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Elastic and inelastic e–C_2F_6 and e–C_3F_8 cross sections from swarm data

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Abstract. The total vibrationally inelastic and momentum-transfer elastic e-C_2F_6 and e-C_3F_8 cross sections are obtained by the best fit of the measured electron drift velocity and diffusion/mobility ratio in pure C_2F_6 and C_3F_8 as well as in their mixtures with Ar.

1. Introduction

Perfluoralkanes are used in different plasma processes (for example etching) and as gaseous dielectrics (discharge switches, radiation research, see Hayashi (1985)). To calculate the rate coefficients of different processes in a gas discharge the electron distribution function $f(u)$ has to be found by solving the Boltzmann equation. For this purpose both the elastic momentum-transfer cross section $Q_{el}(u) = 2\pi \int I_{el}(u, \vartheta)(1-\cos\vartheta)\sin\vartheta\,d\vartheta$ and the total vibrationally inelastic cross section $Q_{in}(u) = 2\pi \int I_{in}(u, \vartheta)\sin\vartheta\,d\vartheta$ should be known with sufficient accuracy. $I(u, \vartheta)$ is the differential cross section of the particular process and u is the energy. A convenient unit for the reduced electric field E/N, $1\ \mathrm{Td} = 1\times10^{-21}\ \mathrm{V\,m^2}$ is used throughout the paper.

2. Method

Determining $Q_{el}(u)$ and $Q_{in}(u)$ using measured values of the drift velocity V_d and the transversal diffusion/mobility ratio D/μ is an ill-posed inverse problem. It is equivalent to solving a Fredholm equation of the first kind (Gurchin *et al* 1970). To convert this ill-posed problem to a well-posed one in the sense of Tikhonov and Arsenin (1977), one needs supplementary information, sometimes rather subjective, to narrow the class of possible solutions. In the particular case of this work, functions $Q_{el}(u)$ and $Q_{in}(u)$ which have as few minima and maxima as possible will be looked for (Vapnic 1979).

The procedure of processing the data (minimisation of the sum of the squared deviation) is described elsewhere (Stefanov 1980, Stefanov *et al* 1988). In short, it consists of:

(i) approximating $Q_{el}(u)$ and $Q_{in}(u)$ by adequate analytical forms containing N constants C_j;

(ii) minimising the function of N variables $F(C_j) = \Sigma[\ln(k_{exp}/k_{calc})]^2$, where $k = V_d$ or D/μ.

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The drift velocity and the ratio transversal diffusion/mobility D/μ were calculated as accepted in a two-term expansion of the Boltzmann equation in a hydrodynamic approximation (Pitchford *et al* 1981, Pitchford and Phelps 1982):

$$V_d = -\tfrac{1}{3}(2e/m)^{1/2} E \int (u/Q_1)(df_0/du)\, du \tag{1}$$

$$D/\mu = -\int (u/Q_1) f_0\, du \left(\int (u/Q_1)(df_0/du)\, du \right)^{-1} \tag{2}$$

where $Q_1 = \Sigma_k N_k [Q_{el}^k(u) + \Sigma_j Q_{in}^{k,j}(u)]$, e is the elementary charge, m is the electron mass, E is the applied electric field, N_k is the number density of the kth gas component, f_0 is the scalar electron distribution function:

$$f(u) = f_0 + f_1 \cos\alpha + \ldots \tag{3}$$

and α is the angle between the electric field and the electron velocity (Pitchford *et al* 1981).

In a uniform electric field, f_0 can be found as a solution of the Boltzmann equation (Smith and Tomson 1981, Pitchford *et al* 1981, Pitchford and Phelps 1982)

$$\tfrac{1}{3}E^2 \frac{d}{du}\left(\frac{u}{Q_1}\frac{df_0}{du}\right) + 2m\frac{d}{du}(u^2 Q_2 f_0) + \frac{2mkT}{e}\frac{d}{du}\left(u^2 Q_2 \frac{df_0}{du}\right) = f_0^* \tag{4}$$

where

$$Q_2 = \sum_k \frac{N_k}{M_k}\left[Q_{el}^k(u) + \sum_j Q_{in}^{k,j}(u) \right]$$

$$f_0^* = \sum_k N_k \sum_j [u f_0(u) Q_{in}^{k,j}(u) - (u + u_{kj}) f_0(u + u_{kj}) Q_{in}^{k,j}(u + u_{kj})]$$

M_k is the mass of the kth gas component; u_{kj} is the threshold of the jth inelastic process of the kth gas component and kT is the thermal energy.

