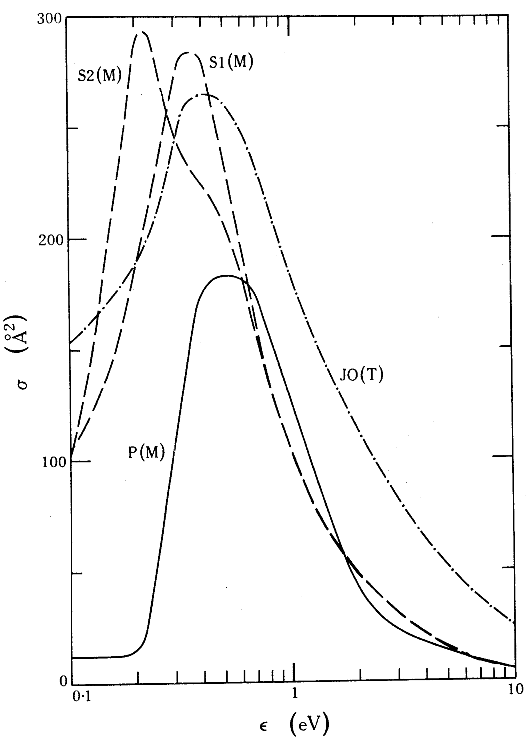

Fig. 7. Momentum transfer and total scattering cross sections for electrons in mercury as a function of electron energy. The momentum transfer cross sections shown are: S1(M), S2(M), Sin Fai Lam (1979) from his Pauli approximation and second-order Dirac potential models respectively; P(M), present result derived from the drift velocity data of Paper I. The total scattering cross section denoted as JO(T) is from Jost and Ohnemus (1979).

were employed to obtain the p-wave phase shifts. The momentum transfer cross section derived from Walker's (1975) phase shifts is shown as W1 in Fig. 5, and it can be seen that there is poor agreement with the present cross section except at higher energies. Drift velocities obtained by using the W1 cross section are compared with the data of Paper I in Fig. 6, and it can be seen that there is a serious disagreement with the experimental data, particularly at low values of E/N. Walker (personal communication) has recently attempted to reduce the difference between his theoretical cross section and that derived in the present work by using an interaction potential which includes an adjustable parameter to vary the strength of the polarization contribution to the interaction potential. The method of calculation of the phase shifts was the same as that used in 1975. The best fit to the present cross section that could be obtained by varying this parameter is shown as W2 in Fig. 5. A comparison between the drift velocities calculated from the W2 cross section and the data of Paper I is shown in Fig. 6. Again the differences at low E/N values are much larger than the estimated experimental error.

Phase shift analyses for electron scattering by mercury have been carried out by Hutt and Bransden (1974) and Hutt (1975) using data including the momentum transfer cross section derived from electron transport data. The momentum transfer cross section obtained from Hutt's (1975) set of phase shifts is shown in Fig. 5 (curve H). The drift velocities calculated using Hutt's momentum transfer cross section are compared with the experimental values of Paper I in Fig. 6.

Recently Sin Fai Lam (1980, present issue pp. 261–81) has carried out a further *ab initio* calculation of the phase shifts for electron scattering by mercury atoms by applying a perturbation method to the nonrelativistic Schrödinger equation. Two different models have been used which he designates the Pauli approximation and the second-order Dirac potential. The momentum transfer cross sections obtained by Sin Fai Lam for these two models are shown in Fig. 7 as S1(M) and S2(M) respectively. It can be seen that there is good agreement with the present σ_m for energies greater than about 0·6 eV but very serious disagreement at lower energies. A comparison of the drift velocities calculated using the cross sections S1 and S2 with the drift velocity values of Paper I is given in Fig. 6. The disagreement over virtually the whole E/N range is greater than the estimated absolute experimental error, as expected from the large differences between the cross sections S1 and S2 and the present cross section at lower energies.

Only drift velocity data were used in deriving the present momentum transfer cross section. Computer tests have shown, however, that $D_\perp/\mu$ (where $D_\perp$ is the transverse diffusion coefficient and μ the electron mobility defined as v_{dr}/E) is much more sensitive to changes in the momentum transfer cross section for electrons in mercury vapour than the drift velocity, and its use would reduce significantly the uncertainty in the derived cross section due to the lack of uniqueness. Unfortunately no accurate $D_\perp/\mu$ values are available since those reported in the literature are derived from measurements on mercury discharges and include effects due to electron–electron interactions.

There have been several measurements of the total scattering cross section for low energy electrons in mercury vapour, the most recent being that of Jost and Ohnemus (1979); see Fig. 7. Unfortunately, in the absence of accurate differential scattering cross section data in this low energy region it is not possible to make detailed comparisons with the present momentum transfer cross section. If the angular scattering calculations of Sin Fai Lam (1980) are used to convert the total scattering cross section to that for momentum transfer it is found that there is fair agreement with the present σ_m curve down to about 0·6 eV, but below this electron energy there is serious disagreement. The Sin Fai Lam calculations indicate that the momentum transfer cross section should be greater than the total scattering cross section for energies below 0·3 eV, whereas it is clear from Fig. 7 that the opposite is the case. To illustrate the discrepancy: at 0·2 eV the present σ_m value is 15 Å^2 while the total scattering cross section of Jost and Ohnemus is 195 Å^2.

4. Conclusions

The momentum transfer cross section for electrons in mercury has been derived over the energy range 0·1–5 eV and has been compared with other momentum transfer cross sections derived from experimental data or obtained by *ab initio* calculations. Although there is fair agreement at energies greater than about 0·6 eV there is serious disagreement at lower energies. The disagreement with previously derived momentum transfer cross sections in this lower energy region is due to the large difference between the drift velocity values at low E/N used in the present derivation and those employed in previous analyses.

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