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Importance of attachment cross-sections of F^- formation for the effective ionisation coefficients in SF_6

Makoto Hayashi and Tetsuo Nimura
Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan

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Abstract. The importance of the attachment cross-section for F^- formation for the effective ionisation coefficients in SF_6 is discussed. The values of the dissociative attachment cross-section q_a for F^- formation for electron energies from 2 to 15 eV are very small compared with the values of q_a for SF_6^- formation at low electron energies. However, the effect of the values of q_a for F^- formation on the effective ionisation coefficients is very great. Calculations were carried out by a two-term Boltzmann equation analysis. It is pointed out that the measured grand total electron–SF_6 cross-sections were inconsistent with the sum of elastic and inelastic cross-sections used by many workers.

1. Introduction

Sulphur hexafluoride, SF_6, is a widely used insulating gas. Many papers on the electron–SF_6 cross-section have been published, and recent reviews have been given by Christophorou (1981), Teich (1981), Christophorou *et al* (1982) and Gallagher *et al* (1983).

A Boltzmann equation analysis and Monte Carlo simulation of electron swarm parameters in a gas have already proved to be a suitable method for calculation of swarm parameters. Comprehensive studies by these methods were published for SF_6 by Kline *et al* (1979), Yoshizawa *et al* (1979), Itoh *et al* (1980), Govinda Raju and Hackam (1981), Yousfi *et al* (1982), Novak and Frechette (1982) and very recently Dincer and Govinda Raju (1983) using a set of cross-section data.

We also calculated electron swarm parameters in SF_6 by a Boltzmann equation analysis and Monte Carlo simulation method. In this paper, discussion is focused mainly on the importance of the very small attachment cross-sections q_a of electron energies from 2 to 15 eV (mainly F^- formation) on the effective ionisation coefficient $(\alpha - \eta)$, the ionisation coefficient minus the attachment coefficient.

In SF_6, the values of q_a are very large, 520×10^{-16} cm^2 at 0 eV (Chutjian 1981). The values of q_a for F^- formation have been measured by Lehmann (1970) and Kline *et al* (1979) and the local maximum value of q_a is 0.060×10^{-16} cm^2 at 5.2 eV, about 10^4 times smaller than the values of q_a at 0 eV. The attention of workers is given to the large values of q_a below electron energies of 0.1 eV, and sometimes they neglect the values of q_a between 2 and 15 eV.

There are many uncertainties about the values of cross-sections for SF_6. The authors point out these uncertainties for the calculation of accurate electron energy distribution functions.

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2. Collision cross-sections

The set of cross-sections q for SF_6 used in the calculations are shown in figure 1. Although detailed discussions about q are not given here, some comments are made.

The values of the elastic momentum transfer cross-section q_m measured by Srivastava *et al* (1976) from 5 to 75 eV have to be corrected by recent exact differential cross-section (DCS) values for He measured by Register *et al* (1980, see Hayashi 1981), and corrected values were used in figure 1. The same corrected values were published independently by Trajmar *et al* (1983). By this correction, the value of q_m at 60 eV is changed from 15×10^{-16} cm^2 to 5.5×10^{-16} cm^2. However, Srivastava *et al*'s DCS values were measured below 135° of scattering angle θ. The contributions of DCS values from 135° to 180° for q_m are very great, about 50–60%, for 40 to 75 eV. We hope to measure the elastic DCS values from 10° or 20° to at least 160° or 170° of θ for electron energies from 1 to 100 eV.

In SF_6, the values of electron drift velocity W at low E/N, below 10 Td, cannot be measured experimentally, because the electron swarm does not reach a steady-state condition with regard to electron attachment. Thus the values of q_m at low electron energies, below 1 eV, cannot be determined by the electron swarm method (Frost and Phelps 1962).

There are neither experimental nor theoretical data for electronic excitation cross-sections q_e, except for one datum at 20 eV for five electronic excitation levels (Trajmar and Chutjian 1977). Thus, many workers assume the values of a single total q_e. A single total q_e approximation is adequate for He and Ne. However, it is not generally adequate to calculate the values of α for molecular gases. Exact values of electron swarm parameters cannot be calculated until the values of q_e for the electronic excitation levels for wide energy ranges are measured precisely.

