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Elastic and inelastic e–CF_4 cross sections at low energies: fit to the experimental data

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Abstract. The momentum transfer elastic and the total vibrationally inelastic electron-CF_4 cross sections at energies 0.02-4 eV are varied until the best fits of the measured electron drift velocity and diffusion/mobility ratio are obtained. The elastic cross section exhibits a well pronounced minimum somewhere in the range 0.2-1.3 eV.

1. Introduction

Tetrafluoromethane is used as a working gas or as an admixture in different gas discharge devices: plasma etchers, e-beam controlled diffuse discharge switches (Hunter *et al* 1985) and gas-filled particle detectors (Christophorou *et al* 1979). To understand the kinetics of processes in a CF_4 plasma (see, for example, Vinogradov *et al* 1984) one needs numerical data of the elastic and different inelastic electron impact cross sections. Inelastic cross sections are available for dissociative attachment (threshold energies 4.6, 5.4 and 6.4 eV, see Christophorou *et al* (1979) and Hunter and Christophorou (1984)), dissociation (threshold 12.5 eV, Winters and Inokuti (1982) and electronic excitation and ionisation (threshold above 12 eV, see, for example, Verhaart *et al* (1978)).

To calculate the rate coefficients of different processes in a gas discharge the electron energy distribution function $f(\varepsilon)$ should be found by solving the Boltzmann equation. Then both the elastic momentum transfer cross section $Q'_{el}(\varepsilon)$ and vibrationally inelastic total cross section $Q^0_{in}(\varepsilon)$ should be known with a sufficient accuracy. For both elastic and inelastic processes $Q^0 = \int I(\theta)\,d\omega$, $Q^1 = \int I(\theta)(1-\cos\theta)\,d\omega$, $I(\theta)$ being the differential cross section of the particular process. Verhaart *et al* (1978) measured $Q^0_{in}(\varepsilon)$ indirectly up to 1.5 eV in arbitrary units. Jones (1986) measured the total elastic cross section Q^0_{el} at $\varepsilon \geqslant 1$ eV (which is different from Q'_{el} needed in kinetic calculations). Masek *et al* (1987) and Slovetzkii and Deriugin (1987) tried to evaluate $Q'_{el}(\varepsilon)$ and $Q^0_{in}(\varepsilon)$ roughly from swarm measurements by using a trial and error procedure similar to that of Frost and Phelps (1962).

The purpose of this work is to process the available swarm data in order to restore $Q'_{el}(\varepsilon)$ and $Q^0_{in}(\varepsilon)$ in the range 0.02-4 eV. The rotationally inelastic collisions are associated with small changes of energy ($\simeq 10^{-4}$ eV) and are therefore included in Q'_{el}.

2. Method

The procedure of processing the data is described in detail by Stefanov (1980). In short it consists in

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(i) approximating $Q'_{el}(\varepsilon)$ and $Q^0_{in}(\varepsilon)$ by adequate analytical forms containing N constants C_j;

(ii) comparing experimental values of drift velocity v_D or diffusion/mobility D/μ with calculated values by forming terms $R_i = \ln(k_{exp}/k_{calc})$ where $k = v_D$ or D/μ;

(iii) minimising the function of N variables $F(C_j) = \sum_{i=1}^{M} R_i^2$.

To obtain the so-called quasisolution of this ill-posed problem the class of functions in which the solution is looked for should be limited to 'smooth enough' functions which do not have too many maxima and minima (see, for example, Tikhonov and Arsenin 1977).

The drift velocity was calculated as

$$v_D = -(eE/3N)(2/m)^{1/2} \int_0^\infty (\varepsilon/Q_{eff})(df_0/d\varepsilon)\, d\varepsilon \tag{1}$$

and the ratio D/μ as

$$D/\mu = -\int_0^\infty (\varepsilon/Q_{eff}) f_0\, d\varepsilon \left(\int_0^\infty (\varepsilon/Q_{eff})(df_0/d\varepsilon)\, d\varepsilon \right)^{-1} \tag{2}$$

where m is the electron mass, $Q_{eff} = Q'_{el} + Q^0_{in}$ and E/N is the ratio of the applied electric field to the molecule number density.

