Correlation of Positronium Annihilation Cross-section of Molecules with Their Topological Features[†]

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Positronium annihilation cross-section of 182 organic compounds containing a variety of functional groups can be very well correlated with the connectivity parameters reflecting the topological features of the molecules. The correlation involving first order valence connectivity term $(^1\chi_v)$, third order cluster valence connectivity term $(^3\chi^v_c)$ and the number of non-hydrogen atoms gives the value of cross-section within the experimental accuracy.

THE positronium annihilation quenching cross-sections (averaged over the velocity distribution of the positronium atoms and expressed as $\left\langle \sigma v \right\rangle_{av}$) are computed[1] from experimentally measured life-times, τ_2, of triplet positronium atoms employing Eq. (1).

$$\left\langle \sigma v \right\rangle_{av} = (M/\rho \; N_0)\,(1/\tau_2) \qquad ..(1)$$

In Eq. (1), M is the molecular weight of the compound, ρ is the mass density and N_0 is the Avogadro number. The available correlations[2-8] of positronium annihilation cross-sections require a knowledge of experimentally determined values of one or the other molecular properties. Molecular connectivity[9], on the other hand, reflects the topology of a molecule and can be calculated from its structural formula. Recently these parameters have been found to correlate with a number of physical[10-14] and biological[15-17] properties. In this paper an attempt has been made to correlate positronium annihilation quenching cross-sections with the connectivity parameters.

Calculations

The vertex connectivity parameter of order $m(^m\chi)$ is calculable from the general Eq. (2) where $^m n_s$ is

$$^m\chi = \sum_{j=1}^{^m n_s} \left[\prod_{i=1}^{m+1} (\delta_i)_j^{-1/2} \right] \qquad ..(2)$$

the number of mth order subgraphs and δ_i is the vertex connectivity for the ith atom. In the present investigations the first order connectivity parameter and the third order cluster terms have been found to correlate most successfully with the annihilation cross-sections. The calculation of these two connectivity parameters is explained taking 2,3-dimethylpentane as a typical example. The numbering and δ values (encircled) for various atoms in this molecule are given in Fig. 1. These parameters have been calculated using Eqs (3) and (4).

$$\chi = \frac{1}{\sqrt{\delta_1\delta_2}} + \frac{1}{\sqrt{\delta_2\delta_3}} + \frac{1}{\sqrt{\delta_3\delta_4}} + \frac{1}{\sqrt{\delta_4\delta_5}}$$
$$+ \frac{1}{\sqrt{\delta_6\delta_2}} + \frac{1}{\sqrt{\delta_7\delta_3}} \qquad ..(3)$$

$$^3\chi_c = \frac{1}{\sqrt{\delta_1\delta_2\delta_3\delta_6}} + \frac{1}{\sqrt{\delta_2\delta_3\delta_4\delta_7}} \qquad ..(4)$$

Positronium annihilation cross-section is a property due to interaction of the positronium atom and the valence electrons of the molecule[18]. Consequently, the valence connectivity terms, $^m\chi^v$, were preferred over simple vertex connectivity parameters. Given a vertex connectivity parameter of first order, the corresponding valence parameter $^1\chi^v$ can be calculated using Eq. (5)

$$^1\chi^v = {}^1\chi - S \qquad ..(5)$$

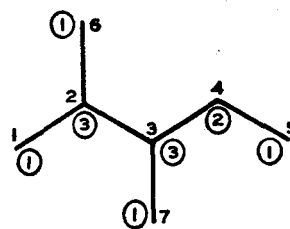Fig. 1 — Numbering of carbon atoms and δ-values (encircled) in the case of 2,3-dimethylpentane

where S is the correction term for a particular functional group. The valence connectivity parameters of higher orders can be calculated using Eq. (2) by replacing δ_i values with δ_i^v values. The valence δ values, δ_i^v can be computed for different atoms in different groups from Eq. (6)

$$\delta_t^v = Z_i - h \qquad ..(6)$$

In Eq. (6) Z_i is the number of electrons in the valence shell of the ith atom and h is the number of hydrogens attached to this atom. For halogens however the δ^v values are selected empirically[9]. The δ^v values employed in the present study are given in Table 1.

In cyclic molecules there is one extra bond as compared to the corresponding open chain isomers. Therefore, in all cyclic molecules correction[11] has been made to account for this extra bond. For cyclic alkanes and alkenes and benzenes correction terms of $1/\sqrt{4}$, $1/\sqrt{6}$ and $1/\sqrt{9}$, respectively have been subtracted from the normal $^1\chi^v$ value. We have repeated the calculations with unmodified values of $^1\chi^v$ as well. The results in two cases are however not significantly different.

