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Study of Electron Thermalization Lengths and Total Initial Ionization Yields in Tetra-alkyl Liquids

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ABSTRACT

Measurements of field dependent ionization currents in nine tetra-alkyl liquids have been used to determine the average electron thermalization lengths and total initial ionization yields.

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In this paper we present and discuss the total initial ionization yields G_{TOT} and the average electron thermalization lengths <y> determined from recent measurements of field dependent ionization currents in tetra-alkyl liquids.

Consider the passage of an ionizing particle through a liquid in an external electric field **E**. The free ion yield $G_{fi}(\mathbf{E})$ is defined as the number of electron-ion pairs liberated when an energy of 100 eV is deposited in the liquid. If P(y,E) is the probability that a thermalized electron separated from its positive ion partner by a distance y will escape geminate recombination,

$$G_{fi}(\mathbf{E}) = G_{TOT} \int_0^\infty D(y)P(y,\mathbf{E})\,dy\ , \tag{1}$$

where D(y) is the distribution of electron thermalization lengths, and G_{TOT} is the number of electron-ion pairs initially formed in the liquid when an energy of 100 eV is deposited by an ionizing particle. In the theory of Onsager[1]:

$$P(y,\mathbf{E}) = \exp(-r_c/y)\,[1 + F(y,\mathbf{E})], \tag{2}$$

where the critical distance $r_c = e^2/\varepsilon kT$, and e is the electronic charge, ε the dielectric constant of the liquid, k is Boltzmann's constant, and T is the temperature (°K). The Onsager function F(y,**E**) is given in Ref. 2 after averaging over the angles between the direction of **E** and the axis between the electron and its parent ion:

$$F(y,\mathbf{E}) = \exp(-U_0)\sum_{n=1}^{\infty} \frac{(U_0)^n}{(n+1)!} \sum_{j=0}^{n-1} (n-j)\,\frac{(r_c/y)^{j+1}}{(j+1)!}\ , \tag{3}$$

where $U_0 = eEy/kT$. Hence given D(y) and G_{TOT} we can predict $G_{fi}(\mathbf{E})$.

In the present paper measurements of $G_{fi}(E)$ for the nine tetra-alkyl liquids listed in Table 1 are used to provide constraints on D(y) and G_{TOT}. The $G_{fi}(E)$ were obtained from calculated dose rates and measured ionization currents. The measurements were made at room temperature using a guard ring type parallel plate ionization chamber exposed to gamma rays produced by 1.95 MeV electrons incident on a 0.25 mm tungsten target. The chamber received a dose rate of about 0.5 μGy/s. Full details of the experimental setup and the method of extracting the $G_{fi}(E)$ can be found in Ref. 3.

The measured $G_{fi}(E)$ are shown in Fig. 1. We have previously noted[3] that the measured $G_{fi}(E)$ for TMS, TMG, TMSn, TES, TESn, TBG, and TBSn suggest that (i) free ion yields for similar tetra-alkyl liquids are the same within the precision of the measurements, independent of the nature of the central group IV atom, and (ii) the yield does depend on the nature of the attached alkyl group, being highest for methyl groups and decreasing as group size increases. The results for TEG and TPG shown in Fig. 1, which have not been previously reported, confirm these observations.

In Fig. 2 we show that the measured $G_{fi}(E)$ in the region $E > 10$ kV/cm are well described by the Onsager predictions (Eq. 1 - 3) obtained using the square of the refractive index (n_D^2) for ε together with a three-dimensional Gaussian form for D(y) and values of G_{TOT} and $<y>$ which give the best least-squares fit to the $E > 10$ kV/cm data. At lower fields we suspect[4] that volume recombination depletes the observed yields, and hence the measured $G_{fi}(E)$ tend to fall below the Onsager predictions for some liquids.

