the corresponding LeFevre values and the values for the perfluoroalkenes average 11% above the LeFevre values. We conclude that the polarity correction is essential for all perfluorocarbons; however, we must await the measurement of more experimental values before we can conclude that the calculated semiempirical polarizabilities are significantly too high.

Table V shows that for substituted fluorocarbons polarity corrections are not unambiguously necessary to obtain satisfactory agreement with the LeFevre values. For C–F–X or C–F–H–X compounds where X is a halogen the calculated values with polarity corrections average 9% below the LeFevre values while the polarizabilities calculated with no polarity corrections average 6% above the LeFevre values. Since the LeFevre values are probably several per cent lower than the true experimental values, we conclude that for C–F–X and C–F–H–X compounds eq 7 with no polarity corrections gives the most satisfactory results. On the other hand, for C–F–H compounds calculated values with polarity corrections average 3% above the LeFevre values while calculated values without polarity corrections average 18% above the LeFevre values. Thus for C–F–H compounds we conclude that eq 6 with polarity corrections should be used. Overall, the Lippincott–Stutman semiempirical method for calculating molecular polarizabilities gives good results with an accuracy of 10% or better. The method has the appeal of being readily extendable to complex molecules and to new molecules for which no experimental data exist; however, the decision of whether to incorporate polarity corrections or not remains largely empirical.

Both the LeFevre and the Lippincott–Stutman method appear to give sufficiently accurate polarizabilities to test for correlations between polarizability and molecular ionization cross sections.

Molecular Electron Ionization Cross Sections at 70 eV

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Electron ionization cross sections at 70 eV have been measured for 62 hydrocarbons, fluorocarbons, and halogen-substituted hydrocarbons and fluorocarbons. These results together with previously measured results on other molecular classes have been tested against proposed correlations of ionization cross sections with polarizability, diamagnetic susceptibility, and additivity of atomic ionization cross sections. None of these correlations is generally valid but each is valid within a given molecular class. It is striking, however, that there is a single linear correlation with diamagnetic susceptibility for all nonfluorine-substituted compounds. Two empirical equations are developed, based on polarizability and based on modified additivity correlations, which reproduce the experimental cross sections for 98 molecules in a wide variety of molecular classes within average deviations of 3 and 4.5%.

I. Introduction

Electron ionization cross sections for atoms and molecules are of importance for evaluation of radiation chemical data, for mass spectrometric studies of ion–molecule reactions and thermodynamic measurements, and for plasma and space physics. They also constitute one of the fundamental problems concerning electron impact collisions. There has been considerable work on both the experimental and theoretical aspects of electron ionization cross sections. Electron ionization cross sections increase rather rapidly with energy from threshold, reach a flat maximum usually between 50 and 80 eV, and decrease slowly at higher energies. At high electron kinetic energy (>1 keV) there is good agreement between the experimental energy dependence of the cross section and simple theory based on the Born approximation.[2] However, the experimental dependence of cross section on molecular structure is not satisfactorily predicted by theory. At lower electron energies which are relevant to mass spectrometric and radiation chemical studies (70 eV) the theory is even more

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(2) B. L. Schram, A. J. H. Boerboom, M. J. van der Wiel, F. J. de Heer, and J. Kistemaker, "Advances in Mass Spectrometry," Vol. 3, W. L. Mead, Ed., Institute of Petroleum, London, 1966, pp 273–286.

approximate and neither theory nor experiment show particularly good agreement in themselves or with each other.[3,4] Lacking a rigorous predictive theory one turns to semiempirical correlations. It is most desirable to find a correlation between cross sections in the approximate energy independent range near 70 eV and some ground-state molecular property. Three such correlations have been suggested which can be partially justified by approximate theory.

Otvos and Stevenson[3a] suggested that atomic ionization cross sections in the approximate energy independent range could be calculated from the average square radius of the electrons with ionization energies less than 35 eV and that molecular cross sections could be calculated by adding the constituent atomic cross sections. Their experimental data seemed to support this postulate. Lampe, Franklin, and Field[3] obtained more extensive experimental data and concluded that the additivity postulate did not hold, but that a general correlation of cross section with polarizability did exist. Stevenson and Schissler[4] reassessed the situation in 1961 and concluded that (a) the additivity postulate does not hold in general but perhaps holds within a given molecular class of compounds, i.e., alkanes; (b) simple classical theory indicates that cross sections should be proportional to the 0.5 power of the polarizability rather than the 1.0 power as suggested by Lampe, Franklin, and Field; and (c) a general correlation may exist between electron ionization cross section and diamagnetic susceptibility. The proposed cross section correlations can be summarized as: (1) additivity of atomic cross sections, (2) linear with polarizability, and (3) linear with diamagnetic susceptibility.

Part of the difficulty preventing definitive statements about semiempirical correlations has been the disagreement in the experimental cross section values. Even the most careful and recent absolute cross section measurements of two different groups of investigators[5,6] show considerable disparity. However, relative cross sections, measured for a variety of molecules showing a wide variation of values of molecular properties, may provide a better test of such correlations. Consequently, we have measured cross sections for 62 molecules which include hydrocarbons, fluorocarbons, and halogen-substituted hydrocarbons and fluorocarbons. Our results complement those of Harrison, et al.,[7] who measured cross sections for hydrocarbons, ethers, ketones, aldehydes, esters, and alkylbenzenes. Analysis of all results shows clearly that none of the three proposed correlations is generally valid but that each of the three correlations is equally valid within a given molecular class. It is striking, however, that there is a single correlation with diamagnetic susceptibility for all nonfluorine-substituted compounds. An empirical equation based on polarizability is developed here which includes most molecular classes of volatile compounds and reproduces the experimental cross sections for 98

molecules within an average deviation of 3%. A more simplified equation based on modified additivity correlations reproduces the experimental cross sections within an average deviation of 4.5%.

II. Experimental Section

All compounds were obtained commercially and were degassed before use. The quoted purities were greater than 99% for most of the compounds; a few of the fluorocarbons were only quoted as greater than 98% pure.

The ion chamber in a Nuclide 12-90G magnetic mass spectrometer was used to measure the total ionization cross section. The total number of positive ions produced by the electron beam in the ion chamber was collected on a negatively biased repeller with the ionization chamber grounded. The positive ion current collected on the repeller showed a broad maximum at -6 V and all measurements were taken at this voltage. Measurements on all compounds were taken with an electron ionizing voltage of 70 eV and on a few compounds with an electron energy of 35 and 20 eV. Other ion source parameters were trap voltage $= 80$ V, trap current $= 50$ μA, ion chamber temperature $= 50°$.

The total ion current was monitored on the repeller by a Keithley 610B electrometer. To prevent leakage currents between the repeller and the ion chamber a repeller guard was installed in the original ion source. Typical ion currents were in the range of 10^{-9} A.