All data were processed at the RCC, Chandigarh on the DECSYSTEM-20.

Results and Discussion

The compounds studied in this paper are listed in Table 2. The observed values of $\left\langle \sigma v \right\rangle_{av}$ for these compounds are those quoted by Gray et al.[6], unless otherwise specified. The $\left\langle \sigma v \right\rangle_{av}$ values for iodo compounds studied by Gray et al. are not reliable due to small intensities and have not been included in the regression analysis. The connectivity parameters for a number of hydrocarbons have been taken from ref. 9 and for rest of the molecules the $^1\chi^v$ and $^3\chi_c^v$ parameters have been calculated according to Eq. (1), using the computer programm KNKTVT developed by us. This program does

TABLE 1 — δ^v VALUES FOR HETEROATOMS IN DIFFERENT GROUPS

Atom	Group	δ^v	Atom	Group	δ^v
O	—O—	6		H—C=	3
	=O	6	Cl	Cl	0.690
	OH	5	Br	Br	0.285
C	—C=	4	F	F	20*

*Contribution due to F in connectivity is to be subtracted

TABLE 2 — COMPARISON OF OBSERVED AND CALCULATED VALUES OF $\left\langle \sigma v \right\rangle_{av}$

No.	Compd.	$\left\langle \sigma v \right\rangle_{av}(\times 10^{14}\,cm^3/sec)$		
		Obs[a]	Calc.	
			Eq. (8)	Eq. (9)
1.	n-Butane	3.65	3.97	3.67(3.71)
2.	n-Pentane	4.69	4.92	4.64(4.68)
3.	n-Hexane	5.56	5.88	5.61(5.64)
4.	n-Heptane	6.63	6.83	6.58(6.61)
5.	n-Octane	7.58	7.79	7.55(7.57)
6.	n-Nonane	8.59	8.74	8.52(8.54)
7.	n-Decane	9.47	9.69	9.49(9.50)
8.	n-Undecane	10.50	10.65	10.46(10.57)
9.	n-Dodecane	11.55	11.60	11.43(11.43)
10.	n-Tridecane	12.38	12.56	12.40(12.40)
11.	n-Tetradecane	13.41	13.51	13.37(13.36)
12.	n-Pentadecane	14.33	14.45	14.30(14.33)
13.	n-Hexadecane	15.38	15.42	15.31(15.30)
14.	n-Heptadecane	16.24	16.37	16.28(16.26)
15.	n-Octadecane	17.08	17.33	17.25(17.23)
16.	2-Methylbutane	4.39	4.70	4.48
17.	2,2-Dimethylpropane	4.08	4.08	3.91
18.	2-Methylpentane	5.34	5.66	5.45
19.	3-Methylpentane	5.48	5.72	5.50
20.	2,3-Dimethylbutane	5.30	5.48	5.34
21.	2,2-Dimethylbutane	5.20	5.20	5.04
22.	3-Methylhexane	6.46	6.67	6.47
23.	2,4-Dimethylpentane	6.27	6.39	6.26
24.	2-Methylpentane	7.27	7.56	7.39
25.	3-Methylpentane	7.22	7.63	7.44
26.	2,5-Dimethylhexane	7.17	7.34	7.23
27.	2,3,4-Trimethylpentane	7.03	7.27	7.20
28.	2,2,4-Trimethylpentane	6.91	6.88	6.82
29.	2,2,4-Trimethylhexane	7.87	7.90	7.83
30.	2,2,5-Trimethylhexane	7.80	7.84	7.79
31.	2,4,6,10-Tetramethyl-pentadecane	17.61	17.58	17.72
32.	Cyclopentane	4.59	4.57	4.56
33.	Cyclohexane	5.65	5.53	5.53
34.	Cycloheptane	6.69	6.48	6.50
35.	Cyclooctane	7.84	7.44	7.47
36.	Cyclododecane	11.93	11.25	11.35
37.	Methylcyclohexane	6.32	6.32	6.38
38.	Ethylcyclohexane	7.25	7.33	7.39
39.	Propylcyclohexane	8.18	8.28	8.36
40.	Butylcyclohexane	9.32	9.24	9.32
41.	Hexylcyclohexane	11.36	11.15	11.27
42.	Methylcyclopentane	5.41	5.37	5.41
43.	Propylcyclopentane	7.23	7.33	7.39
44.	tert-Butylcyclohexane	8.90	8.64	8.84
45.	1,4-Dimethylcyclohexane	7.05	7.12	7.24
46.	cis-1,2-Dimethylcyclohexane	7.13	7.16	7.27
47.	trans-1,2-Dimethyl cyclohexane	7.03	7.16	7.27