The boundary conditions are $f_0(\infty) = 0$, $df_0(\infty)/du = 0$ and f_0 is normalised as $\int \sqrt{u}\, f_0(u)\, du = 1$. To solve equation (4) we used a Runge-Kutta numerical procedure starting the integration from a large energy u_* and then going to low energies. The boundary values of $f_0(u_*)$ and $df_0(u_*)/du$ were chosen arbitrarily but not equal to zero because equation (4) is homogeneous. As a result of this arbitrariness the solution $f_0(u)$ was different only in a narrow interval ($\sim$0.2 eV) of u near u_*. In the remaining range of lower energies, significant to calculate V_d and D/μ, $f_0(u)$ did not depend on the boundary values or on the choice of u_* (provided the latter was large enough).

The numerical procedure was found to coincide within 4% with the results of Pitchford *et al* (1981) on V_d and D/μ using their model methane cross sections. Similar coincidence was found when comparing our routine with the results of Hayashi and Niwa (1987) using their e-C_2F_6 cross sections.

To find an initial approximation of $Q_{in}(u)$ we considered gas mixtures of Ar with small additions of C_2F_6 or C_3F_8. In this case $NQ_{el}(u)$ of C_2F_6 or C_3F_8 is about 100 to 1000 times less than $NQ_{el}(u)$ of the argon buffer gas and provided the latter is known we can find $Q_{in}(u)$ solely. Once an initial approximation of $Q_{in}(u)$ is known then the next step is to find an approximation of $Q_{el}(u)$ from swarm data in pure C_2F_6 or C_3F_8 (Pirgov and Stefanov 1989).

It is hardly correct to determine many inelastic cross sections by fitting the limited set of available swarm data. For this reason we approximated the excitation of all

vibrational modes of C_2F_6 or C_3F_8 by one threshold u_{in} and a unique cross section $Q_{in}(u)$; furthermore we assumed $Q_{in}(u) = Q_{in}^{(1)}(u)$ $(Q_{in}^{(1)}(u) = 2\pi \int I_{in}(u, \vartheta) \times (1 - \cos \vartheta) \sin \vartheta \, d\vartheta)$.

3. Experimental data used

We found two works related to swarm measurements in e-C_2F_6 and e-C_3F_8.

3.1. Drift velocity and diffusion/mobility ratio measurements in pure C_2F_6 and C_3F_8 in the range (280-600 Td) (Naidu and Prasad 1972)

For such large values of E/N the integration procedure should begin at high energies ($\geq$20 eV) where a large set of different inelastic cross sections may become important. We limited our consideration to the range $\leq$10 eV and therefore these data were not used.

3.2. V_d and D/μ measurements (Hunter et al 1985) for Ar/C_2F_6, CH_4/C_2F_6, Ar/C_3F_8 and CH_4/C_3F_8 mixtures and in pure C_2F_6, C_3F_8 in the range (0.1-200 Td)

In view of the fact that up to 12 eV there are no inelastic processes in Ar we considered the data of Ar/C_2F_6 and Ar/C_3F_8.

The dissociative attachment cross sections of C_2F_6 and C_3F_8 were taken from Hunter *et al* (1985) and the data for the e-Ar elastic momentum-transfer cross section from Milloy *et al* (1977) and Spencer and Phelps (1976).

Table 1. Total vibrationally inelastic and momentum-transfer elastic e-C_2F_6 cross sections.

u (eV)	Q_{in} (10^{-20} m^2)	u (eV)	Q_{el} (10^{-20} m^2)
For $0.0825 < u < 0.1056$,		0.0024	85.00
$Q_{in} = 1.03 \times 10^4 \times (u - 0.0825) \times (0.129 - u)$		0.01	22.17
		0.02	6.50
0.1056	5.57	0.04	5.82
0.20	10.67	0.08	4.09
0.35	15.47	0.14	1.00
0.70	16.45		
1.00	12.63	For $0.14 < u < 0.8$, $Q_{el}(u) = 1.0$	
1.39	11.33	0.8	1.00
1.96	13.89	1.0	1.57
2.56	17.47	1.5	3.70
2.90	18.09	2.0	6.52
3.24	17.29	2.6	9.73
4.00	12.11	3.3	11.99
5.00	7.35	4.0	12.28
6.00	5.22	6.0	8.34
8.00	4.18	8.0	6.53

4. Results and discussion

The vibrationally inelastic cross section was approximated as $Q_{in}(u) = au^2 + bu + c$ in the range $u_{in} < u < u_1$. For $u > u_1$, $\ln Q_{in}(u)$ was approximated as a cubic spline with a smooth transition at $u = u_1$. The logarithm of the elastic cross section was approximated by a cubic spline in the whole range of energies.