The distribution function $f = f_0 + f_1 \cos\theta + f_2(3\cos^2\theta - 1)/2 + \ldots$, where θ is the angle between the electric field and the electron velocity (see, for example, Pitchford and Phelps 1982), can be found as a solution of an infinite set of equations for $f_0, f_1, f_2 \ldots$. The first two of them are

$$\begin{aligned}(eE/3N)(\varepsilon\, df_1/d\varepsilon + f_1) &= -\varepsilon f_0 \sum Q^0_{in,k} + \sum (\varepsilon + \varepsilon_k) f_0(\varepsilon + \varepsilon_k) Q^0_{in,k}(\varepsilon + \varepsilon_k) \\ &\quad + (2m/M) \frac{d}{d\varepsilon} \left[\varepsilon^2 (f_0 + kT_g\, df_0/d\varepsilon) \left(Q'_{el} + \sum Q^0_{in,k} \right) \right] \end{aligned} \tag{3}$$

$$\begin{aligned}(eE/N)(\varepsilon\, df_0/d\varepsilon) &= -\varepsilon f_1 \left(Q'_{el} + \sum Q^0_{in,k} \right) + \sum (\varepsilon + \varepsilon_k) f_1(\varepsilon + \varepsilon_k) [Q^0_{in,k}(\varepsilon + \varepsilon_k) - Q'_{in,k}(\varepsilon + \varepsilon_k)] \end{aligned} \tag{4}$$

where T_g is the gas temperature; the summation includes all kth inelastic processes.

It is hardly correct to determine a lot of cross sections by fitting limited experimental material. For this reason we assumed that the excitation of all vibrational modes of CF_4 can be described by one threshold ε_{in} and a unique cross section $Q_{in}(\varepsilon)$ and that $Q^0_{in} = Q'_{in}$ (which is correct in the special case of isotropic inelastic scattering) so that the last term in equation (4) is zero.

Expansion of the set of equations (3) and (4) leads to new equations for $f_2, f_3 \ldots$ which contain higher-order cross sections like $Q^n = \int I(\theta)(1 - \cos^n\theta)\, d\omega$. Therefore in spite of the higher accuracy obtained with many equations (Pitchford *et al* 1981), for practical purposes the set of equations (3) and (4) seems to be adequate. Slovetzkii and Deriugin (1987) also recommended use of the two-term approximation for CF_4 at $E/N = 200$ Td (1 Td $= 10^{-21}$ V m^2) arguing that then the ratio v_D/(mean electron velocity) is small enough.

To solve equations (3) and (4) we developed a Runge-Kutta numerical procedure starting the integration at large energies where f_0, f_1 were chosen arbitrarily and then going to low energies. The numerical procedure was tested by comparing our routine

with the results of Pitchford *et al* (1981) using their model methane cross section. The coincidence of the calculated values of v_D and D/μ was within 4%. Note that in contrast to Pitchford *et al* we accepted Q_{el} (10^{-20} m^2) $= 0.965/\varepsilon - 3.569$ for $0.169 < \varepsilon < 0.256$ eV to provide a smooth transition to the adjacent energy ranges.

3. Experimental data used

We found six experimental works relating to e-CF_4 cross sections in the low-energy range.

(i) Measurements of the drift velocity v_D in the range $E/N = 0.15$-25 Td by Christophorou *et al* (1979).

(ii) Drift velocity measurements in the range 0.1-200 Td (Hunter *et al* 1985). These results are unique because of the wide range of the measurements and because the particular range of 20-60 Td with a negative slope of $v_D(E/N)$ is investigated. The difference of v_D in (i) and (ii) is typically 10% and this may be considered as a rough estimate of the error of the measurement.

(iii) The v_D and D/μ measurements of Naidu and Prasad (1972) in the range $E/N = 120$-280 Td.

(iv) The D/μ measurements of Lakshminarasimha *et al* (1973) in the range 15-200 Td.

(v) Cyclotron resonance measurements of Tice and Kivelson (1967), from which $Q'_{el}(\varepsilon)$ is deduced, in the range 0.01-0.04 eV.

(vi) The derivative of the electron transmission spectrum in the range 0.16-1.5 eV (Verhaart *et al* 1978) may be considered as a relative measurement of the vibrationally inelastic cross section $Q^0_{in}(\varepsilon)$.

The experimental results listed above are shown in figure 1 (v_D) and figure 2 (D/μ).