The dominant source of uncertainty on the extracted G_{TOT} and $<y>$ arises from our lack of knowledge of the form of D(y). To estimate the size of this uncertainty, we consider a simple physical model of the thermalization process in which (a) an electron undergoes N_{COL} collisions before thermalizing, (b) each collision randomizes the electron direction, and (c) the distances x between collisions are distributed with a probability distribution P(x)

= exp(-x/λ) where the mean free path λ is fixed once N_{COL} and <y> have been specified. If $N_{COL} = 1$, the resulting D(y) will be an exponential distribution. As N_{COL} tends towards infinity, the resulting D(y) will tend towards a Gaussian distribution. The distributions D(y/λ) that correspond to $N_{COL} = 1, 2, 5, 10, 20$, and ∞ (Gaussian) have been generated by Monte Carlo, and used to obtain the best fit values of G_{TOT} and <y>. The results for the nine tetra-alkyl liquids are listed in Table 2. The fits do not distinguish between the different forms of D(y); as N_{COL} is changed the quality of the fits does not change significantly. In Fig. 3 we see that as N_{COL} is varied the best fit points for tetra-alkyl liquids with similar molecular structure move along a common curve in the (G_{TOT}, ε<y>) plane, and that this curve depends on the nature of the alkyl group and tends to move to lower ε<y> as the size of the alkyl group increases. In Ref. 4 we presented fit results for five of the tetra-alkyl liquids where we used for D(y) a Gaussian with a polynomial tail. We note here that the resulting fitted values for G_{TOT} and <y> do not differ significantly from the pure Gaussian results.

Before drawing conclusions from these observations we first consider the systematic uncertainties on the experimental measurements, which are described fully in Ref. 3. The uncertainty on the absolute dosimetry common to all liquids is ±10%, which results in an uncertainty of ±10% on the G_{TOT} scale in Fig. 3. The uncertainty on the relative dosimetry between any two liquids is ±7% (±4%) if one (neither) of the liquids contain Sn atoms. This results in relative uncertainties on the G_{TOT} values of one liquid with respect to another of ± 7% (±4%) for liquids with (without) Sn atoms. Finally, there is an uncertainty on the values of ε used to evaluate r_c. The error bars on the $N_{COL} = 1$ and 20 points in Fig. 3 indicate the uncertainties on the fitted G_{TOT} and <y> due to the uncertainty on ε, and were obtained by refitting the data using measured values of ε (Table 1) instead of n_D^2. Note that the resulting uncertainty in the (G_{TOT}, ε<y>) plane tends to move the fitted points along the curves in Fig. 3.

Taking into account the uncertainties discussed above, for the D(y) we have considered, we conclude:

(i) The product of the dielectric constants and the average thermalization lengths ε<y> are in the ranges 300 ± 100 Å for the tetramethyl liquids, 140 ± 60 Å for the tetraethyl liquids, 150 ± 50 Å for tetrapropylgermane, and 190 ± 70 Å for the tetrabutyl liquids.

(ii) The total initial yields G_{TOT} (pairs per 100 eV) are in the ranges 5.6 ± 3.1 for the tetramethyl liquids, 9 ± 6 for the tetraethyl liquids, 4.3 ± 2.5 for tetrapropylgermane, and 2.5 ± 1.5 for the tetrabutyl liquids.

(iii) A previous analysis[5] of G_{fi} data for liquid hydrocarbons assumed that both the G_{TOT} and the form of D(y) are the same for all the liquids, and that G_{TOT} is equal to the yield in vapor phase (~4 pairs per 100 eV). Our results show that if (a) the form of D(y) is common to all the tetra-alkyl liquids then the G_{TOT} must vary considerably, or if (b) the value of G_{TOT} is common to all the tetra-alkyl liquids then it is indeed ~ 4 pairs per 100 eV, however the form of D(y) must vary considerably, being essentially an exponential distribution for the tetra-butyl liquids and approximately Gaussian for TEG.

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Table 1 : Some properties of the tetra-alkyl liquids measured.