The total ion current I_t for a given gas with ionization cross section, Q_t, is given by the equation

$$I_t = Q_t I_e dN \qquad (1)$$

where I_e is the ionizing electron current, d is the ionizing path length, and N is the number of molecules per cubic centimeter in the ion source. Since N is proportional to the pressure a plot of I_t vs. pressure should be linear with a slope proportional to the ionization cross section of the compound being measured. This relationship will hold only if the gas flow has similar characteristics into and out of the ion source. In our system a gold foil leak was used to admit gas to the ion source. This was shown to have effusive flow characteristics over the reservoir pressure range of 100 to 15 Torr in which we worked. The reservoir pressure was monitored by a Wallace-Tiernan gauge. The inlet system was heated with heating tape to 50°.

(3) (a) J. W. Otvos and D. P. Stevenson, J. Amer. Chem. Soc., **78**, 546 (1956); (b) F. W. Lampe, J. L. Franklin, and F. H. Field, ibid., **79**, 6129 (1957).

(4) D. P. Stevenson and D. O. Schissler in "The Chemical and Biological Actions of Radiations," Vol. V, M. Haissinsky, Ed., Academic Press Ltd., London, 1961, Chapter 2.

(5) R. K. Asundi and M. V. Kurepa, J. Electron. Control, **15**, 41 (1963).

(6) D. Rapp and P. Englander-Golden, J. Chem. Phys., **43**, 1464 (1965).

(7) A. G. Harrison, E. G. Jones, S. K. Gupta, and G. P. Nagy, Can. J. Chem., **44**, 1967 (1966).

Table I: Total Electron Ionization Cross Sections (cm² × 10¹⁶)

Code no.	Compound	No. of runs	70 eV Cross sec.	Std dev	No. of runs	35 eV Cross sec.	Std dev	No. of runs	20 eV Cross sec.	Std dev
					Rare Gases					
1.	He	7	0.417	0.11						
2.	Ne	7	0.563	0.06						
3.	Ar	16	(3.62)	0.35	7	(2.85)	0.04	13	(0.820)	0.08
4.	Kr	9	5.30	0.19	5	4.07	0.12	8	1.77	0.04
5.	Xe	4	7.50	0.14	5	6.34	0.31	7	4.33	0.28
					n-Alkanes					
6.	CH_4	6	4.67	0.17	6	3.65	0.16	14	1.62	0.02
7.	C_2H_6	4	8.51	0.22	5	6.45	0.28	7	3.32	0.08
8.	c-C_3H_6	4	10.6	0.14						
9.	C_3H_8	4	11.5	0.36	5	8.91	0.32	7	4.79	0.12
10.	C_4H_{10}	4	15.3	0.54	5	11.4	0.44	7	6.45	0.23
11.	C_5H_{12}	4	18.6	0.81						
12.	C_6H_{14}	5	22.5	1.3						
					Alkenes					
13.	C_2H_4	4	6.93	0.21						
14.	C_3H_6	4	10.2	0.61						
15.	i-C_4H_8	4	13.3	0.50						
16.	1-C_4H_8	4	13.7	0.65						
17.	cis-2-C_4H_8	4	13.9	0.56						
18.	$trans$-2-C_4H_8	4	13.8	0.47						
19.	1,3-C_4H_6	2	13.1	0.04						
					n-Perfluoroalkanes					
20.	CF_4	4	4.68	0.13	5	2.22	0.06	13	0.260	0.03
21.	C_2F_6	4	7.79	0.29	5	3.89	0.04	8	0.610	0.07
22.	C_3F_8	4	10.5	0.43	5	5.52	0.08	8	1.07	0.10
23.	c-C_4F_8	5	12.5	0.84						
24.	C_4F_{10}	4	13.5	0.55	5	7.25	0.07	9	1.62	0.14
25.	C_6F_{14}	4	19.5	0.64						
					Perfluoroalkenes					
26.	C_2F_4	4	6.16	0.18						
27.	C_3F_6	4	9.16	0.41						
28.	2-C_4F_8	4	12.2	0.37						
29.	1-C_7F_{14}	4	21.2	0.70						
30.	c-C_6F_{10}	4	16.1	0.44						
					C–F–Cl Compounds					
31.	CF_3Cl	3	7.79	0.11	5	5.15	0.16	8	2.02	0.05
32.	CF_2Cl_2	3	11.2	0.41	5	8.52	0.37	8	4.20	0.22
33.	$CFCl_3$	3	14.6	0.24	5	11.7	0.30	5	6.26	0.47
34.	C_2F_5Cl	4	10.9	0.06						
35.	1,2-$C_2F_4Cl_2$	4	14.3	0.11						
36.	1,1,2-$C_2F_3Cl_3$	4	17.6	0.27						
					C–F–Br Compounds					
37.	CF_3Br	4	9.07	0.37						
38.	CF_2Br_2	4	14.2	0.62						
					C–F–I Compounds					
39.	CF_3I	4	10.9	0.48						
40.	C_2F_5I	4	13.5	0.68						
41.	i-C_3F_7I	4	16.6	0.42						

Table I (*Continued*)

Code no.	Compound	No. of runs (70 eV)	Cross sec. (70 eV)	Std dev (70 eV)	No. of runs (35 eV)	Cross sec. (35 eV)	Std dev (35 eV)	No. of runs (20 eV)	Cross sec. (20 eV)	Std dev (20 eV)
				C–F–H Compounds						
42.	CH_3F	4	4.46	0.20	5	3.03	0.09	8	1.27	0.06
43.	CH_2F_2	3	4.56	0.23	5	2.75	0.03	8	0.940	0.03
44.	CHF_3	4	4.47	0.17	5	2.41	0.03	8	0.547	0.04
45.	$1,1\text{-}C_2H_4F_2$	4	7.77	0.12						
46.	$1,1\text{-}C_2H_2F_2$	4	6.40	0.21						
				Other C–F–X Compounds						
47.	CHF_2Cl	3	7.92	0.13	5	5.66	0.28	8	2.58	0.11
48.	$CHFCl_2$	3	11.5	0.21	5	9.12	0.25	8	4.96	0.33
49.	CF_2ClBr	4	11.1	1.0						
50.	$CF_2ClCFClI$	7	27.2	6.1						
51.	$CF_2ClCHFI$	5	19.8	1.1						
52.	CF_2ClCH_3	4	11.0	0.15						
53.	$CF_2BrCFClBr$	5	23.4	1.3						
54.	$CF_2BrCHFCl$	4	15.8	0.62						
				Alkyl Halides						
55.	CH_3Cl	4	8.68	0.30						
56.	C_2H_5Cl	4	12.0	0.21						
57.	$n\text{-}C_3H_7Cl$	4	15.6	0.21						
58.	$n\text{-}C_4H_9Cl$	5	19.9	1.2						
59.	CH_2Cl_2	4	12.4	0.32						
60.	CH_2ClBr	5	14.7	0.95						
61.	$CHCl_2Br$	7	21.8	4.9						
62.	CH_3Br	4	10.1	0.42						

Table II: Comparison of Literature Values of Ionization Cross Sections ($cm^2 \times 10^{16}$)