The main problem is to choose values for v_D at high E/N from the data of (ii) and (iii) which differ by a factor of 1.5. Although not staying on a firm ground one may argue the choice as follows. We expect that for large E/N the dependence of v_D on n in the sequence of perfluoroalkanes C_nF_{2n+2} is likely to be smooth. This is the case in (ii) at $E/N = 100$-200 Td for $n = 1$-3 (see figures 6-8 of Hunter *et al* (1985)). On the contrary, in (iii) $v_D(n)$ becomes smooth only for $n = 2$-4 but for $n = 1$ (CF_4) v_D is about a factor of 1.5 higher than what is expected from the extrapolated smooth dependence (figure 1 of Naidu and Prasad (1972)). Adding this to the fact that (ii) is in pretty good agreement with (i) we chose experiment (ii) for further consideration and did not take into account v_D from (iii).

To avoid costly computations, of all data we used as an input for the minimisation procedure described in § 2 only 22 'generalised' experimental points, 16 'smoothed' values of v_D of the experiment (ii) in the range 0.1-200 Td and 6 values of D/μ (two from the experiment (iv) at $E/N = 60$ and 80 Td and four averaged values of (iii) and (iv) at $E/N = 125$-200 Td). Comparing (iii) and (iv) one estimates the accuracy of D/μ measurements to be about 15%. Values of D/μ at lower E/N were assumed to be less accurate and were not taken into account.

Experiments (v) and (vi) were not considered as input data and were used to check the final solutions.

Calculations of v_D and D/μ up to $E/N = 200$ Td require integration of the Boltzmann equation for $\varepsilon \leqslant 12$ eV. The dissociative attachment cross section Q_{diss} was considered as a representative of high-energy inelastic processes. It was taken from

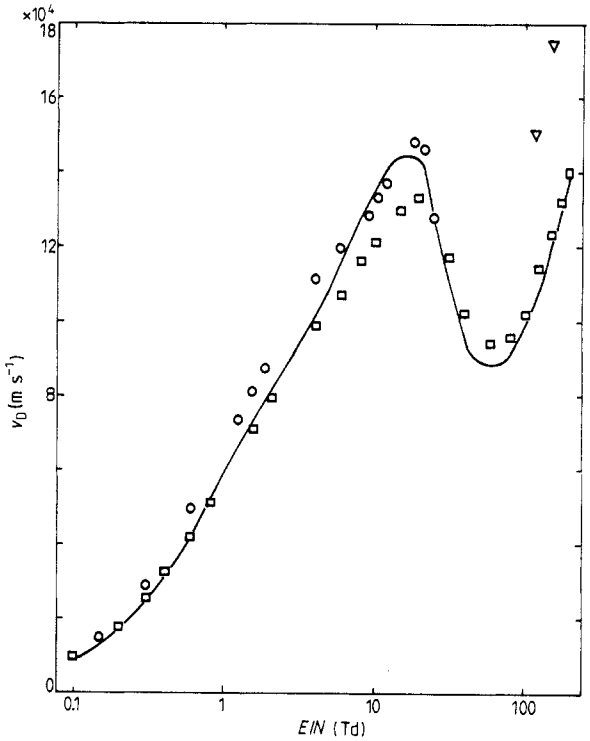

Figure 1. Electron drift velocity in CF_4 as function of E/N in Td ($1\ \text{Td} = 10^{-21}\ \text{V m}^2$). Experimental values: □, Hunter *et al* (1985); ○, Christophorou *et al* (1979); ▽, Naidu and Prasad (1972). Curve: values calculated using the results of this work.

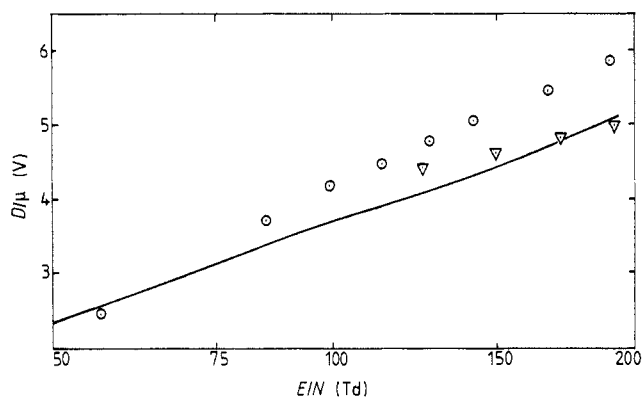

Figure 2. Electron diffusion/mobility ratio in CF_4. Experimental values: ○, Lakshminarasimha *et al* (1973); ▽, Naidu and Prasad (1972). Calculated values are shown by the curve.