Liquid						
Name	Acronym	Formula	Purity (%)	T (°K)	$\varepsilon^{a)}$	n_D^2
Tetramethylsilane	TMS	$(CH_3)_4Si$	≥ 99.9	295	1.92	1.846
Tetramethylgermane	TMG	$(CH_3)_4Ge$	≥ 99.9	295	2.01	1.924
Tetramethylstannane	TMSn	$(CH_3)_4Sn$	≥ 99.9	295	2.25	2.076
Tetraethylsilane	TES	$(C_2H_5)_4Si$	≥ 99	295	$2.08^{b)}$	2.036
Tetraethylgermane	TEG	$(C_2H_5)_4Ge$	≥ 99.9	297	2.13	2.082
Tetraethylstannane	TESn	$(C_2H_5)_4Sn$	97	295	$-^{b)}$	2.170
Tetrapropylgermane	TPG	$(C_3H_7)_4Ge$	97	297	2.15	2.105
Tetrabutylgermane	TBG	$(C_4H_9)_4Ge$	99.9	295	2.12	2.120
Tetrabutylstannane	TBSn	$(C_4H_9)_4Sn$	≥ 99	295	2.23	2.173

(a) Dielectric constant, our measurements. (b) These values differ from the measured ε given in Ref. 4. The old values for these liquids were incorrect, and resulted in our inability to fit the TES and TESn data. We do not have a reliable measurement of ε for TESn.

Table 2 : Fit results for <y> (Å) and G_{TOT} (pairs per 100 eV).

Liquid	$N_{COL}=1$		$N_{COL}=2$		$N_{COL}=5$		$N_{COL}=10$		$N_{COL}=20$		$N_{COL}=\infty$	
	<y>	G_{TOT}	<y>	G_{TOT}	<y>	G_{TOT}	<y>	G_{TOT}	<y>	G_{TOT}	<y>	G_{TOT}
TMS	137	5.2	174	3.9	200	3.1	205	3.0	215	2.8	214	2.8
TMG	120	5.6	153	4.2	180	3.2	188	3.1	197	2.9	197	2.8
TMSn	92	7.4	122	5.2	147	3.9	153	3.7	162	3.5	161	3.4
TES	41	10.5	57	6.7	74	4.2	79	3.8	85	3.5	86	3.3
TEG	37	13.3	51	8.3	65	5.5	68	5.2	75	4.5	77	4.2
TESn	44	8.4	61	5.4	76	3.8	81	3.4	89	3.0	90	2.8
TPG	48	5.9	65	4.0	82	2.7	84	2.7	92	2.4	97	2.1
TBG	60	3.4	81	2.3	100	1.6	107	1.5	110	1.5	115	1.3
TBSn	59	3.5	78	2.5	96	1.8	103	1.6	110	1.5	115	1.3

Figure Captions

Fig. 1 Free Ion Yields shown as a function of applied electric field for (a) tetramethylsilane, tetramethylgermane, and tetramethylstannane; (b) tetraethylsilane, tetraethylgermane, and tetraethylstannane; (c) tetrabutylgermane and tetrabutylstannane; and (d) tetrapropylgermane compared with tetraethyl- and tetrabutyl-germane.

Fig. 2 Comparison of field dependent free ion yields with Onsager predictions (curves, see text) obtained using a Gaussian form for D(y) and the best fit values for G_{TOT} and $<y>$ (see Table 2, columns corresponding to $N_{COL} = \infty$).

Fig. 3 Onsager fit results for the nine tetra-alkyl liquids in the G_{TOT} versus $\varepsilon<y>$ plane. The curves are there to guide the eye. For each liquid, the best fit points are shown for the electron thermalization range distribution corresponding to $N_{COL} = 1$ (at the high G_{TOT} end of the curves), 2, 5, 10, 20, and ∞ (at the low G_{TOT} end). The error bars are on the $N_{COL} = 1$ and $N_{COL} = 20$ points, and indicate the uncertainty due to the assumed value of the dielectric constant.