Compound	This work[a,d] 70 eV	3b[a,e] 75 eV	3a[a,f] 75 eV	7[a,g] 75 eV	3a[a,h] 75 eV	6[b] 70 eV	5[c] 70 eV	5[b] 70 eV	Average[i]	% av dev
He	0.417	0.397	0.310		0.287	0.420	0.310	0.355	0.357	13
Ne	0.563	0.632	0.598	0.584		0.671	0.550	0.619	0.602	5.5
Ar	(3.62)	(3.62)	(3.62)	(3.62)	(3.62)	(3.62)	(3.62)	(3.62)	(3.62)	...
Kr	5.30	5.33	5.41	5.32	5.35	5.50	5.6	5.70	5.44	2.2
Xe	7.50	7.52		7.68		6.70	7.6	8.00	7.50	3.6
CH_4	4.67	4.78	2.56	4.80	3.58	4.78			4.76	0.8
C_2H_6	8.51	8.59	4.75	8.60	5.30				8.61	0.9
C_3H_8	11.5	11.4	6.37	11.9	7.40				11.6	1.7
$n\text{-}C_4H_{10}$	15.3	14.5	8.96	14.8	9.50				15.2	2.6
$n\text{-}C_5H_{12}$	18.6	19.1		18.1	11.7				18.9	1.1
$n\text{-}C_6H_{14}$	22.5	22.9		21.3					22.8	0.9
C_2H_4	6.93	6.85	3.95	6.28	4.25	7.44			6.88	4.5
C_3H_6	10.2	10.0	5.78	9.20	6.40				9.80	4.1
$c\text{-}C_3H_6$	10.6	11.1		10.7					10.8	1.9
$i\text{-}C_4H_8$	13.3	13.3								
$1\text{-}C_4H_8$	13.7			11.8	8.60					
$cis\text{-}2\text{-}C_4H_8$	13.9									
$trans\text{-}2\text{-}C_4H_8$	13.8									
$1,3\text{-}C_4H_6$	13.1									
CH_3Cl	8.68	5.41	9.70							
CH_3Br	10.1	6.40								
C_2H_5Cl	12.0		12.4							

[a] Cross sections determined on a negatively biased repeller in a mass spectrometer. [b] Absolute cross sections. [c] Comparative cross sections determined on a Lozier type apparatus. [d] Nuclide 12-90G mass spectrometer used. [e] CEC 21-620 cycloidal mass spectrometer used. [f] Westinghouse LV mass spectrometer used. [g] AEI MS-10 mass spectrometer used. [h] CEC Diatron-20 mass spectrometer used. [i] Reference 3a values for hydrocarbons are not included.
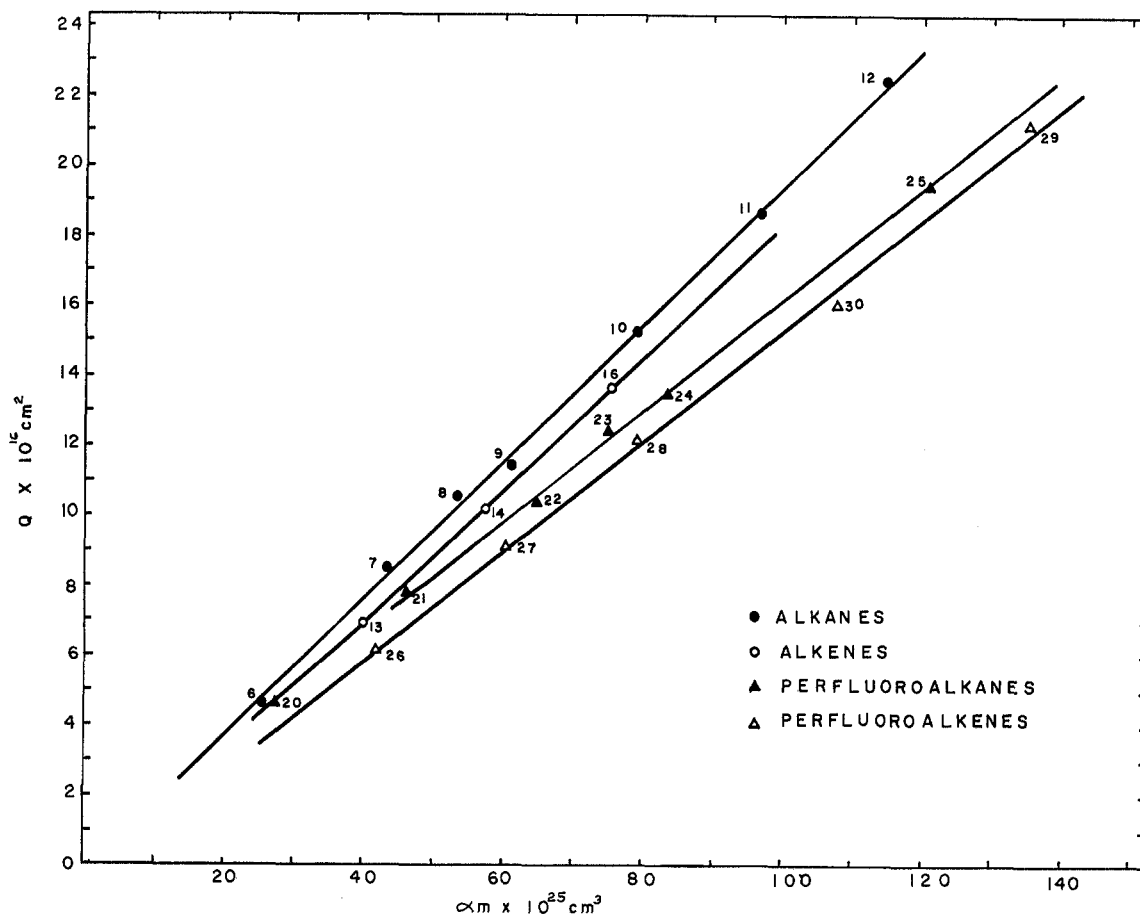
Figure 1. Total electron ionization cross sections (Q) vs. molecular polarizabilities (α_m) for alkanes, alkenes, perfluoroalkanes, and perfluoroalkenes.

As indicated by Harrison, et al.,[7] liquid nitrogen trapping of the cold system may interfere with the ion current measured because of changes in pumping speed as the liquid level decreases. This problem is most serious for gases condensable at liquid nitrogen temperature. We also found this to be a serious problem and that it could be alleviated by using methanol–Dry Ice mixtures as the trap coolant instead of liquid nitrogen. Our pumping system was a 4-in. Consolidated Vacuum Corp. unit with a Model BCN baffle.

All current vs. reservoir pressure plots were linear. The slopes of the plots were determined by a computer least-squares fit to the experimental points. The standard deviation of this fit was generally within 1%. The precision was less for molecules with very low and very high cross sections. Four or more pressure plots were determined for all molecules except for three plots for six molecules and only two plots for one molecule. The standard deviations of these slopes or the total ionization cross section for most of the molecules was less than 4% and the average deviation was less than 2%. Some indication of the day-to-day reliability of the apparatus is that the standard deviation of argon slopes determined over a number of different days was only 10% while the average deviation was about 5%.