Hunter and Christophorou (1984) as $Q_{diss}=0$ at $\varepsilon<4.8$ eV and $Q_{diss}(m^2)=1.58\times10^{-22}\exp\{-[(\varepsilon-7.3)/(1+0.16|\varepsilon-6|^{1.5})]^2\}$ for $\varepsilon\geq4.8$ eV.

4. Results and discusion

The logarithm of the elastic cross section $Q'_{el}(\varepsilon)$ was approximated in the range $(0, \varepsilon_0)$ by a cubic spline. At $\varepsilon>\varepsilon_0$ Q'_{el} was assumed to be a weak linear function in agreement with Jones (1986) who showed that the total cross section is a weak function of the energy at $\varepsilon\geq1$ eV. The parameter ε_0 was included as a variable in the minimisation procedure and the final result was $\varepsilon_0=1.505$ eV. The vibrationally inelastic cross section was approximated by means of four parameters $C, \alpha, \beta, \varepsilon_1$:

$$Q^0_{in}=C(u-1)u^{-\alpha}\ln(\beta u) \qquad u=\varepsilon/\varepsilon_1. \tag{5a}$$

When $\beta<1$ then the threshold of vibrational excitation was taken as $\varepsilon_{in}=\varepsilon_1/\beta$ to avoid negative values of $\ln(\beta u)$.

To resolve possible resonances in Q^0_{in} we tried to add narrow Gaussian distributions to $Q^0_{in}(\varepsilon)$ of equation (5) but in the process of minimisation they always disappeared.

The best solution for $Q'_{el}(\varepsilon)$ is given in table 1 and shown by the full curve in figure 3 and for $Q^0_{in}(\varepsilon)$ by the full curve in figure 4 which corresponds to the equation

$$Q^0_{in}=15.5\times10^{-20}\,m^2(u-1)u^{-2.272}\ln(0.898u) \qquad u=\varepsilon/0.1417\text{ eV} \tag{5b}$$

with a threshold $\varepsilon_{in}=0.158$ eV. The sum of squared deviations for this solution is $F=\Sigma_{i=1}^{22}R_i^2=0.086$ and it corresponds to a standard (RMS) deviation of 6.4%. The

Table 1. The momentum transfer elastic e-CF_4 cross section.

ε (eV)	Q'_{el} (10^{-20} m^2)
0.007	15.0
0.013	9.7
0.021	6.0
0.031	4.0
0.042	3.0
0.056	2.34
0.071	1.96
0.088	1.67
0.107	1.35
0.128	1.02
0.150	0.75
0.175	0.56
0.201	0.42
0.229	0.31
0.259	0.20
Q'_{el} = const	
1.315	0.20
1.385	0.68
1.458	4.19
1.532	12.31
1.608	12.35
For $\varepsilon>1.504$, Q'_{el} $=12.3+0.5(\varepsilon-1.504)$	

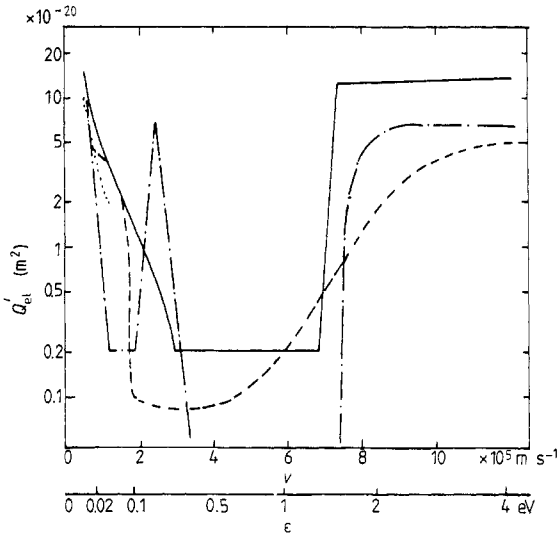

Figure 3. Electron-CF_4 momentum transfer elastic cross section. Full curve, results of this work; · · · ·, derived from the measurements of Tice and Kivelson (1967); - - -, Masek *et al* (1987); — · —, Slovetzkii and Deriugin (1987). The electron velocity is $v(10^5\ \mathrm{m\ s^{-1}}) = 5.93\ \varepsilon^{1/2}\ (\mathrm{eV}^{1/2})$.