		Obs[a]	Eq. (8)	Eq. (10)
48.	Methyl alcohol	1.72	1.67	1.59
49.	Ethyl alcohol	2.56	2.68	2.61
50.	n-Propyl alcohol	3.56	3.64	3.56
51.	n-Butyl alcohol	4.57	4.59	4.51
52.	n-Octyl alcohol	8.25	8.41	8.33
53.	n-Dodecyl alcohol	12.24	12.23	12.14
54.	Isoamyl alcohol	5.35	5.33	5.37
55.	Isopropyl alcohol	3.40	3.48	3.48
56.	Isobutyl alcohol	4.57	4.37	4.42
57.	sec-Butyl alcohol	4.47	4.49	4.46
58.	tert-Butyl alcohol	3.93	4.05	4.33
59.	Propyleneglycol	4.03	4.16	4.14

—Contd.

TABLE 2—*Contd.*

No.	Compd.	$\langle \sigma v \rangle_{av} \times 10^{14}$ (cm³/sec)	
		Obs[a]	Calc.
60.	Cyclopentanol	5.26	5.14 5.11
61.	Cyclohexanol	6.45	6.09 6.06
62.	Benzyl alcohol	6.32	6.35 6.34
63.	Diethyl ether	4.43	4.57 4.49
64.	Diisopropyl ether	5.94	5.36 5.45
65.	Anisole	6.52	6.32 6.29
66.	Benzyl ether	12.38	11.90 11.96
67.	Ethyl vinyl ether	4.24	4.27 4.20
68.	Dioxane	4.71	4.99 4.93
69.	Tetrahydrofuran	4.58	4.40 4.32
70.	Isobutylene oxide	4.22	4.06 4.16
71.	Acetaldehyde	2.61	2.51 2.43
72.	Butyraldehyde	4.36	4.45 4.37
73.	Benzaldehyde	6.38	6.24 6.22
74.	Acetone	3.36	3.32 3.31
75.	Methyl ethyl ketone	4.49	4.34 4.31
76.	Methyl pentyl ketone	7.40	7.20 7.17
77.	Methyl hexyl ketone	8.46	8.16 8.12
78.	Methyl isobutyl ketone	6.15	6.03 6.12
79.	Acetophenone	7.93	8.11 8.12
80.	Acetylacetone	5.40	5.67 5.70
81.	Cyclohexanone	5.88	5.96 5.93
82.	Acetic acid	2.74	3.12 3.08
83.	Propionic acid	3.67	4.13 4.08
84.	Butyric acid	4.68	5.08 5.03
85.	Octanoic acid	8.43	8.90 8.85
86.	Isopropyl formate	4.73	4.93 4.94
87.	Methyl propionate	4.79	4.99 4.94
88.	Benzyl benzoate	12.92	12.45 12.51
89.	Benzyl salicylate	12.46	13.09 13.18
90.	Bis-(2-ethoxyethyl sebacate	20.16	20.72 20.72
91.	Bis-(2-ethylhexyl) adipate	23.59	23.12 23.22
92.	Pentyl acetate	7.39	7.87 7.83
93.	*n*-Propyl formate	4.81	5.08 5.01

No.	Compd.	Obs	Eq. (8)	Eq. (11)
94.	1-Chloropropane	4.02	4.09	3.96
95.	1-Chlorobutane	4.86	5.04	4.94
96.	1-Chloroheptane	7.68	7.91	7.88
97.	1-Chlorododecane	12.77	12.68	12.78
98.	1-Chlorohexadecane	16.32	16.50	16.70
99.	1-Chlorooctadecane	18.31	18.40	18.66
100.	2-Chloropropane	3.85	3.74	3.74
101.	2-Chlorobutane	4.84	4.78	4.73
102.	1,2-Dichlorobenzene	6.20	6.68	6.50
103.	Chlorocyclohexane	6.47	6.41	6.33
104.	*cis*-1,2-Dichloroethylene	3.73	3.81	3.63
105.	*trans*-1,2-Dichloroethylene	3.74	3.81	3.63
106.	Trichloroethylene	4.52	4.63	4.54
107.	1,2,4-Trichlorobenzene	6.82	7.60	7.48
108.	1-Chloronaphthalene	9.08	8.76	8.51
109.	Chlorobenzene	6.01	5.75	5.51
110.	1-Bromoethane	3.38	3.60	3.53
111.	1-Bromopropane	4.60	4.55	4.51
112.	1-Bromobutane	5.28	5.51	5.49
113.	1-Bromopentane	6.30	6.46	6.47
114.	1-Bromooctane	9.54	9.33	9.41
115.	1-Bromodecane	11.41	11.23	11.37
116.	1-Bromotetradecane	15.70	15.05	15.29
117.	1-Bromohexadecane	17.71	16.96	17.25
118.	2-Bromobutane	5.33	5.08	5.16
119.	Bromobenzene	5.41	6.04	5.89
120.	*o*-Fluorotoluene	5.79	6.05	5.70
121.	*m*-Fluorotoluene	5.67	6.04	5.70
122.	*p*-Fluorotoluene	5.82	6.04	5.70
123.	Fluorobenzene	4.59	5.20	4.82
124.	Fluorohexane	5.96	6.10	5.89