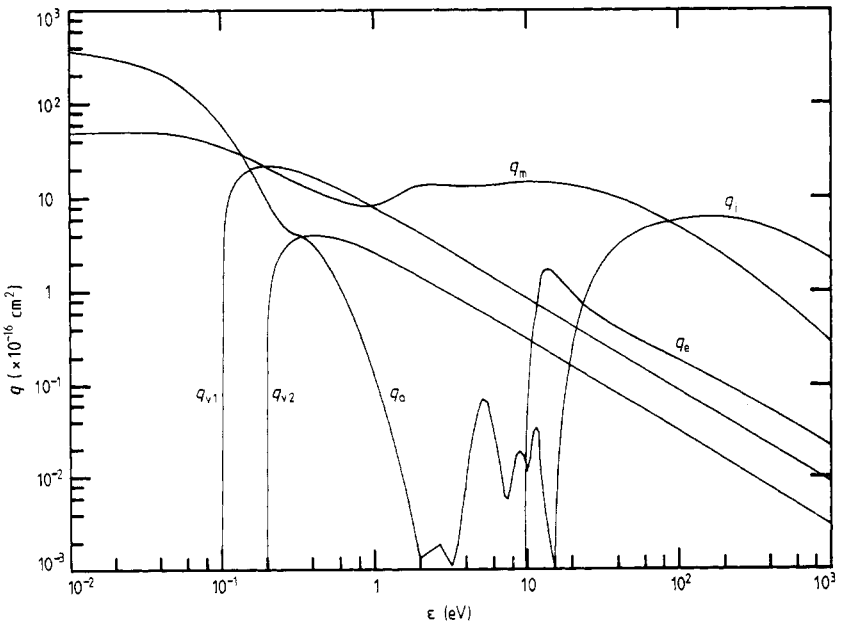

Figure 1. Cross-sections for e–SF_6 collisions used in the calculations.

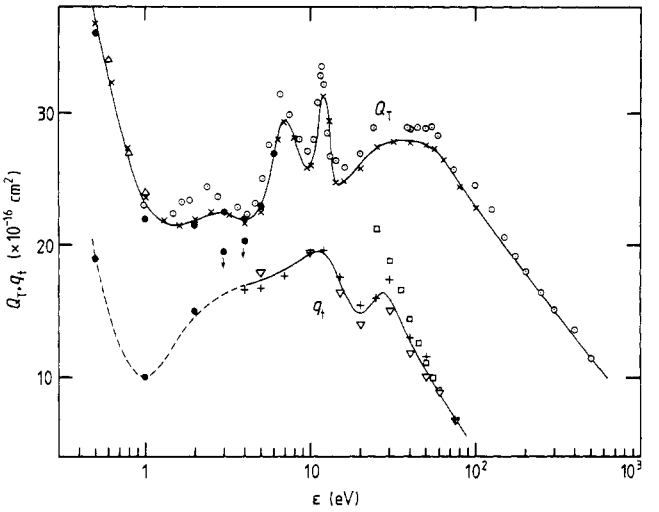

Figure 2. Grand total collision cross-section Q_T and total elastic collision cross-section q_t for e–SF_6. For Q_T: × Kennerly and Bonham (1969), △ Ferch *et al* (1982), ⊙ Kauppila *et al* (1983). For Q_T and q_t: ● Rohr (1979). For q_t: + corrected values calculated by the authors for the measured values of Srivastava *et al* (1976), □ Benedict and Gyemant (1978) from theory, ▽ Trajmar *et al* (1983). At low electron energies of q_t, the experimental data are few and scattered, and the values of q_t are shown by the dashed curve.

There is no information about values of the dissociation cross-section q_d. The values of q_d should be included in the cross-section set to calculate the swarm parameters. The values of ionisation cross-section q_i shown in figure 1 are total ionisation cross-sections. For the exact calculations of swarm parameters, the values of partial ionisation cross-section values having different threshold voltage are needed.

Kennerly and Bonham (1979), Rohr (1979), Ferch *et al* (1982) and very recently Kauppila *et al* (1983) measured the values of total collision cross-section Q_T including the values of inelastic cross-sections. These Q_T values are shown in figure 2 along with the values of total elastic cross-section q_t. The values of Q_T almost coincide, and agree surprisingly well in shape with theoretical q_t values given by Dehmer *et al* (1978). However, the values of

$$Q_T = q_t + q_v + q_e + q_i + q_a$$

calculated using the values of q given in figures 1 and 2, are much smaller than the experimental values of Q_T given in figure 2, as shown in table 1. The same inconsistency appears for the values of cross-sections used by other workers.