III. Results

A. Ionization Cross Sections. Relative electron ionization cross sections were measured for 62 molecules at 70 eV and for 19 molecules at 35 and 20 eV. These cross sections were always measured relative to the cross section for argon and are assigned absolute values based on Asundi and Kurepa's value[5] for the argon ionization cross section of 3.62×10^{-16} cm^2 at 70 eV. It should be pointed out that the absolute ionization cross section for argon is not generally agreed upon by different groups of recent workers.[6] Our measured cross sections at 35 and 20 eV are assigned absolute values based on argon of 2.85×10^{-16} cm^2 (35 eV) and 0.820×10^{-16} (20 eV). These values are those of Rapp and Englander-Golden[6] multiplied by 1.15. The factor, 1.15, normalizes Rapp and Englander-Golden's data for argon at 70 eV to the data of Asundi and Kurepa[5] for argon at 70 eV. The cross sections are summarized in Table I together with the number of current–pressure plots used for each determination and the standard deviation of these independent determinations.

Cross sections for rare gases, alkanes, and alkenes have been measured by several investigators. Table II summarizes the literature results that can be compared to our values; all values have been renormalized to a
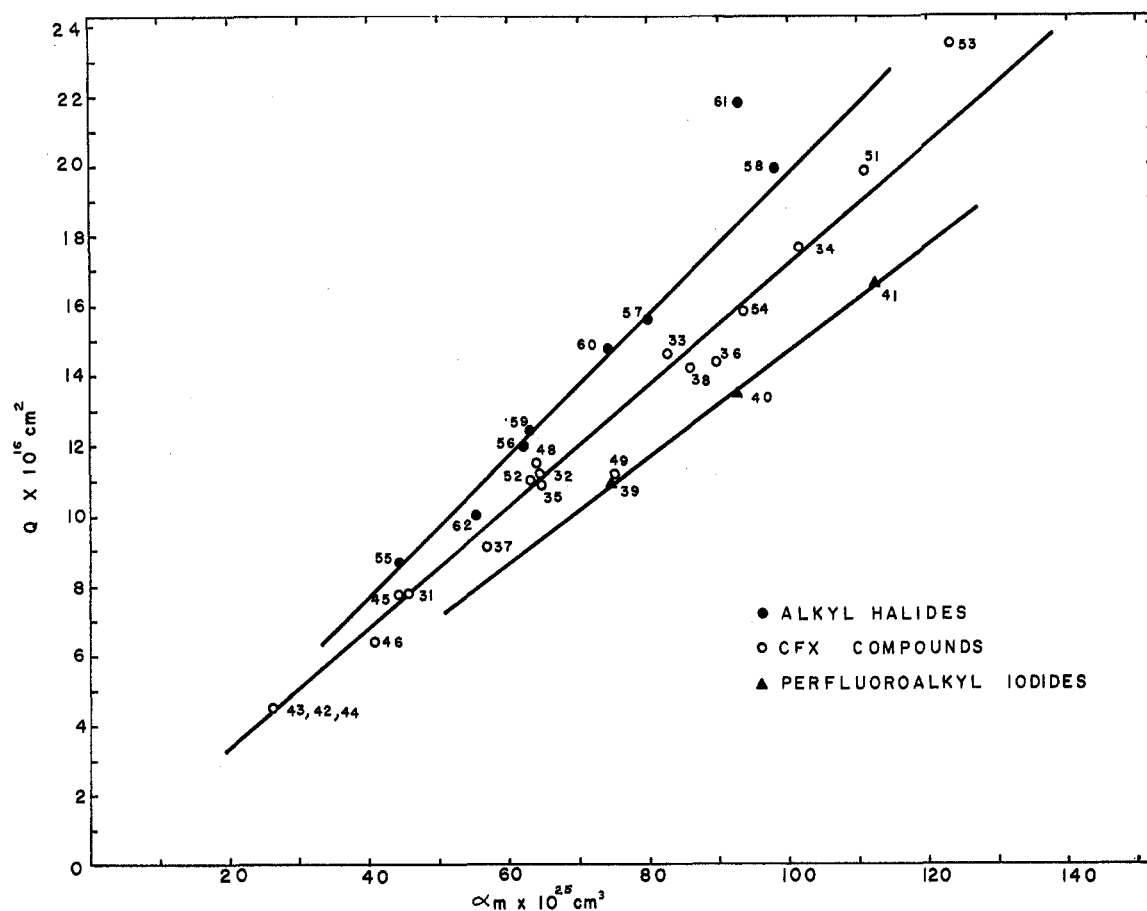
Figure 2. Total electron ionization cross sections (Q) vs. molecular polarizabilities (α_m) for alkyl halides, CFX compounds, and perfluoroalkyl iodides.

Table III: Numerical Key in Compound Identification in the Figures

Code no.	Alkynes	Code no.	Ketones
63.	HCCH	85.	CH_3COCH_3
64.	CH_3CCH	86.	$C_2H_5COCH_3$
65.	C_2H_5CCH	87.	n-$C_3H_7COCH_3$
66.	n-C_3H_7CCH	88.	n-$C_5H_{11}COCH_3$
67.	n-C_4H_9CCH	89.	n-$C_6H_{13}COCH_2$
68.	n-$C_5H_{11}CCH$	90.	$C_2H_5COC_2H_5$
	Ethers		**Aldehydes**
69.	CH_3OCH_3	91.	CH_3CHO
70.	$C_2H_5OCH_3$	92.	C_2H_5CHO
71.	$C_2H_5OC_2H_5$	93.	i-C_3H_7CHO
72.	n-$C_4H_9OCH_3$		
73.	t-$C_4H_9OCH_3$		
74.	$C_3H_7OC_3H_7$		
	Esters		**Alkyl benzenes**
75.	$HCOOCH_3$	94.	C_6H_6
76.	$HCOOC_2H_5$	95.	$CH_3C_6H_5$
77.	$HCOOC_3H_7$	96.	$C_2H_5C_6H_5$
78.	$HCOOCH(CH_3)_2$	97.	n-$C_3H_7C_6H_5$
79.	$HCOOC_4H_9$	98.	n-$C_4H_9C_6H_5$
80.	$HCOOCH_2CH(CH_3)_2$		
81.	n-$C_4H_9COOCH_3$		
82.	CH_3COOCH_3		
83.	n-$C_3H_7COOCH_3$		
84.	$CH_3COOC_2H_5$		

cross section of 3.62×10^{-16} cm² for argon. The agreement of our values with those of other groups is generally good except for the values of Otvos and Stevenson.

B. Correlation of Cross Sections with Molecular Parameters. The correlation of ionization cross sections with molecular polarizability is tested in Figures 1–3. The cross sections listed in Table I are plotted in 1 and 2 while the cross sections in Figure 3 are from Harrison, *et al.*,[7] and are renormalized to our data. The numbers in the figures refer to the number of the compound in Tables I and III. The polarizabilities used are calculated from LeFevre's bond polarizabilities[8] and are tabulated by Beran and Kevan.[9] Polarizability values calculated by the Lippincott–Stutman method[9] give similar correlations to those shown in Figures 1–3.[10] Figure 1 shows separate linear correlations for alkanes, alkenes, perfluoroalkanes, and perfluoroalkenes. No single linear correlation holds for these different molecular types. The fluorocarbons show smaller cross sections for a given molecular polarizability than do the hydrocarbons; this will be found to be generally true.