TABLE 2—*Contd.*

No.	Compd.	$\langle \sigma v \rangle_{av} \times 10^{14}$ (cm³/sec)		
		Obs[a]		Calc.
		Obs	Eq. (8)	Eq. (12)
125.	Benzene	4.80	4.83	4.78
126.	Benzene-*d*[b]	4.74	4.83	4.78
127.	1,2,4-Trimethylbenzene	7.40	7.36	7.34
128.	Toluene	5.64	5.67	5.63
129.	Ethylbenzene	6.72	6.68	6.57
130.	*n*-Butylbenzene	8.33	8.59	8.40
131.	*n*-Amylbenzene	9.39	9.55	9.32
132.	*n*-Octylbenzene	12.32	13.25	12.37
133.	*s*-Butylbenzene	8.31	8.48	8.34
134.	*t*-Butylbenzene	7.99	8.03	8.02
135.	Cumene	7.17	7.47	7.39
136.	*o*-xylene	6.61	6.52	6.49
137.	*m*-xylene	6.56	6.50	6.48
138.	*p*-xylene	6.49	6.50	6.48
139.	Cyclohexylbenzene	10.03	10.09	10.06
140.	Tetrahydronaphthalene	8.56	8.20	8.25
141.	Ethynylbenzene	6.07	6.25	6.42

No.	Compd.	Obs	Eq. (8)	Eq. (13)
142.	Hexene-1	5.59	5.55	5.62
143.	Dodecene-1	11.16	11.27	11.27
144.	4-Methylpentene-1	5.27	5.33	5.50
145.	Pentene-2(*cis* 66.8%)	4.64	4.60	4.68
146.	Pentene-2 (*cis* 98.5%)	4.62	4.60	4.68
147.	Hexene-2(*cis* 50.8%)	5.74	5.55	5.62
148.	Hexene-2(*cis* 82.2%)	5.56	5.55	5.62
149.	Heptene-2(*cis* 79.1%)	6.55	6.50	6.56
150.	Heptene-2(*cis* 98.6%)	6.48	6.50	6.56
151.	Octene-2(*cis* 69%)	7.55	7.46	7.50
152.	Octene-2(*cis* 97.5%)	7.49	7.46	7.50
153.	*trans*-4-Methylpent-2-ene	5.33	5.36	5.52
154.	*cis*-4-Methylpent-2-ene	5.21	5.36	5.52
155.	2-Methylpent-2-ene	5.74	5.38	5.53
156.	2-Methylpent-1-ene	5.33	5.39	5.54
157.	2,3-Dimethylbut-1-ene	5.31	5.24	5.46
158.	2,4,4-Trimethylpent-2-ene	7.23	6.68	7.03
159.	2,4-Hexadiene	5.26	5.24	5.55
160.	2,3-Dimethylbut-2-ene	5.47	5.23	5.48
161.	2-Hexyne	5.79	5.37	5.58
162.	3-Hexene[c]	6.16	5.58	6.62
163.	1-Hexyne	5.58	5.40	5.59
164.	3-Hexyne	6.05	5.42	5.59
165.	1,5-Hexadiene	5.63	5.22	5.55
166.	1,4-Hexadiene	5.84	5.22	5.56
167.	1,3-Hexadiene	5.39	5.26	5.56
168.	1,3-Pentadiene	4.72	4.28	4.61
169.	1,4-Pentadiene	5.04	4.26	4.61
170.	Cyclopentane	4.26	4.36	4.63
171.	Cyclohexane	5.35	5.31	5.57
172.	1,3-Cyclohexadiene	5.36	5.09	5.52
173.	1,4-Cyclohexadiene	5.37	5.08	5.52
174.	1,5-Cyclooctadiene	7.58	6.99	7.40
175.	*n*-Butylamine	5.34	4.67	
176.	Aniline	6.38	5.50	
177.	Di-*n*-butylamine	8.66	8.49	
178.	Tri-*n*-butylamine	12.53	12.23	
179.	Acetonitrile	2.88	2.43	
180.	Butyronitrile	5.97	6.20	
181.	Nitromethane	2.58	3.02	
182.	Pyridine	4.77	4.98	