Table 1. Comparison of experimental and summarised values of total collision cross-section Q_T ($\times 10^{-16}$ cm^2).

ε (eV)	Q_T (Kennerly)	Q_T (Σq)
1	23.6	21
10	26.0	21
30	27.8	20
100	22.8	12

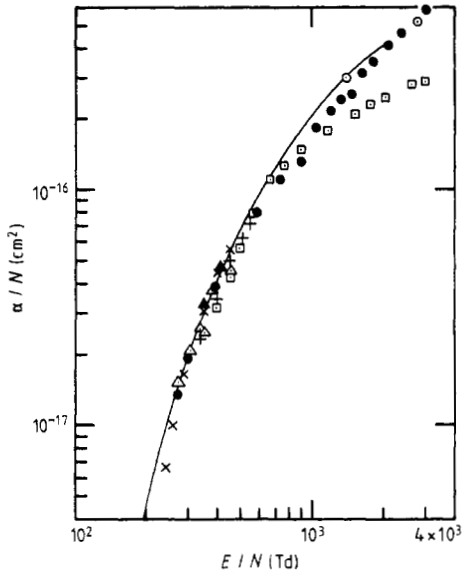

Figure 3. Ionisation coefficient α. —— Present calculated values by Boltzman equation. ⊙ Present calculated values by MCS. × Geballe and Harrison (1955), △ Bhalla and Craggs (1962), ▲ Boyd and Crichton (1971), ⊡ Maller and Naidu (1976), + Kline *et al* (1979), ● de Urquijo-Carmona (1980).

The values of attachment cross-section q_a used in these calculations are as follows, SF_6^- formation measured by Chutjian (1981), SF_5^- by Christophorou *et al* (1971), F^- by Lehmann (1970), and F_2^-, SF_4^-, SF_3^- and SF_2^- by Kline *et al* (1979). Summations of these values are shown in figure 1.

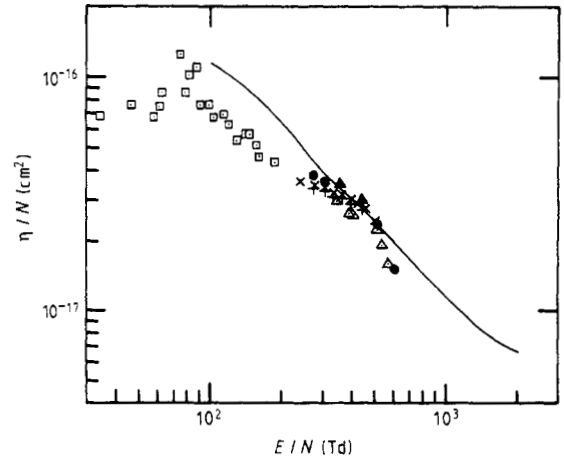

Figure 4. Attachment coefficient η. —— Present calculated values by Boltzman equation. ⊡ McAffee and Edelson (1963), × Geballe and Harrison (1955), + Bhalla and Craggs (1962), ▲ Boyd and Crichton (1971), △ Kline *et al* (1979), ● de Urquijo-Carmona (1980).

3. Calculated results

The method of calculation is given in the previous papers of Hayashi (1982), and Hayashi and Nimura (1983). The gas temperature is 300 K. The two-term Boltzmann equation analysis and Monte Carlo calculations were carried out for two ranges, 100–2000 Td and 283–5600 Td, respectively.

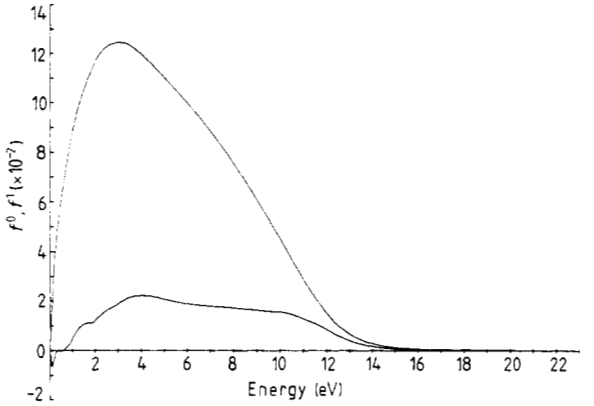

Figure 5. Electron energy distribution function; E/N = 100 Td. Upper, f^0, lower, f^1. There are no depressions at electron energies around 0.18 and 2 eV shown by Yoshizawa *et al* (1979).

