

## Cross Sections for Electron Scattering in Nitrogen

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### *Abstract*

New measurements of electron drift velocities in mixtures of nitrogen and argon have been analysed to determine the normalization factor for the vibrational excitation cross sections for nitrogen. The validity of applying a two-term solution of the Boltzmann equation in these mixtures is demonstrated. The derived cross sections are shown to be consistent with earlier transport data in pure nitrogen.

### 1. Introduction

Accurate values of low energy cross sections can often be obtained only by combining the results from both swarm and beam experiments. In particular, while low energy beam experiments can accurately provide the shape of a cross section, they cannot provide accurate absolute values. Electron swarm experiments can be used to solve this deficiency. In the case of nitrogen, for example, the single collision experiments of Schulz (1964) reliably established the shape of the vibrational cross sections, as confirmed both by later experiments (Ehrhardt and Willman 1967; Wong 1976) and by theoretical calculations (Birtwistle and Herzenberg 1971; Schneider *et al.* 1979). However, the absolute values of the cross sections are less certain.

This paper presents an analysis of recent measurements of electron drift velocities in argon-nitrogen mixtures (Haddad 1983) which shows that Schulz's (1964) vibrational cross sections require renormalization to be consistent with these data. The analysis confirms an earlier conclusion (Engelhardt *et al.* 1964) based on an analysis of transport data in pure nitrogen.

As pointed out by Engelhardt and Phelps (1964), the analysis of swarm measurements in a binary mixture of this type has some advantages over the more conventional method based on the analysis of drift and diffusion data for the pure molecular gas. In mixtures of argon with relatively small concentrations of nitrogen (say less than 5%), the electron motion is dominated by elastic scattering from the argon atoms and inelastic scattering from the nitrogen molecules. Provided the momentum transfer cross section for argon is known accurately, measurements of the electron drift velocity in such mixtures can be used to determine the inelastic cross sections for nitrogen. Once these inelastic cross sections are established the momentum transfer cross section for nitrogen can be derived from an analysis of the transport data in pure nitrogen.

The technique has two main advantages. Firstly, the calculated values of the drift velocity in the mixture are more sensitive to changes in the vibrational cross sections than the calculated transport data in pure nitrogen. Our calculations show that the drift velocity in a 1% mixture of nitrogen in argon is about three times more sensitive to changes in the normalization factor for the vibrational cross sections than similar data in pure nitrogen. Secondly, measurements of the drift velocity in argon–nitrogen mixtures can be analysed with sufficient accuracy using a solution of the Boltzmann equation which relies on a two-term spherical harmonic representation of the velocity distribution function. In contrast, cross sections derived from measurements of both  $v_{dr}$  (the drift velocity) and  $D_{\perp}/\mu$  (the ratio of the lateral diffusion coefficient to mobility) in pure nitrogen can only be analysed with sufficient accuracy by avoiding this approximation (Pitchford and Phelps 1982). Although the error involved in calculating the drift velocity in pure nitrogen using a two-term solution of the Boltzmann equation is quite small (of the order of 2% or less, see Pitchford and Phelps 1982), the error involved in calculating  $D_{\perp}/\mu$  using such a solution ranges from about 2% at 10 Td (1 Td  $\equiv 10^{-17}$  V cm<sup>2</sup>) to about 10% at 70 Td. At 70 Td an error of 10% in  $D_{\perp}/\mu$  translates into an error in the cross sections of the same order of magnitude. This implies that if measured values of  $D_{\perp}/\mu$  are interpreted using a two-term solution of the Boltzmann equation, the derived cross-section set would be in error by about 10%. Measurements of transport coefficients are typically accurate to 1% or 2% (Elford 1971), so that it is important to avoid errors in the solution of the Boltzmann equation which are of this order or larger.

In Section 2 we describe the transport data used in the analysis. Section 3 reviews the cross sections used as the starting point for the analysis and in Section 4 we discuss the calculations that were made to determine the cross-section set which provides the best fit to the experimental transport data. In Section 5 we summarize and discuss our results.