4.1. C_2F_6

The best solutions for $Q_{el}(u)$ and $Q_{in}(u)$ are given in table 1 and are shown by the full curve in figure 1. Our value of the vibrational threshold $u_{in} = 0.0825$ eV was obtained as a solution and is in good agreement with the known values of the vibrational excitation energies of different modes (Hunter *et al* 1985) $0.08 < u_{in} < 0.16$ eV.

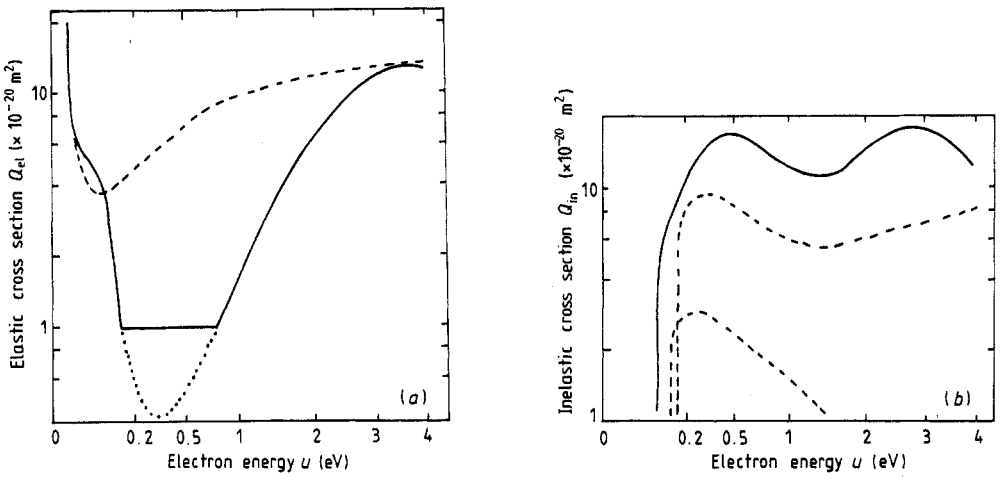

Figure 1. Electron-C_2F_6 momentum transfer (a) and vibrationally inelastic (b) cross sections as a function of the electron energy in eV. ——, results of this work; - - -, derived from Hayashi and Niwa (1987); ···, form of Q_{el} near the minimum obtained as a solution. The horizontal axes are linear for $\sqrt{u}$.

The form of $Q_{el}(u)$ near the minimum obtained as a solution is shown in figure 1(a) by a dotted curve. Changing it to $Q_{el}(u) = \text{const} = 1 \times 10^{-20}$ m^2 (the full curve in figure 1(a)) leads to variation of the calculated values of V_d and D/μ by less than 1%; therefore in the region $0.14 < u < 0.8$ eV, $Q_{el}(u) \leqslant 1 \times 10^{-20}$ m^2. This uncertainty can be explained by the fact that the Boltzmann equation contains the values of $\Sigma_k [Q^k_{el}(u) + \Sigma_j Q^{k,j}_{in}(u)]$ and $\Sigma_k \Sigma_j Q^{k,j}_{in}(u)$ and does not contain $Q^k_{el}(u)$ explicitly. Therefore in the range where $Q^k_{el} \ll \Sigma_j Q^{k,j}_{in}(u)$ the exact value or shape of Q^k_{el} are of little importance and cannot be found from a swarm data analysis. A similar situation was reported in the case of CF_4 (Stefanov *et al* 1988).

The calculated values of V_d are shown in figure 2 (full curves). The sum of squared deviations for this solution is $F = 0.237$, and it corresponds to a RMS deviation of 7.8% (the maximum deviation is 22%).