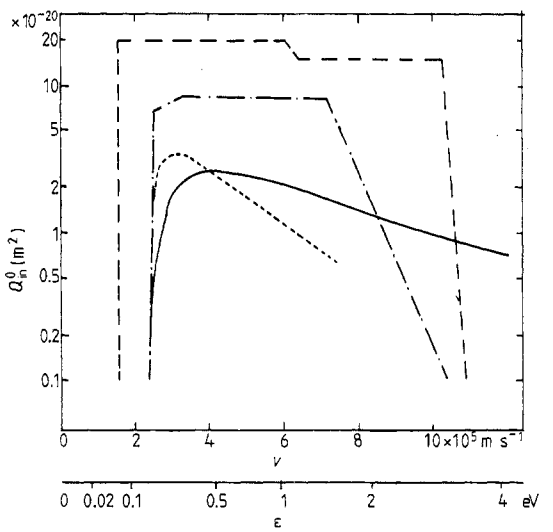

Figure 4. Vibrationally inelastic total e-CF_4 cross section. Full curve, results of this work; · · · ·, derivative of the electron transmission spectrum in arbitrary units (Verhaart *et al* 1978); - - -, Masek *et al* (1987); — · —, Slovetzkii and Deriugin (1987).

maximum deviation is 12%. The calculated values of v_D and D/μ are shown by full curves in figures 1 and 2.

In fact the solution for $Q'_{el}(\varepsilon)$ in the range $\varepsilon = 0.22$–1.3 eV (further denoted as range A) has two maxima and two minima (not shown in the figure) bounded by 0.13 and 0.6×10^{-20} m^2. These oscillations were assumed to be an artefact for the following reason. The Boltzmann equation contains the values of $Q_{eff} = Q'_{el} + Q^0_{in}$ and of Q^0_{in} and does not contain Q'_{el} explicitly. Therefore in the range A where $Q'_{el} \ll Q^0_{in}$ the exact value or shape of $Q'_{el}(\varepsilon)$ are of little importance and cannot be found from a swarm data analysis. This is proved by the fact that both the oscillating solution and the full curve $Q'_{el}(\varepsilon)$ of figure 3 with $Q'_{el} = \text{const} = Q_A = 0.2\times10^{-20}$ m^2 at the minimum have the same sum of squared deviations $F = 0.086$.

Figure 5(a) shows the dependence of F on the accepted value of Q_A. The only conclusion about the minimum of $Q'_{el}(\varepsilon)$ based on a swarm analysis is that it is situated somewhere in the range A and its value is less than 0.4×10^{-20} m^2. Figure 5(b) represents the change of F when Q'_{el} is increased and Q'_{in} is decreased by the same value Δ in the range A. It shows that Q'_{el} and Q'_{in} are well separated within an accuracy of the order of 0.3×10^{-20} m^2 in the range A.

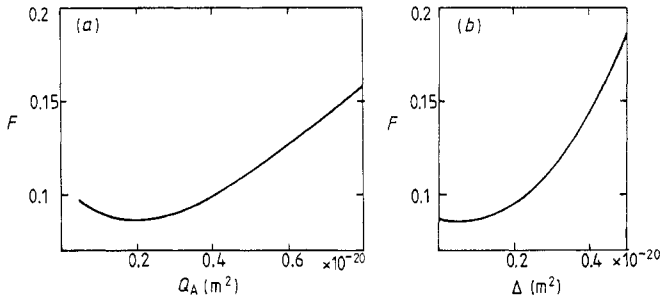

Figure 5. The sum of squared deviations F versus (a) the value of Q'_{el} in the minimum (Q_A); (b) the supplement Δ, when $Q'_{el} \to Q'_{el} + \Delta$ and $Q^0_{in} \to Q^0_{in} - \Delta$.

Assuming $Q_{diss} = 0$ resulted in changes of v_D and D/μ of about 1%. Therefore for $E/N \leq 200$ Td these quantities are not sensitive to the choice of any high-energy inelastic cross section. To check the assumption of only one vibrational mode an infinite number of vibrational modes (ε_{in} changed to ε in equations (3) and (4)) was assumed. Then the result of the procedure was a very poor approximation of the experiments ($F = 15$).