(8) R. J. W. LeFevre, *Advan. Phys. Org. Chem.*, **3**, 1 (1966).
(9) J. A. Beran and L. Kevan, *J. Phys. Chem.*, **73**, 3860 (1969).
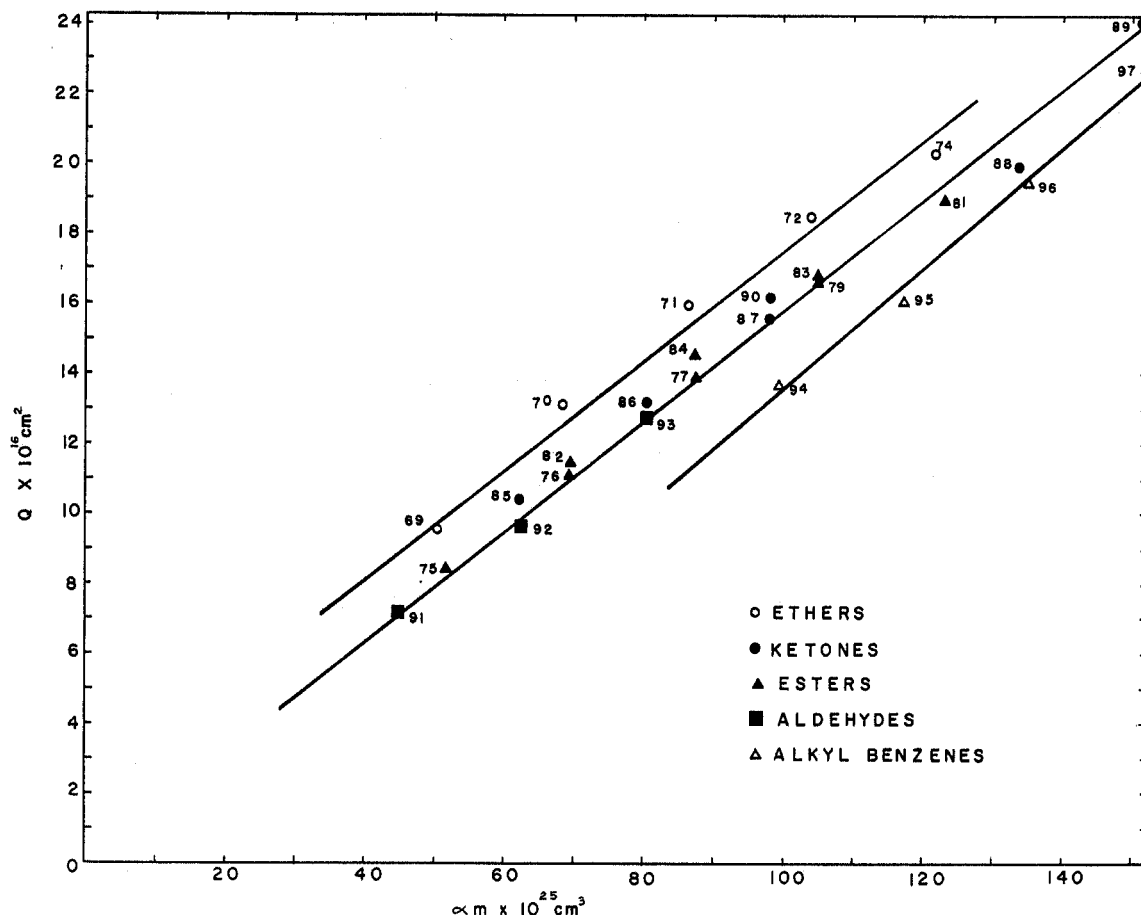(10) J. A. Beran, Ph.D. Thesis, University of Kansas, 1968.

Figure 3. Total electron ionization cross sections (Q) vs. molecular polarizabilities (α_m) for ethers, ketones, esters, aldehydes, and alkyl benzenes.

Figure 2 shows separate correlations for alkyl halides, for C–F–Cl, C–F–Br, C–F–H, and other C–F–X compounds, and for perfluoralkyl iodides. A few of the more complexly substituted compounds such as numbers 50, 53, and 61 in Table I do not fall in any of the correlations indicated in Figure 2. Figure 3 shows results on other molecular classes. The ketones, esters, and aldehydes all form a single linear correlation while the ethers and the alkyl benzenes each form other linear correlations.

In Figures 4–6 the correlation of ionization cross sections with molecular diamagnetic susceptibility is tested. The pertinent diamagnetic susceptibilities have been calculated[9] by the semiempirical method of Haberditzl.[11] Figure 4 illustrates separate linear correlations for alkanes, alkenes, perfluoroalkanes, and perfluoroalkenes. In contrast to the polarizability correlation the alkene lines lie above the alkane lines for both protiated and fluorinated compounds in Figure 4. In Figure 5 the alkyl halides show a linear correlation with diamagnetic susceptibility as do the three perfluoroalkyl iodides. However, the CFCl, CFBr, CFH, and CFX compounds show poor correlation with diamagnetic susceptibility which contrasts with their rela-

tively good correlation with polarizability in Figure 2. The molecular classes in Figure 6 all seem to fit a single linear correlation in contrast to the several separate correlations observed when plotted against polarizability in Figure 3. The esters all lie below the single correlation line drawn in Figure 6 and so deviate slightly from the above generalization.

Otvos and Stevenson[8a] originally suggested that molecular ionization cross sections are given by the sum of the constituent atomic cross sections. Mann[12] has recently calculated atomic cross sections in a more rigorous fashion than done by Otvos and Stevenson. Lin and Stafford[13] have used Gryzinski's[14] classical equation to calculate maximum atomic cross sections. Of the three theoretical evaluations of atomic cross sections, Mann's calculations appear to agree slightly better than the other calculations with the experimental data available.[10] Figure 7 tests the atomic cross section additivity postulate for alkanes, perfluoroalkanes,

(11) W. Haberditzl, Angew. Chem. Int. Ed., 5, 288 (1966).

(12) J. B. Mann, J. Chem. Phys., 46, 1646 (1967).

(13) S. S. Lin and F. E. Stafford, ibid., 48, 3885 (1968).