## 2. Transport Data

The new analysis of electron swarm data for nitrogen undertaken in this paper uses recent measurements of drift velocity in argon–nitrogen mixtures (Haddad 1983). However, the set of derived cross sections for nitrogen must be consistent not only with these new data but also with existing swarm data in pure nitrogen. A previous analysis of swarm data in pure nitrogen by Engelhardt *et al.* (1964) was based on a comprehensive set of measurements available at that time. We have elected to use more recent values of  $v_{dr}$  and  $D_{\perp}/\mu$  for pure nitrogen measured in our laboratory (as summarized by Huxley and Crompton 1974), combined with the measurements of  $v_{dr}$  in argon–nitrogen mixtures referred to above. These measurements all have the advantage that error limits have been established (see Elford 1971 for a discussion of the accuracy of this type of measurement). Our comparisons between measured and calculated values of  $v_{dr}$  in pure nitrogen are restricted to an upper limit of 60 Td by the availability of data of the required accuracy, while for  $D_{\perp}/\mu$  the onset of the inadequacy of the two-term solution sets an upper limit of about 10 Td (see Section 4).

In particular, for pure nitrogen we have used data for  $v_{dr}$  at 293 K from 0.02 to 60 Td (Lowke 1963), data for  $v_{dr}$  and  $D_{\perp}/\mu$  at 77 K from 0.06 to 6 Td (Lowke 1963; Crompton and Elford, unpublished results 1966) and data for  $D_{\perp}/\mu$  at 293 K from 0.02 to 10 Td (Crompton and Elford, unpublished results 1965). In addition we

have used drift velocity data for mixtures containing 0.1%, 1.0% and 5.0% of nitrogen in argon measured at 293 K (Haddad 1983). These measurements were made with  $E/N$  ranging from 0.1 to 5 Td, 0.06 to 10 Td and 0.1 to 10 Td respectively.

### 3. Cross-section Data

To calculate transport parameters over the ranges of  $E/N$  for which experimental data are available, we need the scattering cross sections for all energetically possible processes in both argon and nitrogen.

For argon Milloy *et al.* (1977) determined the momentum transfer cross section  $\sigma_m$  from an analysis of measurements of  $D_{\perp}/\mu$  as a function of  $E/N$  at 294 K (Milloy and Crompton 1977) and  $v_{dr}$  as a function of  $E/N$  at 90 and 293 K (Robertson 1977). The value of  $\sigma_m$  was determined over the energy range 0–4 eV, taking account of the additional constraint imposed by the fact that the cross section should conform to a modified effective range expansion (O'Malley 1963) in the low energy region ( $<0.32$  eV). This cross section was altered slightly by Haddad and O'Malley (1982) who extended the energy range of the modified effective range expansion. This improved cross section is used in the present work. At energies above 4 eV we have used the data of A. V. Phelps (personal communication). We have also used data for the argon electronic excitation cross sections from Schaper and Scheibner (1969) and ionization cross sections from Smith (1930).

For nitrogen the initial cross sections were based on a set recommended by Phelps (personal communication) and include cross sections for rotation, vibration, electronic excitation and momentum transfer.

In nitrogen many rotational transitions with very closely spaced thresholds (of the order of meV) must be considered. Their separate effects cannot be resolved. Consequently, only the energy dependence and normalization of the family of rotational cross sections can be verified from an analysis of transport data, and not the validity of a single cross section.

As many as 30 rotational cross sections and their associated super-elastic cross sections have been used in the present analysis. It has therefore been convenient to use algebraic expressions for the various cross sections for direct rotational excitation and then adjust one or two parameters to obtain the best fit to the experimental data. The studies of Gerjuoy and Stein (1955) and Dalgarno and Moffett (1963) both provide convenient algebraic expressions, but previous work (Engelhardt *et al.* 1964) has shown that the fit to the experimental data is significantly poorer with the Dalgarno–Moffett formula: we have therefore used the Gerjuoy–Stein formula. The effective quadrupole moment, the only adjustable parameter in this formula, was set initially to  $1.04 ea_0^2$  (Engelhardt *et al.* 1964).