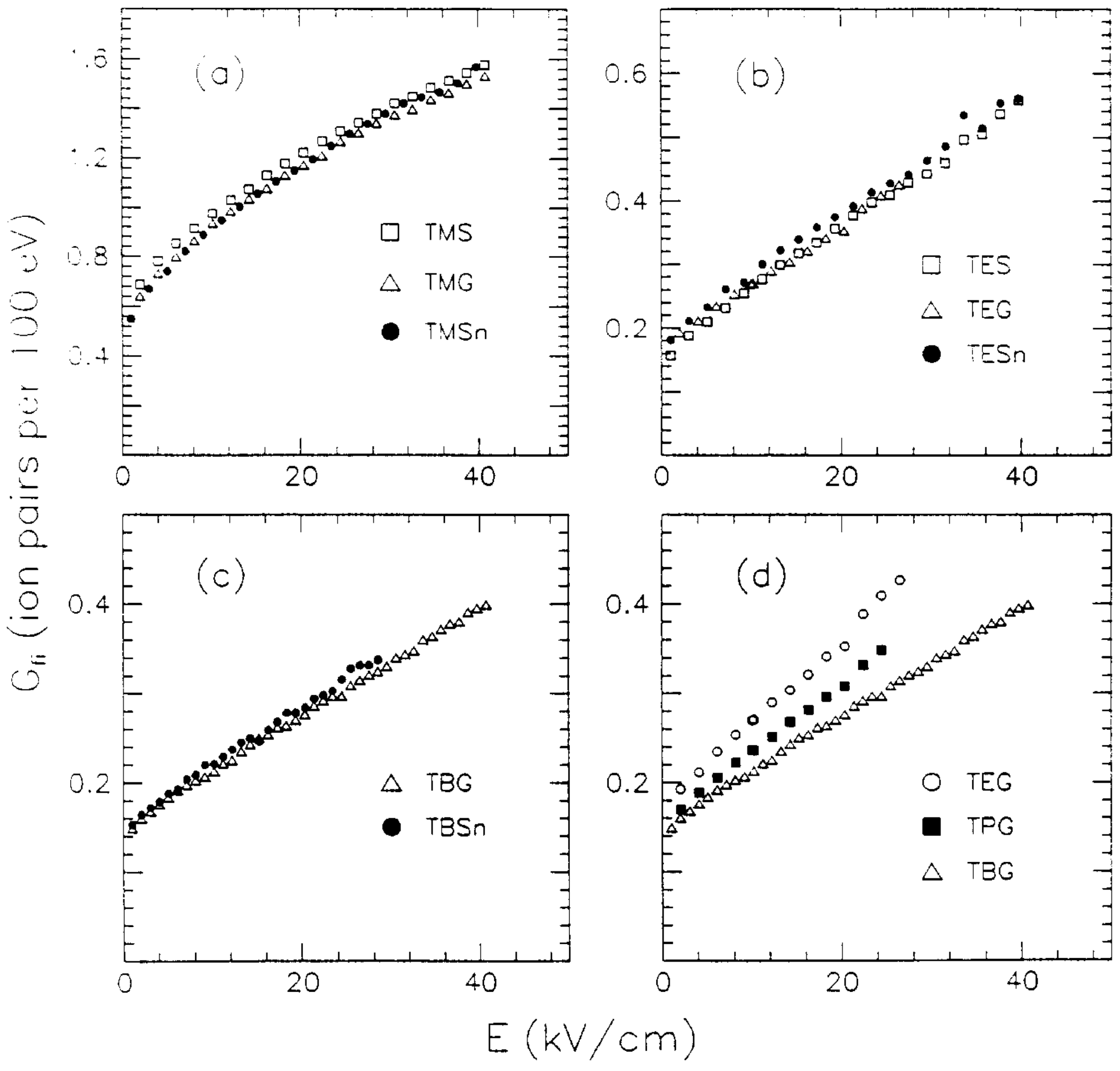

(a)
1.6
1.2
0.8
0.4
TMS
TMG
TMSn
(b)
0.6
0.4
0.2
TES
TEG
TESn
(c)
0.4
0.2
TBG
TBSn
(d)
0.4
0.2
TEG
TPG
TBG
0
20
40
G_{fi} (ion pairs per 100 eV)
E (kV/cm)