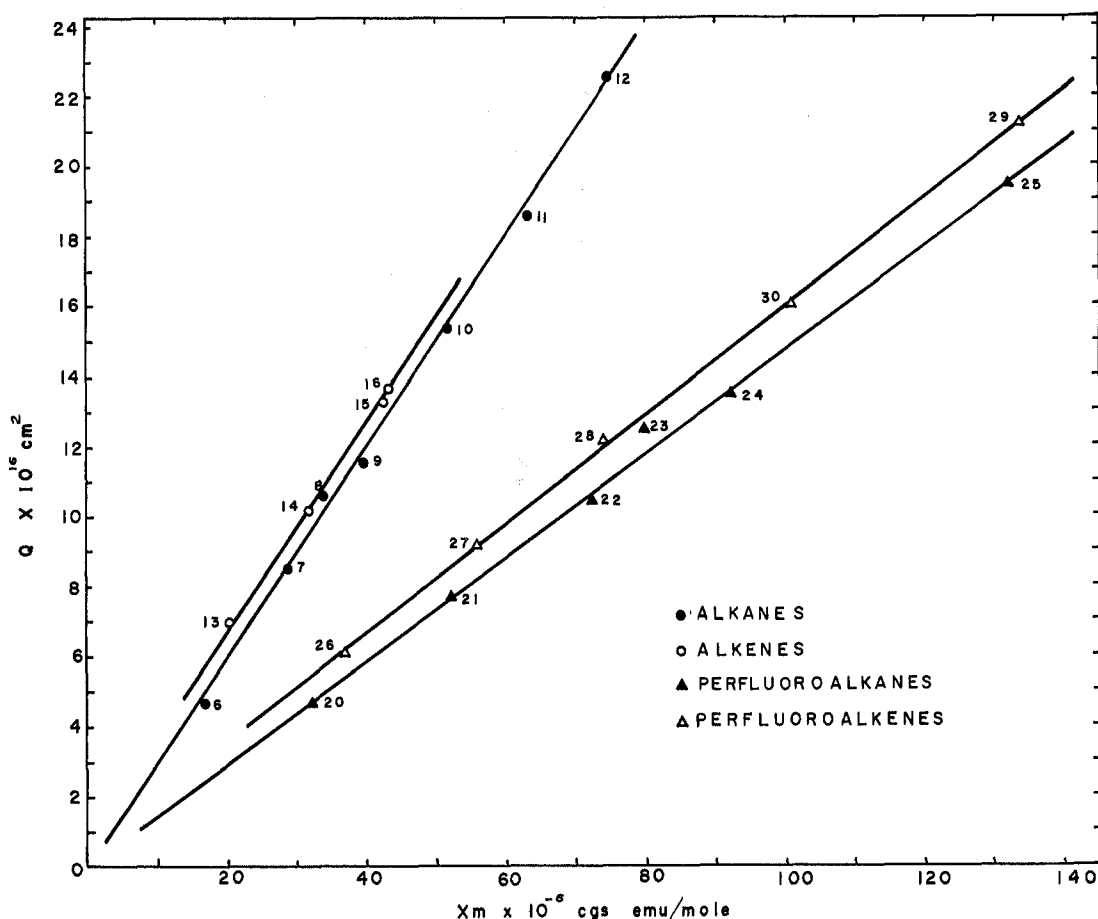(14) M. Gryzinski, Phys. Rev., 138, A322, A336 (1965).

Figure 4. Total electron ionization cross sections (Q) vs. diamagnetic susceptibility (χ_m) for alkanes, alkenes, perfluoroalkanes, and perfluoroalkenes.

and several other molecular classes with Mann's calculated atomic cross sections. The correlations with other calculated values are similar. The dotted line in Figure 7 is of unit slope on which the points should fall if the additivity postulate were obeyed. Even with the improved values for the atomic cross sections it is apparent that the additivity postulate does not hold generally.

IV. Discussion

A. Semiempirical Correlations. Figures 1-7 show that the electron ionization cross sections do not form a single correlation with polarizability, diamagnetic susceptibility, or additivity of atomic cross sections. However, linear correlations within a molecular class are found for each of the three molecular properties. It is interesting that fluorine-substituted compounds show no anomalous behavior.

The polarizability correlations within each molecular class in Figures 1-3 have about the same slopes. Thus these slopes can be superimposed by multiplying the cross sections by a single coefficient for each molecular class. Small changes in slope for a molecular class can be incorporated into an equation with factors of the form n_x^R which represent the number of x atoms raised

to the power R. By utilizing these concepts a general semiempirical equation (I) has been developed which gives total ionization cross sections at 70 eV as a function of the molecular polarizability, α_m, calculated by the δ-function method with bond polarity corrections.[9]

Equation I gives calculated total ionization cross sections with an average deviation of 3% from the experimental cross sections of some 100 molecules reported in this paper and in ref 7. For the determination of the total ionization cross section of any molecule in the molecular classes studied only its polarizability need be known. The δ-function model of molecular polarizability[15] provides a general method for calculating the polarizability of any molecule to the accuracy needed for eq I. For example, the total ionization cross section of CF_3COCF_3 ($\alpha_m = 74.9 \times 10^{-25}$ cm³) should be approximately equal to

$$Q_{CF_3COCF_3} = \frac{1}{5.6 \times 10^{-9} \text{ cm}} (6^{-0.1}) \times$$

$$[\alpha_m - 4.3(3)] = 9.26 \times 10^{-16} \text{ cm}^2$$

For compounds containing more than one iodine atom,

(15) E. R. Lippincott and J. M. Stutman, *J. Phys. Chem.*, **68**, 2926 (1964).
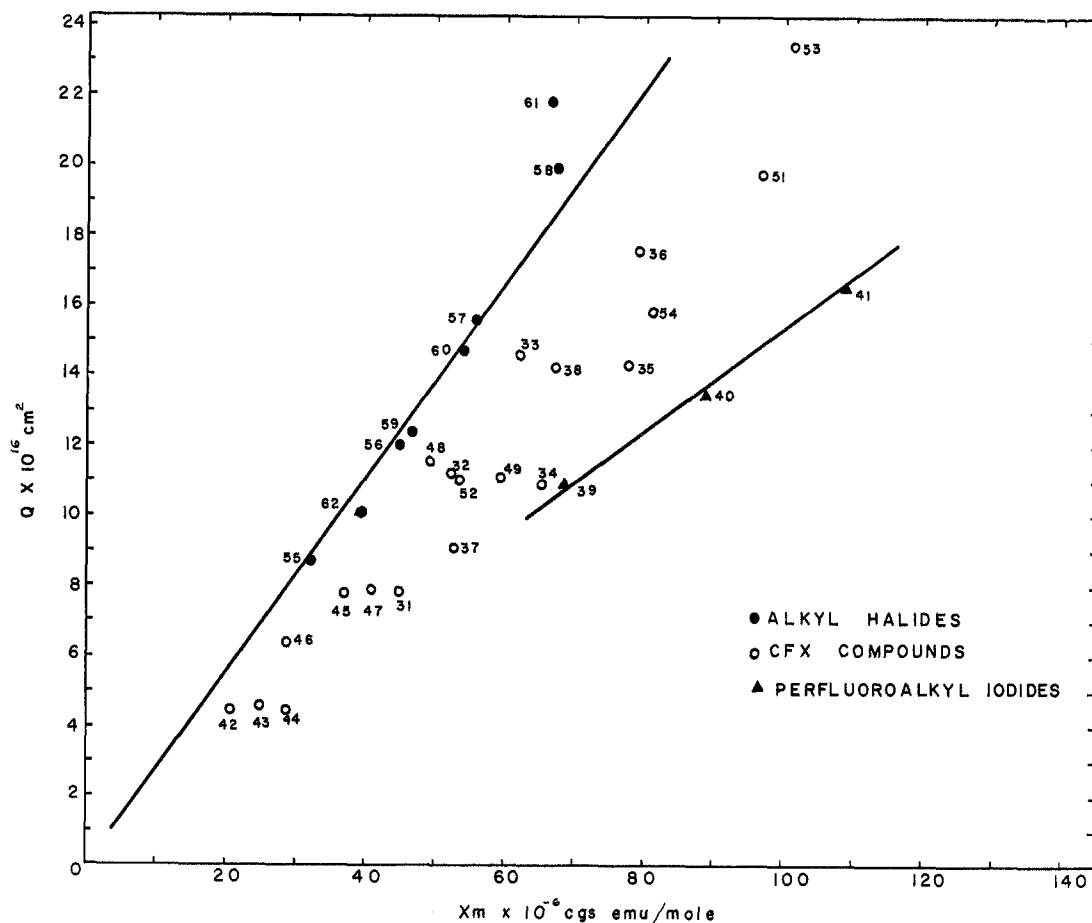
Figure 5. Total electron ionization cross sections (Q) vs. diamagnetic susceptibility (χ_m) for alkyl halides, CFX compounds, and perfluoroalkyl iodides.