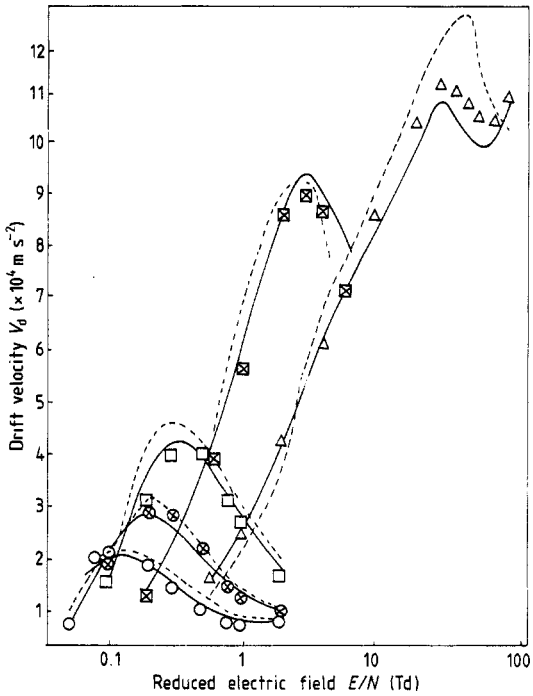

Figure 2. Electron drift velocity in Ar/C_2F_6 mixtures as a function of E/N in Td (1 Td = 1 × 10^{-20} V m^2). ——, results of this work; - - -, results derived with our routine using cross sections of Hayashi and Niwa (1987). Experimental values from Hunter *et al* (1985): ○, 0.1% C_2F_6; ⊗, 0.2% C_2F_6; □, 0.5% C_2F_6; ⊠, 10% C_2F_6; △, 100% C_2F_6.

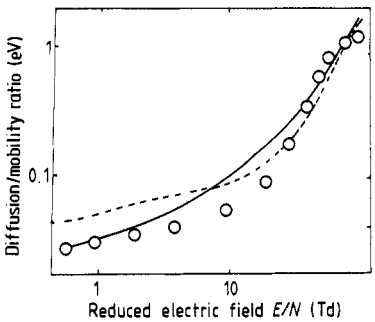

Figure 3. Electron diffusion/mobility ratio in C_2F_6 as a function of E/N in Td (1 Td = 1 × 10^{-20} V m^2). ——, calculated values; - - -, results derived with our routine using cross sections of Hayashi and Niwa (1987); ○, experimental values from Hunter *et al* (1985).

The calculated values of D/μ are shown in figure 3 ($F = 1.49$; RMS = 42%). We accepted that V_d is more accurate than D/μ because the calculation of D/μ needs more terms in the series (3). (For methane V_d(six terms)/ V_d(two terms) = 0.97; D/μ(six terms)/D/μ(two terms) = 0.75 at 6.6 Td (Pitchford *et al* 1981).) Besides, the error of D/μ measurements is about twice that of V_d.

The cross sections found by Hayashi and Niwa (1987) (broken curves in figure 1) are similar to our results especially when the sum $Q_{el}+\Sigma Q_{in}$ and the sum ΣQ_{in} are considered (the Boltzmann equation contains $Q_{el}+\Sigma Q_{in}$ and ΣQ_{in} as discussed above). Using their cross sections, we calculated V_d and D/μ as shown by the broken curves in figures 2 and 3.

4.2. C_3F_8

The best solutions for $Q_{el}(u)$ and $Q_{in}(u)$ are given in table 2 and are shown in figure 4. The procedure used in this work leads to a value of the vibrational threshold 0.27 eV which is unexpectedly high compared with CF_4 and C_2F_6. We did not find values for the vibrational excitation energies of different modes of C_3F_8 in the literature.

Table 2. Total vibrationally inelastic and momentum-transfer elastic e-C_3F_8 cross sections.

u (eV)	Q_{in} (10^{-20} m^2)	u (eV)	Q_{el} (10^{-20} m^2)
For $0.27 < u < 0.28$,		0.002	96.00
$Q_{in} = 1.97 \times 10^4 \times (u - 0.27) \times (0.287 - u)$		0.01	63.23
		0.02	16.79
0.28	1.38	0.04	1.89
0.36	4.13	0.07	0.83
0.49	8.43	0.12	2.04
0.64	9.17	0.20	6.57
0.80	7.60	0.36	10.11
1.00	5.56	0.64	10.91
1.54	3.78	0.80	11.41
2.00	4.84	1.00	13.21
2.60	8.02	1.50	21.70
3.24	12.25	2.20	34.67
4.00	15.76	3.00	39.63
4.41	16.17	4.00	30.91
5.50	13.37	6.00	10.05
8.00	6.02	8.00	4.98

The calculated values of V_d are shown in figure 5 by the full curve ($F = 0.278$, RMS = 7.2%, maximum deviation 24%).