In addition to the direct rotational excitation processes, the effect of rotational excitation via the  $^2\Pi_g$  resonance state must also be taken into account. We have used the data of Phelps (personal communication) for this purpose.

The shapes of the vibrational cross sections were initially taken from Schulz (1964), whose single collision experiments\* were limited to energies above about 1.4 eV. Thus it is necessary to use the results of the analysis of swarm data for the low energy

\* Single collision experiments become increasingly difficult towards lower energies and the cross sections derived from analyses of swarm data are expected to be more reliable in this region (say less than 2 eV).

region of the cross sections. The initial choice was the results of the analysis by Engelhardt *et al.* (1964).

The set of cross sections in nitrogen was completed using 11 electronic excitation cross sections together with appropriate scaling factors, a total ionization cross section, and the momentum transfer cross section, from the work of Phelps (personal communication). Of these remaining cross sections only the momentum transfer cross section was subsequently modified.

#### 4. Numerical Solutions of the Boltzmann Equation

Solutions of Boltzmann's equation provide a method of calculating electron transport coefficients from a given set of cross sections. In solving this equation it is usual to invoke the two-term approximation in order to save computational expense. However, the two-term approximation is known to be inadequate when the ratio of inelastic to elastic cross sections is large (Reid 1979), and we know from previous work (Pitchford and Phelps 1982) that the two-term approximation breaks down in pure nitrogen at moderately high values of  $E/N$ .

One effect of the presence of the monatomic gas in the mixture is to scale down the inelastic cross sections so that they become a less significant fraction of the 'total' elastic cross sections (i.e. in this case the weighted sum of the elastic cross sections for argon and nitrogen). Thus, the two-term approximation becomes more valid. We have therefore been able to employ the two-term approximation in much of the analysis of the data, although we used a multi-term code to verify the accuracy of the transport parameters calculated with the two-term code.

A multi-term solution of the Boltzmann equation requires not only cross sections for all the relevant processes but also angular distributions for each of them. The angular distributions for elastic scattering are the most important because there are many more elastic than inelastic collisions. Since argon is the largest component in the mixtures (a minimum of 95%), we must represent the angular distributions for electrons scattered by argon as accurately as possible. In the low energy range (0.01–1.8 eV) we used the calculations of D. Walker (personal communication) which are consistent with the experimental measurements of D. Andrick (personal communication) where the two studies overlap. The experimental data were used in the energy range 2.0–20.0 eV. Outside the range of these data (0.01–20.0 eV) the angular factors were taken to be those at the appropriate upper or lower limit.

For nitrogen we adopted isotropic angular distributions for the scattered electrons: reliable data for low energy electron scattering from nitrogen are not plentiful and, in any case, the angular factors for nitrogen do not strongly influence the results.

Values of  $v_{dr}$  and  $D_{\perp}/\mu$  in the mixtures were calculated using a multi-term solution of the Boltzmann equation as developed by Lin *et al.* (1979). In Fig. 1 the results of these calculations for a 5% nitrogen-in-argon mixture are compared with the corresponding two-term results. It can be seen that the differences between the two-term and multi-term results for  $D_{\perp}/\mu$  are as large as 13%, whereas the corresponding differences for  $v_{dr}$  are always less than 2%. This confirms the fact that we can analyse our measurements of the *drift velocity* in the mixtures using a two-term solution of the Boltzmann equation; the results and discussion which follow are based on an analysis using the two-term code (Gibson 1970). However, any cross-section analysis based on experimental data for  $D_{\perp}/\mu$  in the mixtures, as well as for  $v_{dr}$ , would need to be carried out using a multi-term solution.