a factor of approximately $n_I{}^{0.3}$ should be included in eq I.

$$Q_{\text{exptl}} = \frac{1}{5.6 \times 10^{-9} \text{ cm}} \, n_F{}^{-0.1} n_{Cl}{}^{0.16} n_{Br}{}^{0.255} \times$$

$$\begin{bmatrix} \alpha_m \text{ (alkanes)} \\ 0.91\alpha_m \text{ (alkenes)} \\ \alpha_m + 4.2 - 4.0(n_C - 2)\text{(ethers)} \\ \alpha_m - 4.3n_C \text{ (ketones)} \\ \alpha_m - 4.0(n_C + 1)\text{(aldehydes)} \\ \alpha_m - 4.5n_C \text{ (esters)} \\ \alpha_m - 4.2(n_C + 2)\text{(alkylbenzenes)} \end{bmatrix} \times$$

$$\begin{bmatrix} 0.925 & \text{(monofluoro compounds)} \\ 1.1 & \text{(monochloro compounds} \\ 1.1 & \text{(monobromo compounds)} \\ 1.1 & \text{(monoiodo compounds)} \end{bmatrix} \quad \text{(I)}$$

where $n > 1$; if $n = 0$, let $n_x{}^R = 1$. α_m is the δ-function molecular polarizability with bond polarity corrections and is in units of $\times 10^{-25}$ cm^3.

In contrast to the polarizability correlations which have about the same slope, the diamagnetic susceptibility correlations in Figures 4–6 show distinctly different slopes for hydrocarbons and fluorocarbons. Further-

more, partially fluorine-substituted compounds do not form very good linear correlations within a given molecular class like CFCl or CFH compounds. Instead, these compounds scatter widely between the two slopes defined by alkanes and perfluoroalkanes. It is possible that some of this scatter is due to inaccurate values of χ_m. As the data stand, however, it is difficult to devise a semiempirical equation like eq I which is based on χ_m.

If the fluorine-substituted compounds in Figures 4–6 are ignored, it is most striking that all of the remaining molecular classes (alkanes, alkenes, alkyl halides, ethers, esters, ketones, and aldehydes) do fall on a single linear correlation passing through the origin with no adjustments being necessary. The equation is

$$Q(\times 10^{16} \text{ cm}^2) = 0.278\chi_m \times$$

$$(\times 10^{-6} \text{ cgs emu/mol}) \quad \text{(II)}$$

Equation II is consistent with Stevenson's suggestion[4] of a *general* correlation between ionization cross section and diamagnetic susceptibility. However, the fluorine-substituted compounds disprove the apparent generality of this correlation. More extensive and accurate experimental values of χ_m for fluorine-substituted compounds could possibly change this conclusion but
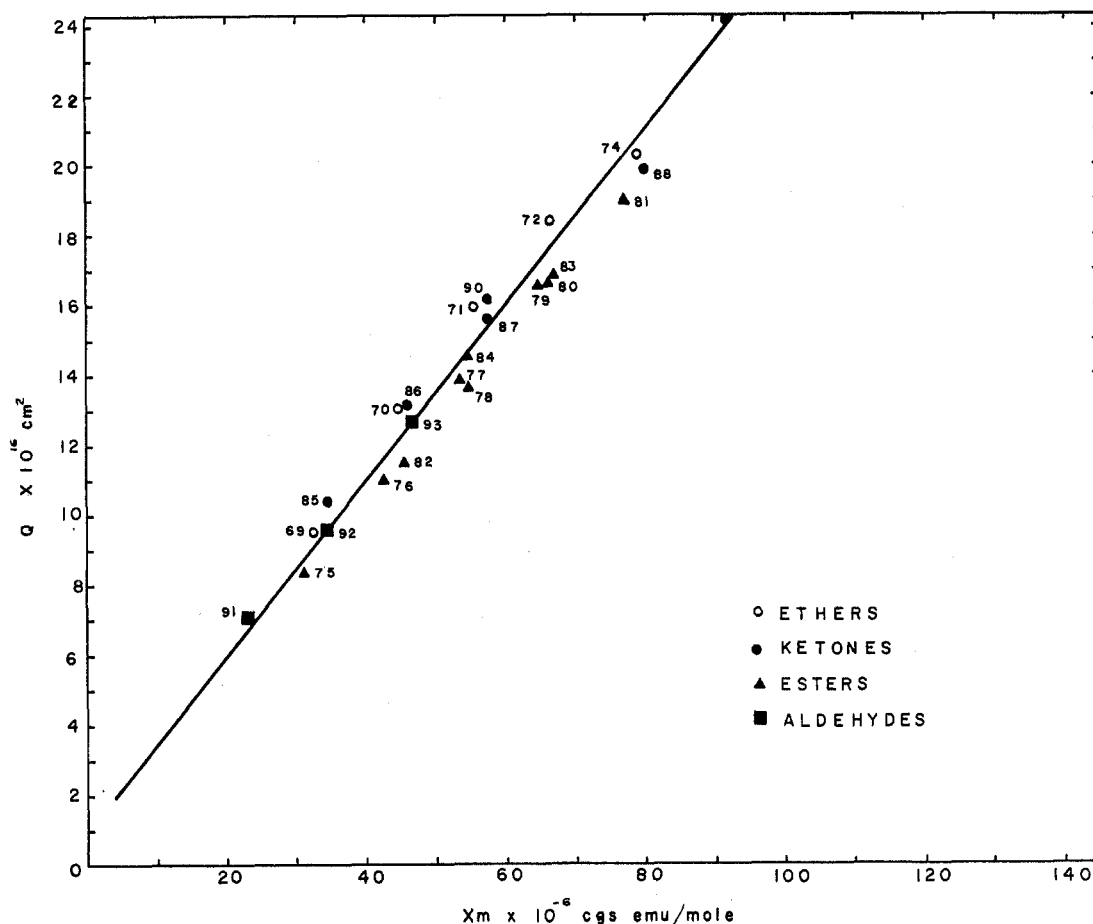
Figure 6. Total electron ionization cross sections (Q) $vs.$ diamagnetic susceptibility (χ_m) for ethers, ketones, esters, and aldehydes.

the experimental values available do not make it seem likely.[9] It is, however, true that for nonfluorine-substituted compounds ionization cross sections do show a single general correlation with diamagnetic susceptibility and not with polarizability.