To get a better approximation we fixed $Q_{el}(u)$ and $Q_{in}(u)$ for C_2F_6 and C_3F_8 and tried to find another $Q_{in}(u)$ (two inelastic cross sections model). The maximum change of the drift velocity in this case was less than 1%.

When the dissociative attachment cross section was taken into account (both for C_2F_6 and C_3F_8) the maximum change of the drift velocity was less than 1%. According to Blevin *et al* (1985) the electron number loss process due to attachment effects the drift velocity $1+\overline{\nu_a}/(\nu_{el}+\nu_{in})$ times (here $\overline{\nu_a}$ is the average attachment collision frequency, ν_{el} and ν_{in} are the elastic and inelastic collision frequencies). In the range of interest $\overline{\nu_a}/(\nu_{el}+\nu_{in}) \leq 0.02$.

The existence of the second maximum in the vibrational cross sections of C_2F_6 and C_3F_8 was checked as follows. An energy (u_2) was chosen near the first maximum and another form of $Q_{in} = a(u-u_2)+Q_{in}(u_2)$ was looked for in the range $u > u_2$. After

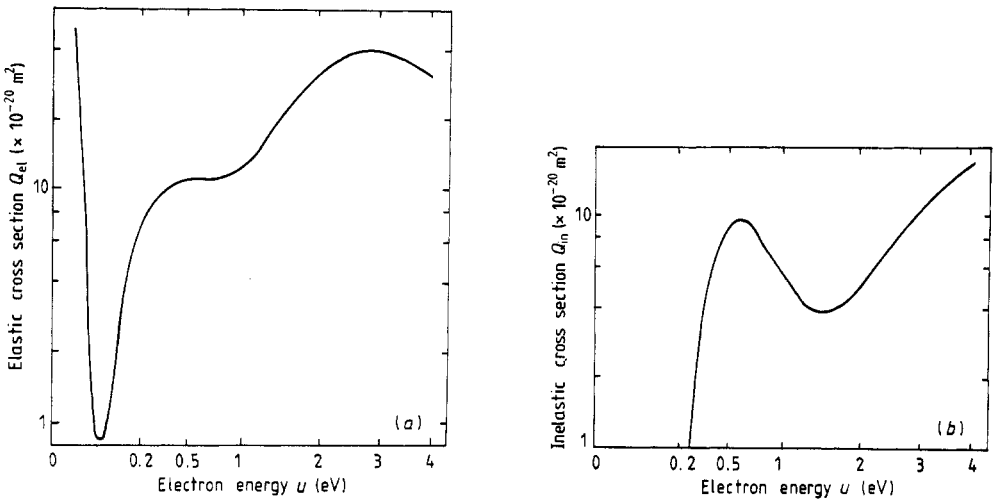

Figure 4. Electron-C_3F_8 momentum transfer (a) and vibrationally inelastic (b) cross sections as a function of the electron energy. The horizontal axes are linear for $\sqrt{u}$.

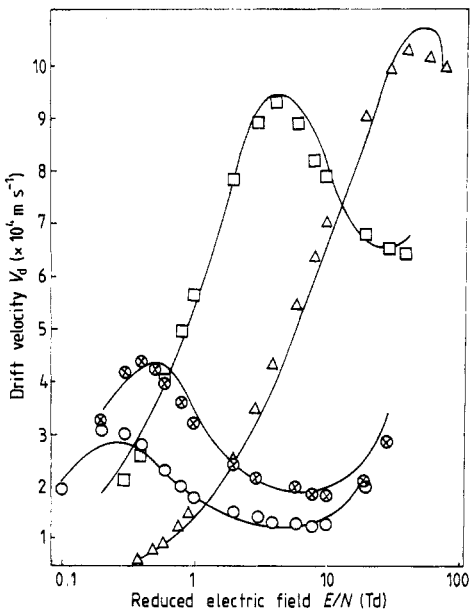

Figure 5. Electron drift velocity in Ar/C_3F_8 mixtures as a function of E/N in Td (1 Td = 1 × 10^{-20} V m^2). ——, results of this work. Experimental values from Hunter *et al* (1985): ○, 0.2% C_3F_8; ⊗, 0.5% C_3F_8; □, 10% C_3F_8; △, 100% C_3F_8.

minimisation of the parameters a and u_2 the results were:

for C_2F_6 $\quad a = -1.37 \times 10^{-20}$ m^2 eV^{-1} $\quad u_2 = 0.82$ eV

for C_3F_8 $\quad a = -0.99 \times 10^{-20}$ m^2 eV^{-1} $\quad u_2 = 0.71$ eV.