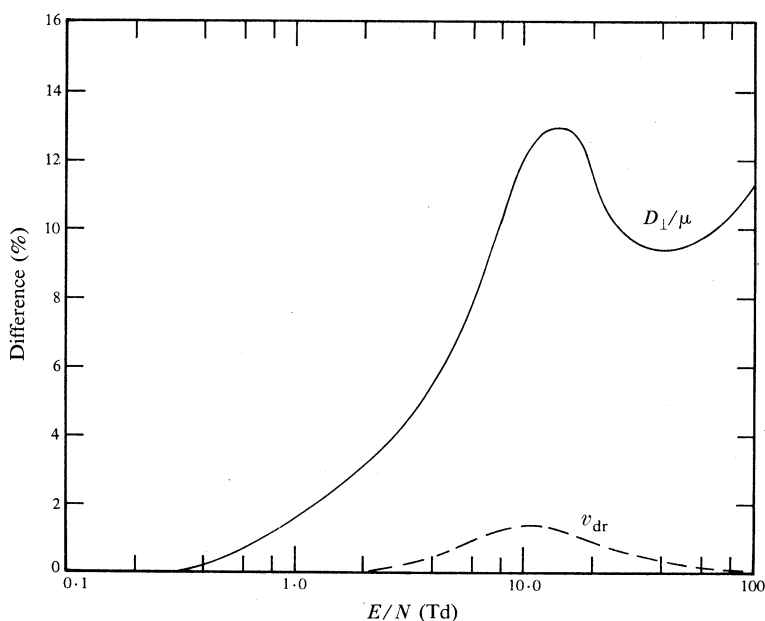


Fig. 1. Differences in the transport parameters, calculated using two-term and multi-term solutions of the Boltzmann equation, for a mixture of 5% nitrogen in argon.

## 5. Results and Discussion

The present analysis aims to investigate the consistency of a set of vibrational cross sections in nitrogen with the complete set of transport data described in Section 2. The best fit to the *drift velocity* measurements in the mixtures required a normalizing factor of 1.4 applied to all the vibrational cross sections with the exception of the low energy ( $< 1.6$  eV) region of the  $v = 0-1$  cross section. With this value of the normalizing factor the maximum difference between predicted and measured values was found to be of the order of 5%, and occurred in the low  $E/N$  regions of the 1% and 5% nitrogen-in-argon mixtures. This disagreement could not be reduced by changing either the normalizing factor or the rotational cross sections. However, the disparity could be reduced by altering the  $v = 0-1$  cross section in the region between 0.3 and 1.2 eV. It is important to note that in the circumstances referred to above the  $v = 0-1$  cross section (at low energies) is the only process influencing the calculated drift velocities to any significant extent.

The fit to the drift velocity data has allowed us to refine the vibrational cross sections in nitrogen, with respect to (a) the low energy region of the  $v = 0-1$  cross sections and (b) the normalizing factor for the remainder of the cross sections. We now use these adjusted cross sections to predict the values of the entire set of transport coefficients in pure nitrogen. The most significant discrepancies (of the order of 5%) occur in the following regions:

- (1) for the 77 K data around  $E/N = 0.2$  Td;
- (2) for the 77 K data around  $E/N = 2$  Td;
- (3) for the 293 K data in the range  $1 \leq E/N \leq 10$  Td.

At 77 K and  $E/N \approx 0.2$  Td, the average energy is less than 0.1 eV, and only the rotational excitation cross sections significantly affect the calculations. The magnitude of these cross sections is determined by a single parameter (the effective quadrupole moment) which initially was set at  $1.04 ea_0^2$ . Altering this parameter to  $1.06 ea_0^2$  improves the agreement between calculated and experimental transport coefficients in the range 0.06–0.6 Td, for temperatures of both 77 and 293 K.

The largest remaining discrepancies now occur where the average energy is of the order of 0.5–2.0 eV. The calculated transport coefficients in this region are sensitive to both the low energy  $v = 0-1$  cross section and the momentum transfer cross section. However, the *mixture* measurements are *very sensitive* to the low energy  $v = 0-1$  cross section and *very insensitive* to the momentum transfer cross section. Since we believe we have accurately determined the low energy  $v = 0-1$  cross section from the mixture data, we have made small modifications to the nitrogen momentum transfer cross section in the region 0.3–1.9 eV in order to obtain a better match to the measured transport data in pure nitrogen. This improves the fit to both the 77 K data (from about 0.6–6.0 Td) and the 293 K data (from about 0.8–20 Td).