Figure 1

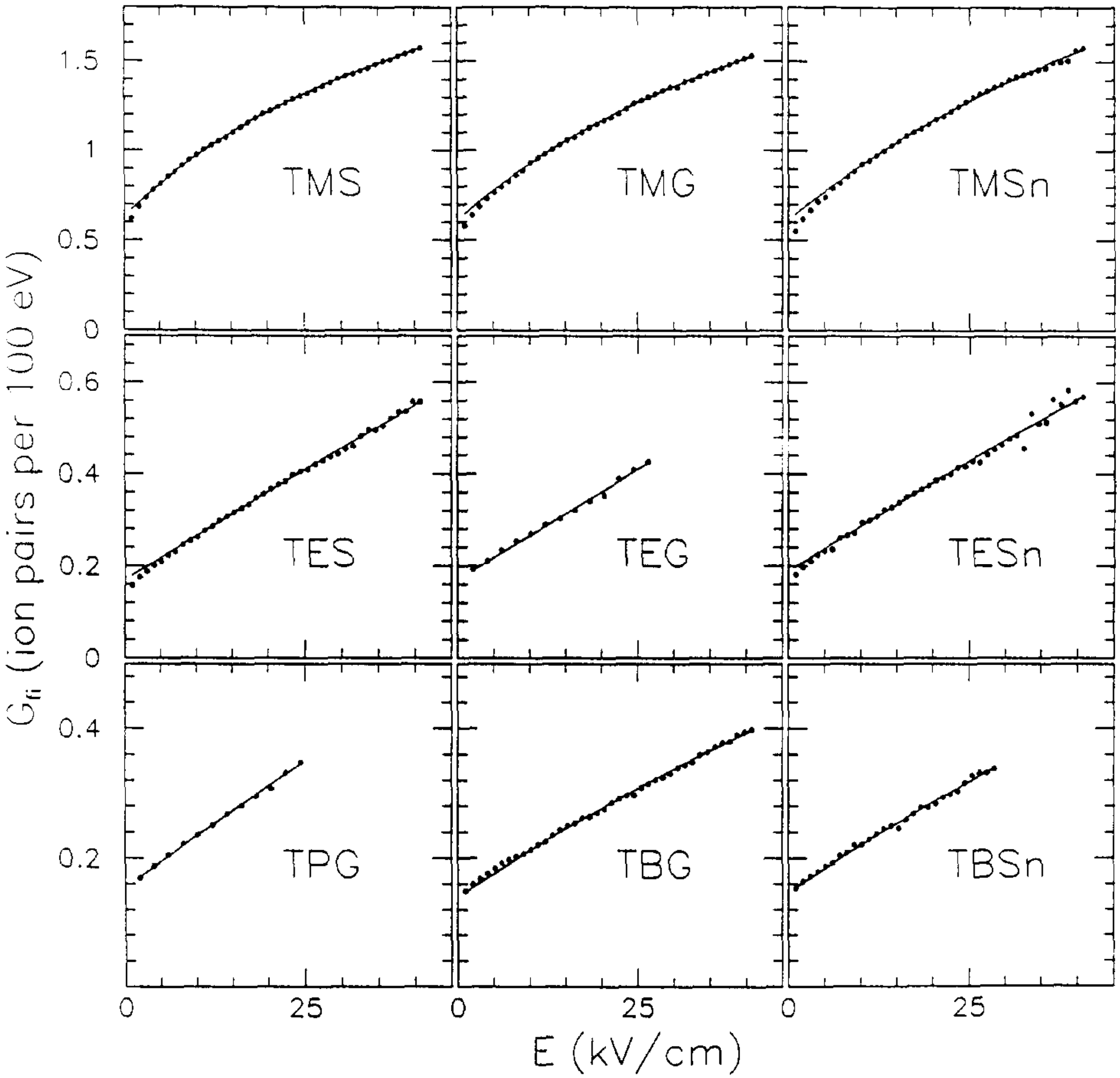
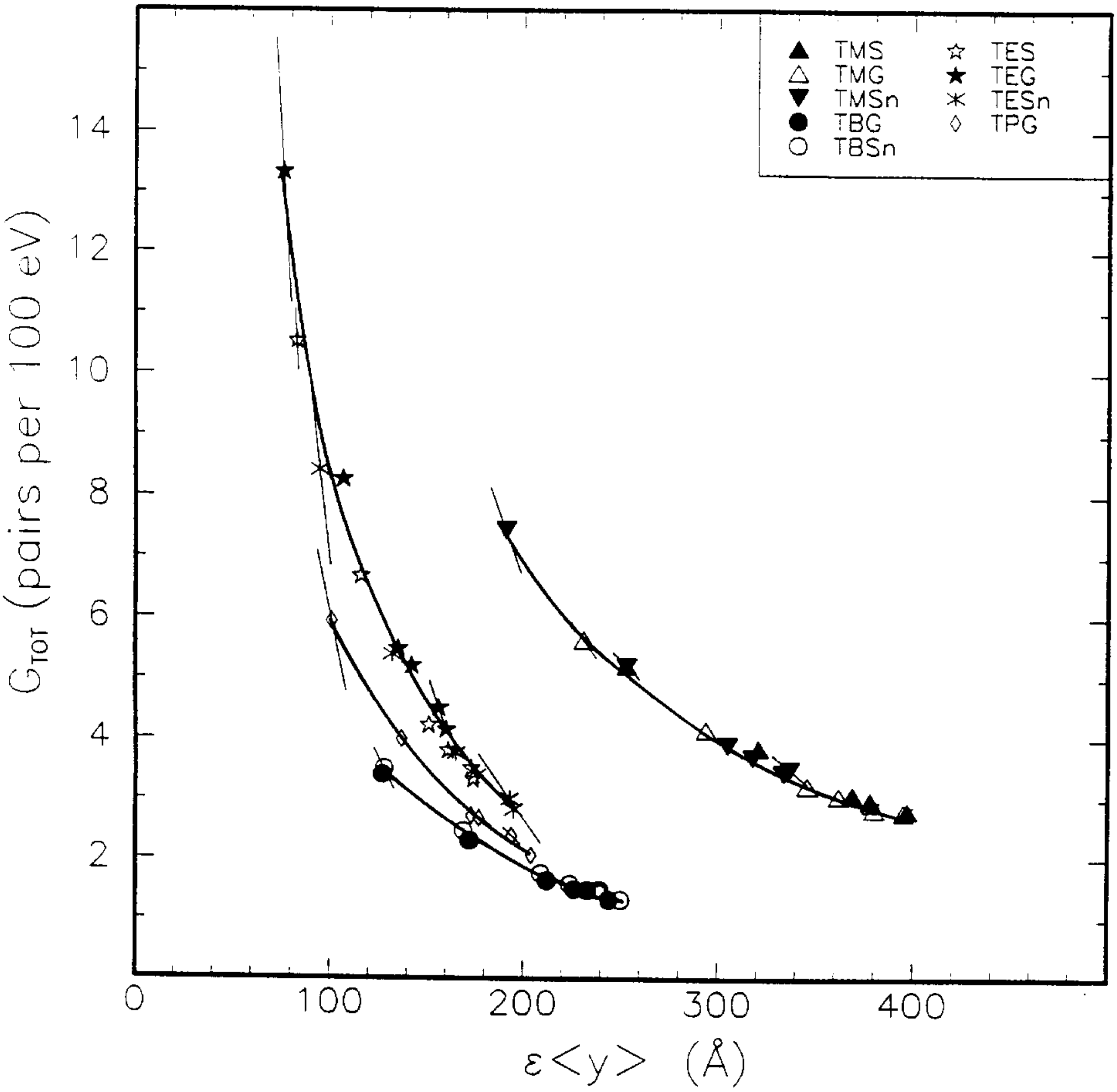

TMS
TMG
TMSn
TES
TEG
TESn
TPG
TBG
TBSn
0
0.5
1
1.5
0
0.2
0.4
0.6
0.2
0.4
0
25
0
25
0
25
G_{fi} (ion pairs per 100 eV)
E (kV/cm)

Figure 2



▲ TMS
△ TMG
▼ TMSn
● TBG
○ TBSn
☆ TES
★ TEG
✱ TESn
◊ TPG
G_{TOT} (pairs per 100 eV)
14
12
10
8
6
4
2
0
100
200
300
400
ε<y> (Å)

Figure 3