In this case the RMS deviations of V_d were substantially larger: 12 and 31% respectively.

Table 3. Variation of the cross section (sensitivity analysis). The figures in the second column show the ratio of the calculated values using changed cross sections compared with the standard one accepted in this work. Values in parentheses are E/N (in Td) at which the maximum change takes place. The figures in the third column show the range of E/N (in Td) in which values changed more than 5%.

	C_2F_6		C_3F_8	
$Q_{el} \rightarrow 2Q_{el}$ in the range (eV)	V_d changed / V_d obtained	E/N (Td)	V_d changed / V_d obtained	E/N (Td)
0.0024–0.02	<2%	—	<4%	—
0.02–0.08	0.56 (2)	0.6–20	1.11 (0.8)	0.4–8
0.08–0.15	<5%	—	<5%	—
0.15–1.01	<2%	—	1.14 (20)	0.4–30
1.01–4	1.10 (60)	50–80	1.27 (80)	60–80
4–8	<2%	—	<4%	—
$Q_{in} \rightarrow 2Q_{in}$				
0.0825–0.1056	1.19 (4)	1–10	—	—
0.27–0.28	—	—	<2%	—
0.1056–0.35	1.62 (30)	4–60	—	—
0.28–0.35	—	—	1.18 (10)	2–20
0.35–0.80	1.65 (40)	10–80	1.47 (60)	6–80
0.80–1.58	1.44 (60)	10–100	1.33 (80)	40–80
1.58–4.29	1.40 (80)	10–100	1.16 (80)	60–80
4.29–8.00	<2%	—	<4%	—
Threshold is changed to (eV)				
0.101	2.06 (10)	1–100	—	—
0.22	—	—	1.33 (0.4)	0.4–80

Table 4. Comparison between the total vibrationally inelastic and momentum-transfer elastic e-CF_4, e-C_2F_6 and e-C_3F_8 cross sections. Figures in parentheses are related to the second maximum of Q_{in}. CF_4: a, results of Hayashi (1985); b, Curtis *et al* (1988); c, Stefanov *et al* (1988). C_2F_6: d, Hayashi and Niwa (1987); e, present work.

Q_{el}		min (10^{-20} m^2)	at (eV)	max (10^{-20} m^2)	at (eV)
CF_4	a	~0.7	~0.2	~7	~7
	b	~0.01	~0.15	~6	~2
	c	≤0.2	0.26–1.31	~12	~4
C_2F_6	d	~3.5	~1	~12	~5
	e	≤1	0.14–0.8	~12	~4
C_3F_8	e	~0.8	~0.07	~40	~3.5
Q_{in}		Threshold (eV)	max (10^{-20} m^2)	at (eV)	
CF_4	a	~0.11	~10	~0.3	
	b	~0.16	~7	~0.3	
	c	0.16	~3	~0.5	
C_2F_6	d	~0.12	~10 (~9)	~0.3 (~4.5)	
	e	0.083	~17 (~18)	~0.7 (~3)	
C_3F_8	e	0.27	~9 (~16)	~0.65 (~4)	

Therefore, it seems that the second maximum in Q_{in} for both C_2F_6 and C_3F_8 is not an artefact.

More results concerning the sensitivity analysis of the obtained solutions are given in table 3. It shows that $Q_{in}(u)$ and $Q_{el}(u)+Q_{in}(u)$ in C_2F_6 and C_3F_8 proposed here are accurate to within a factor of two except near the ends of the interval 0.02–4 eV.

4.3. Comparison of CF_4, C_2F_6 and C_3F_8

In table 4 Q_{el} and Q_{in} of the three first perfluoralkanes are compared. The following regularities are observed. The Ramsauer minimum in Q_{el} takes place at lower energies when the molecular mass increases. There is a maximum in $Q_{el}(u)$ situated in the range 3.5 to 4.5 eV for all three fluoralkanes. The maximum of $Q_{in}(u)$ is in the range 0.5 to 0.7 eV. In C_2F_6 and C_3F_8 a second maximum of Q_{in} in the range 3 to 4 eV appears with $Q_{in}=10$ to 20×10^{-20} m^2.

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