Calculated values of α/N and η/N are shown in figures 3 and 4, along with the experimental values of Geballe and Harrison (1955), Bhalla and Craggs (1962), McAffee and Edelson (1963), Boyd and Crichton (1971), Maller and Naidu (1976), Kline *et al* (1979) and de Urquijo-Carmona (1980). Some examples of electron energy distribution functions f^0 and f^1 are shown in figures 5, 6 and 7. In figure 7, the total attachment cross-sections q_a are shown together. The electron energy for the maximum of f^0 is about

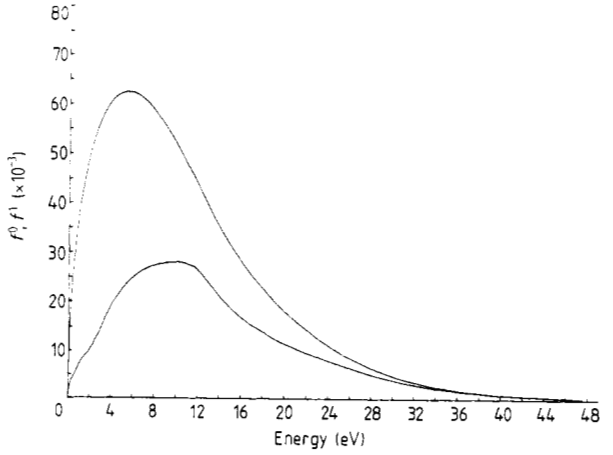

Figure 6. Electron energy distribution function; E/N = 800 Td. The values of f^1 are about half of the values of f^0.

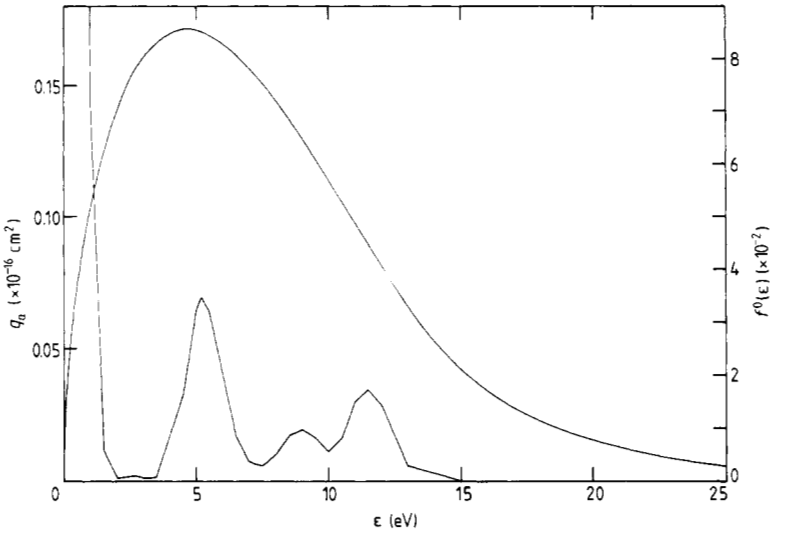

Figure 7. Electron energy distribution function f^0, for E/N = 400 Td, and total attachment cross-section q_a.

5 eV and there are few electrons in the swarm below 0.1 eV. We thought that the values of q_a for about 5 eV were important. Then, the influence of the values of q_a for separated energy ranges are calculated precisely, as discussed below.