More results concerning the sensitivity analysis of the solution obtained are given in table 2. It shows that the $Q'_{el}(\varepsilon)$ and $Q^0_{in}(\varepsilon)$ in CF_4 proposed here are accurate to within a factor of about 1.5 in the range $\varepsilon = 0.02$–4 eV except for Q'_{el} in the range A. The most important feature of Q'_{el} is its sharp increase between 1.4 and 1.5 eV which is essential to explain the correct behaviour of the dependence $v_D(E/N)$ in the region of negative slope.

Cross sections of other swarm analyses are presented in figures 3 and 4. The dotted curve in figure 3 represents Q'_{el} of Tice and Kivelson (1967) found by measuring the cyclotron resonance in CF_4. It agrees pretty well with our results. At $\varepsilon > 1.5$ eV our Q'_{el} coincides within 20% with the values of the total elastic cross section measured by Jones (1986).

Table 2. Variation of the cross sections (sensitivity analysis). The figures in the last two columns (not in brackets) show the ratio of the calculated values using changed versus standard cross section accepted in this work. Values in brackets are E/N (in Td) at which the maximum change takes place.

Variation	Max. change of v_D or D/μ, factor of v_D	D/μ
Q'_{el} increased by a factor of two in the	0.58 (0.1)	
range $\varepsilon = 0.007$–0.22 eV	0.55 (0.2)	
Same, 1.315–1.504 eV	1.18 (30)	0.88 (60)
Same, 1.504–12 eV	0.58 (150)	1.12 (150)
Position of the knot $\varepsilon = 1.504$	1.10 (30)	
shifted to $\varepsilon = 1.6$ eV	1.10 (40)	0.93 (60)
At $\varepsilon > 1.504$ eV $Q'_{el} = 12.3 - 0.5(\varepsilon - 1.504)$	1.67 (150)	0.79 (150)
	1.93 (200)	0.74 (200)
Q^0_{in} increased by a factor of two in the	0.90 (0.1)	
range $\varepsilon = 0.158$–0.455 eV	0.91 (0.4)	0.94 (60)
Same, 0.455–0.86 eV	1.17 (30)	0.86 (60)
Same, 0.86–1.39 eV	1.10 (30)	0.83 (60)
Same, 1.39–2.3 eV	1.47 (30)	0.85 (60)
Same, 2.3–12 eV	$\leq 5\%$	$\leq 1\%$

A comparison with other data on Q^0_{in} is made in figure 4. Our value of the vibrational threshold $\varepsilon_{in} = 0.158$ eV was obtained as a solution and it practically coincides with $\varepsilon_{in} = 0.159$ eV cited by Verhaart *et al* (1978). Note that Slovetzkii and Deriugin (1987) were assuming their elastic cross section to be equal to $Q'_{el} + Q^0_{in}$. To obtain the real elastic cross section Q'_{el} shown in figure 3 we subtracted Q^0_{in} from their elastic cross section. Then $Q'_{el}(\varepsilon)$ becomes negative in the range 0.4–1.5 eV. This is approximately our range A where the minimum of $Q'_{el}(\varepsilon)$ is situated.

When solving the Boltzmann equation Masek *et al* (1987) neglected Q'_{in} in those terms of equations (3) and (4) which contain the sum $Q'_{el} + Q^0_{in}$. In our opinion this leads to substantial errors. To fit the experimental data Masek *et al* arbitrarily assumed $Q'_{in}/Q^0_{in} = 0.7$. However, even in this case it is not clear whether their calculations fit v_D in the range $E/N = 0.1$–10 Td (see their figure 3).

5. Conclusion

The momentum transfer elastic e-CF_4 cross section Q'_{el} and the total vibrationally inelastic cross section Q^0_{in} proposed in this work are in good agreement with the available experimental material over a wide range of E/N including the region of negative differential conductivity. They can be used for solving the Boltzmann equation and computing the transport coefficients up to $E/N = 200$ Td. The elastic cross section exhibits a well pronounced Ramsauer minimum somewhere in the range 0.22–1.3 eV. Both Q'_{el} and Q^0_{in} seems to be accurate to within a factor of about 1.5 except for the region of the minimum of Q'_{el}.

Further improvement of the procedure of restoring the electron-CF_4 cross sections may be achieved by increasing the variety and the accuracy of the experimental material, for example by measuring the electron distribution function. Then more elaborate models including different vibrational modes may be useful.

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