Linear correlation for different molecular classes with additivity of atomic cross sections is demonstrated in Figure 7. This type of correlation is equivalent to one between ionization cross section and the number of different kinds of atoms in the molecule. Such modified additivity correlations have been derived previously for several molecular classes.[7] We have generalized this approach and derived eq III in which n_X is the number of X atoms and n_{CC} refers to the number of carbon–carbon bonds irrespective of bond type. The factors 2.21, 0.3, and 1.68 in front of the number of carbon, hydrogen, and oxygen atoms, respectively, are Mann's[12] calculated atomic cross sections normalized to 3.62 for argon. Equation III gives calculated total ionization cross sections with an average deviation of 4.5% from the experimental cross sections of some 100 molecules reported in this paper and in ref 7.

The two semiempirical equations (I and III) that have been derived in this work can be applied to most

$$
Q_{\text{exptl}} = 1.34 \times \begin{bmatrix} 2.21n_C \\ +0.3n_H \\ +0.16n_F \\ +3.3n_{Cl}(\text{chlorohydrocarbons}) \\ +2.9n_{Cl}(\text{chlorohalohydrocarbons}) \\ +4.33n_{Br} \\ +5.3n_I \\ +1.68n_O \\ -0.4n_{CC}(\text{alkenes}) \text{ no. of CC bonds} \end{bmatrix} \times
$$

$$
\begin{bmatrix} 0.9 & (\text{ethers}) \\ 0.7 & (\text{esters}) \\ 0.76 & (\text{ketones}) \\ 0.73 & (\text{aldehydes}) \\ 0.7 & (\text{alkylbenzenes}) \\ 0.7 & (\text{alkynes}) \end{bmatrix} \times 10^{-16} \text{ cm}^2 \quad \text{(III)}
$$

molecules that can be vaporized into a mass spectrometer. Equation I appears to be more accurate. It has the disadvantage, however, of being somewhat cumbersome to use and requires the polarizability of the molecule to be known or calculable. Equation III is much easier to use than eq I. It has the added feature that no other property of the molecule has to be known
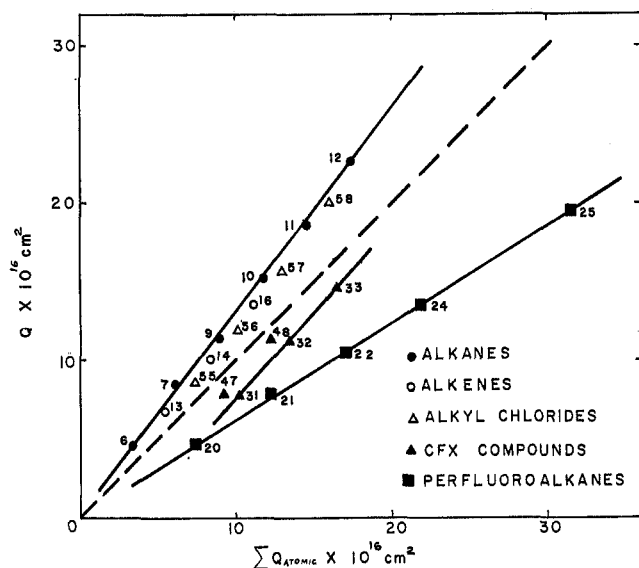
Figure 7. Total electron ionization cross sections (Q) vs. the sum of atomic electron ionization cross sections for alkanes, alkenes, alkyl chlorides, CFX compounds, and perfluoroalkanes.

except its molecular formula. It appears that eq II can be validly used for nonfluorine-substituted compounds if the diamagnetic susceptibility is known.

B. Hydrogen vs. Fluorocarbon Cross Sections. One of the interesting findings in this work is that ionization cross sections for fluorocarbons are less than those for the corresponding hydrocarbons. Pairs of molecules which show this trend are C_2F_6 (7.79) vs. C_2H_6 (8.51), C_3F_8 (10.5) vs. C_3H_8 (11.5), C_4F_{10} (13.5) vs. C_4H_{10} (15.3), C_2F_4 (6.16) vs. C_2H_4 (6.93), and C_3F_6 (9.16) vs. C_3H_6 (10.2). Also whenever a fluorine atom is substituted for a hydrogen atom in a molecule the cross section decreases and when substituted for another halogen atom the cross section decreases substantially. Typical examples of this trend in cross sections appear in the compounds CF_3Cl (7.79) vs. CHF_2Cl (7.92) and CF_3Br (9.07) vs. CH_3Br (10.1).

These observations are real since total ionization efficiency curves for fluorocarbons as well as for hydrocarbons show that 70 eV electron energy is about 5–15 eV above the energy at which the maximum total ionization cross section occurs. Thus the measurements are compared in the nearly energy-independent region for the ionization cross section.

However, it would seem that the decrease in 70-eV ionization cross section with increasing fluorine substitution reflects the somewhat unique properties of the ground-state fluorine atom. The high electronegativity and high ionization potentials of fluorine compared to hydrogen and other halogen atoms are emphasized in Table IV. For fluorosubstituted hydro- or halohydro-

Table IV: Ionization Potentials[a] and Electronegativities[b] of Some Elements

| Element | Ionization potentials[c] | | | | Electro-negativity |
	I	II	III	IV	
Ar	15.68	27.76	40.75	...	0
H	13.527	...	...	...	2.1
F	17.34	34.81	62.35	86.72	4.0
Cl	12.952	23.76	39.69	53.16	3.0
Br	11.80	19.1	25.7	...	2.8
I	10.6	19.4	...	...	2.5

[a] "Handbook of Chemistry and Physics," 44th ed, The Chemical Rubber Publishing Co., Cleveland, 1963. [b] Pauling's electronegativity scale. [c] Units of volts.

carbons, fluorine, because of its high electronegativity, not only has its own lone-pair orbital electrons bound tightly but also increases the energy of the electron pair in the C–F bond. This qualitatively decreases the probability of ionization of the entire molecule. One expects the chemical properties of fluorine to be an even more decisive factor at electron impact energies below the energy of the maximum total ionization cross section.

The total ionization cross sections for the series CH_nF_{4-n} at 70 eV are nearly the same but as the energy is decreased from 70 to 35 to 20 eV, a trend in cross sections develops in which $CH_4 > CH_3F > CH_2F_2 > CHF_3 > CF_4$. This fact is also shown in the perfluoroalkane and the CF_nCl_{4-n} series. As the electron energy decreases, the slope of the cross section vs. polarizability decreases for the perfluoroalkanes and increases for the CF_nCl_{4-n} series.