In figure 8, calculated and measured values of $(\alpha - \eta)/N$ are shown. The lowest curve with circles shows the values for SF_6 and the symbols G, K and M are experimental values for comparison. The uppermost curve shows the values of $(\alpha - \eta)/N$ calculated assuming the values of q_a lower than 2 eV to be equal to zero; that is, values of q_a only from 2 to 15 eV are employed. The middle curve with triangles shows the values of

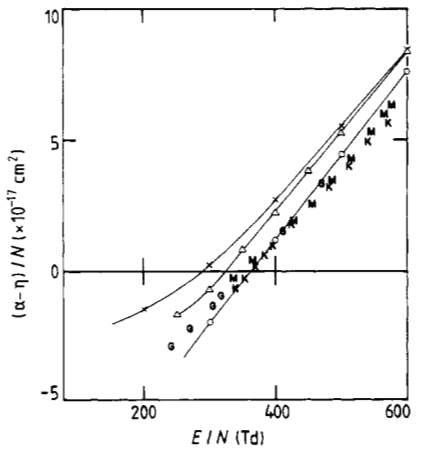

Figure 8. Effective ionisation coefficient $(\alpha - \eta)$. —○—: present calculated values for true SF_6. The symbols G, K and M are experimental values measured by Geballe and Harrison (1955), Kline *et al* (1979) and Maller and Naidu (1976), respectively. —×— and —△—: see text.

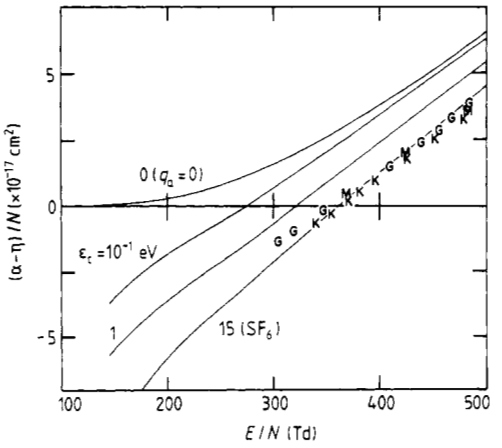

Figure 9. Effective ionisation coefficient $(\alpha - \eta)$. The parameter is critical electron energy ε_c, see text. The lowest curve is for true SF_6. Symbols G, K, M as defined in Figure 8 caption.

$(\alpha - \eta)/N$ assuming the values of q_a from 2 to 15 eV to be equal to zero. This figure has already been given in the report of the 3rd Swarm Seminar (Hayashi *et al* 1983).

The other calculated results for the effect of q_a are shown in figures 9 and 10. In these figures, a parameter ε_c was chosen. Values of q_a are assumed to be zero for all electron energies above ε_c. The lowest curve of $\varepsilon_c = 15$ eV in figure 9 shows the values of $(\alpha - \eta)/N$ for SF_6. In figure 10, the end-points on the right-hand side of the curves are values of $(\alpha - \eta)/N$ for SF_6. From these figures, it is concluded that the small values of q_a between 2 and 15 eV are very important for the values of $(\alpha - \eta)/N$ in SF_6. The

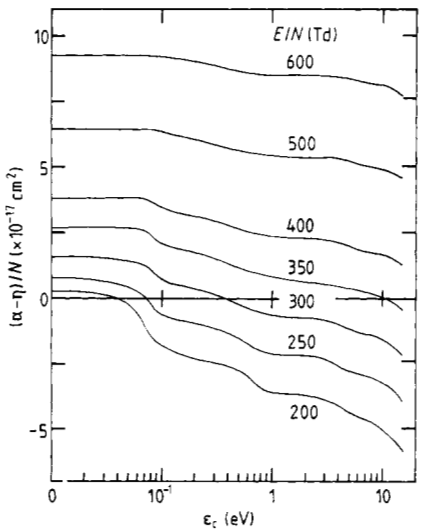

Figure 10. Effective ionisation coefficient $(\alpha - \eta)$ as a function of critical electron energy ε_c. The parameter is E/N. Details see text. The right-hand ends of the curves are values of $(\alpha - \eta)/N$ for true SF_6.

electrons having the energy of 5 or 12 eV, for example, disappear suddenly by dissociative attachment and exert a great influence on the electron swarm.

The values of q_a for C_4F_6 and C_4F_8 for the energy range from 0.04 to about 1 eV was measured by Christodoulides *et al* (1979). In these perfluorocarbons, the values of q_a for the electron energies between 1 and 10 eV should be measured.

4. Conclusion

The importance of the attachment cross-section q_a for F^- formation for the electron energies between 2 and 15 eV for the effective ionisation coefficients in SF_6 is discussed using Boltzmann equation analysis. The values of q_a for F^- formation are very small compared with the values of q_a for SF_6^- formation at low electron energies. However, the exact values of q_a for F^- formation are very important for the calculations of electron swarm parameters in SF_6.