With these three minor alterations (to the low energy  $v = 0-1$  cross section, the effective quadrupole moment, and the momentum transfer cross section), we obtain a maximum discrepancy between calculated and measured values of about 2%, with one exception which will be discussed shortly.

With the adjusted cross sections a change in the normalization factor for the vibrational cross sections to 1.3 or 1.5 produces maximum discrepancies of about 4%. The value of 1.4 is in accord with the value of 1.5 derived by Levron and Phelps (1979) using a different set of transport data, but is significantly different from the factor of 1.9 which Tachibana and Phelps (1979) obtained from their fit to data for the excitation and ionization rate coefficients.

The exception to this remarkably good fit to a wide range of transport data is the region above  $E/N = 2$  Td in the 0.1% nitrogen-in-argon mixture. Here the difference between calculated and measured values increases from 2% at 2 Td to 6% at 5 Td. In this region, the transport coefficients are sensitive to the excitation cross sections in both nitrogen and argon. Furthermore the momentum transfer cross section for argon is not as accurately known at these high (>4 eV) energies as at the lower energies. Because a number of cross sections simultaneously affect the results in this region, we do not uniquely identify any one of them as the source of the discrepancy. Our calculations do show, however, that a small change to the argon momentum transfer cross section in the energy range from about 5 to 15 eV will reduce the disagreement between theoretical and experimental values to less than 2%. This change involves a maximum modification of the cross section of about 9% at around 12 eV with smaller modifications at both higher and lower energies. Changes of this order of magnitude in either the argon or nitrogen electronic excitation cross sections are not large enough to achieve the same good fit to the experimental data.

We have made calculations for the transport data in pure argon from 1–10 Td using this modified momentum transfer cross section. Unfortunately, there are large variations between the measured transport data from different laboratories (Dutton 1975). The only conclusion that we can make from this comparison is that our

modified argon momentum transfer cross section leads to calculated transport parameters which are not inconsistent with these data.

During the course of this analysis we examined another set of vibrational cross sections consisting of the  $v = 0-1$  and  $v = 0-2$  cross sections of Wong (1976), together with the other vibrational cross sections of Schulz (1964). Wong measured absolute differential cross sections with a scattering angle of  $90^\circ$ . Since vibrational excitation is essentially a pure  $^2\Pi_g$  resonance process, the total cross sections can be obtained by multiplying the differential cross sections by  $(14/15)4\pi$  (Dubé and Herzenberg 1979). Wong's  $v = 0-1$  cross section was blended to the low energy  $v = 0-1$  cross section (see Section 3) at about 1.3 eV.

Using this set of vibrational cross sections a satisfactory fit to all the transport data is obtained without any renormalization (i.e. with a normalizing factor of 1.0), although it is necessary to make minor adjustments to the initial cross-section set as follows:

- (1) An effective quadrupole moment of  $1.06 ea_0^2$ —the same as in the previous case.
- (2) A modified low energy  $v = 0-1$  cross section—slightly different to both the Engelhardt *et al.* (1964) analysis and the results from the previous set.
- (3) Small modifications to the nitrogen momentum transfer cross section between 0.3 and 1.9 eV—similar to our other case.

In addition, we again obtain a better fit to the high  $E/N$  data in the 0.1% mixture when we use the modified argon momentum transfer cross section described previously.

These results using this alternative set of cross sections are a direct consequence of the higher values for the  $v = 0-1$  and  $v = 0-2$  cross sections given by Wong (1976) and may indicate that Schulz's (1964) cross sections are too low. However, in order to verify this, it will be necessary to obtain a *complete* set of self-consistent vibrational cross sections for comparison with the swarm data.

## 6. Conclusions

A normalization factor of 1.4 for Schulz's (1964) nitrogen vibrational cross sections provides a good fit to a large body of experimental swarm data in nitrogen and argon-nitrogen mixtures. If the shape and relative magnitudes of these cross sections are regarded as known, the quality of the fit to the data suggests that this factor is unlikely to be in error by more than 10%. It is apparent, however, that a set of reliable single collision measurements of the *relative* vibrational cross sections is required; in order for the swarm analysis to provide definitive results for the absolute values.

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