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References

Benedict M G and Gyemant I 1978 *Int. J. Quant. Chem.* **13** 597–603
Bhalla M S and Craggs J D 1962 *Proc. Phys. Soc.* **80** 151–60
Boyd H A and Crichton G C 1971 *Proc. IEEE* **118** 1872–7
Christodoulides A A, Christophorou L G, Pai R Y and Tung C M 1979 *J. Chem. Phys.* **70** 1156–68
Christophorou L G 1981 *Proc. 2nd Int. Swarm Seminar, Oak Ridge* IV-6, (Oak Ridge, TN: ORNL)
Christophorou L G, McCorkle D L and Carter J G 1971 *J. Chem. Phys.* **54** 253–60, Erratum 1972 *J. Chem. Phys.* **57** 2228
Christophorou L G, James D R and Pai R Y 1982 *Applied Atomic Collision Physics* vol 5 (New York: Academic Press) pp 88–167
Chutjian A 1981 *Phys. Rev. Lett.* **46** 1511–4
Dehmer J L, Siegel J and Dill D 1978 *J. Chem. Phys.* **69** 5205–6
de Urquijo-Carmona J 1980 *PhD Thesis* University of Manchester, from Teich T H (1981)
Dincer M S and Govinda Raju G R 1983 *J. Appl. Phys.* **54** 6311–6
Ferch J, Raith W and Schröder K 1982 *J. Phys. B: At. Mol. Phys.* **15** L175–8
Frost L S and Phelps A V 1962 *Phys. Rev.* **127** 1621–33
Gallagher J W, Beaty E C, Dutton J and Pitchford L C 1983 *J. Phys. Chem. Ref. Data* **12** 109–52
Geballe R and Harrison M A 1955, in *Basic Processes of Gaseous Electronics* ed. L B Loeb (Los Angeles: University of California Press) p 415
Govinda Raju G R and Hackam R 1981 *J. Appl. Phys.* **52** 3912–20
Hayashi M 1981 *Rep. IPPJ-AM-19* (Institute of Plasma Physics, Nagoya University) pp 1–62
—— 1982 *J. Phys. D: Appl. Phys.* **15** 1411–8
Hayashi M and Nimura T 1983 *J. Appl. Phys.* **54** 4879–82
Hayashi M, Nimura T and Ushiroda S 1983 *Proc. 3rd Int. Swarm Seminar, Innsbruck* pp 66–71
Itoh H, Shimozuma M and Tagashira H 1980 *J. Phys. D: Appl. Phys.* **13** 1201–9
Kauppila W E, Dababneh M S, Hsieh Y-F, Kwan Ch K, Smith S J, Stein T S and Uddin M N 1983 *Proc. 13th ICPEAC, Berlin* p 303

Kennerly R E and Bonham R A 1979 *J. Chem. Phys.* **70** 2039–41
Kline L E, Davies D K, Chen C L and Chantry P J 1979 *J. Appl. Phys.* **50** 6789–96
Lehmann B 1970 *Z. Naturf.* **25A** 1755–7
Maller V N and Naidu M S 1976 *Proc. IEE* **123** 107–8
McAffee K B and Edelson D 1963 *Proc. Phys. Soc.* **81** 382–4
Novak J P and Frechette M 1982 *J. Phys. D: Appl. Phys.* **15** L105–10
Register D F, Trajmar S and Srivastava S K 1980 *Phys. Rev.* **A21** 1134–51
Rohr K 1979 *J. Phys. B: At. Mol. Phys.* **12** L185–8
Srivastava S K, Trajmar S, Chutjian A and Williams W 1976 *J. Chem. Phys.* **64** 2767–71
Teich T H 1981 *Proc. 2nd Int. Swarm Seminar, Oak Ridge* IV-4 (Oak Ridge, TN: ORNL)
Trajmar S and Chutjian A 1977 *J. Phys. B: At. Mol. Phys.* **10** 2943–9
Trajmar S, Register D F and Chutjian A 1983 *Phys. Rep.* **97** 216–356, see 346–7
Yoshizawa T, Sakai Y, Tagashira H and Sakamoto S 1979 *J. Phys. D: Appl. Phys.* **12** 1839–52
Yousfi M, Miegeville Y, Chatwiti A and Segur P 1982 *Proc. Int. Conf. on Gas Discharges and their Applications* (London: IEE) pp 343–6