(a) Ref. 6; (b) hydrogen and deuterium treated on same footing; and (c) ref. 8.

Values in parentheses have been calculated using Eq. (7)

TABLE 3 — GENERAL AND GROUP REGRESSIONS WITH THEIR STATISTICS

Eq. No.	Group	Compound[a]	Regression[c]
8	General (All compounds)	1-182	$0.5334 (0.0160)^b$ $N + 0.8417 (0.0320)^1\chi^v - 0.2450 (0.0570)^3\chi_c^v + 0.2242 (0.0553)$ $n = 182; \ r = 0.996; \ s = 0.303(3.545); \ F_{3,178} = 8200; \ EV = 0.993$
9	Alkanes	1-47	$0.8675(0.0578) \ N + 0.2048(0.1130) \ ^1\chi^v - 0.3207(0.0431) \ ^3\chi_c^v - 0.1904(0.0765)$ $n = 47; \ r = 0.999; \ s = 0.152(3.515); \ F_{3,43} = 8123; \ EV = 0.998$
10	Compounds containing oxygen	48-93	$0.5464(0.0335)N + 0.8140 (0.0843)^1\chi^v + 0.0544(0.2143) \ ^3\chi_c^v + 0.1343 (0.0907)$ $n = 46; \ r = 0.998; \ s = 0.309 (4.249); \ F_{3,42} = 2814; \ EV = 0.995$
11	Halogen compounds	94-124	$0.4819(0.0312)N + 0.9967(0.0566) \ ^1\chi^v - 0.0685(0.2418) \ ^3\chi_c^v - 0.0192 (0.1325)$ $n = 31; \ r = 0.998; \ s = 0.294 (4.316); \ F_{3,27} = 2149; \ EV = 0.995$
12	Benzenes and derivatives	125-141	$0.7600 (0.0801)N + 0.3095 (0.1376) \ ^1\chi^v - 0.2371 (0.1431) \ ^3\chi_c^v - 0.2936(0.3217)$ $n = 17; \ r = 0.997; \ s = 0.160 (1.932); \ F_{3,13} = 772; \ EV = 0.993$
13	Unsaturated compounds	142-174	$0.8525 (0.1237) \ N + 0.1781 (0.2271) \ ^1\chi^v - 0.2367 (0.1363) \ ^3\chi_c^v + 0.0545(0.2765)$ $n = 33; \ r = 0.984; \ s = 0.23 (1.255); \ F_{3,29} = 298; \ EV = 0.965$

(a) Numbering of compounds is same as in Table 2; (b) standard errors of the regression coefficients (c) $n=$ sample size; $r =$ correlation coefficient; $s =$ standard error of the estimate; values in the parentheses are standard errors of the observed data : $F = F$-ratio; the subscripts are two degrees of freedom; and $EV =$ amount of explained variance.

not require precounting of the subgraphs (unpublished).

Of the number of correlations tried the one involving three variables, viz. $^1\chi^v$, $^3\chi_c^v$ and N, the number of atoms other than hydrogen in a molecule, is found to be the most significant (Eq. 8. Table 3). The values of cross-section calculated according to this correlation are compared with the observed values in Table 2. The average deviation of the predicted values is little less than 4%. The maximum deviation observed in rare cases is less than 20% and most of the compounds have deviation less than $\pm 5\%$ of the experimental values.

A closer look at Table 2 clearly reveals that the deviation is more for small molecules, particularly those containing oxygen, and for alkenes. For the compounds of former class there are specific intermolecular interactions and the molecular structure is not simple. In the second case the observed values for $\left\langle \sigma v \right\rangle_{av}$ correspond to cis-trans mixtures.

In both these cases the connectivity parameters cannot be calculated accurately and hence the deviation.

It has been reported[6] that for molecules having the same molecular formula but different degree of branching the positronium life-times are different. Gray et al. have reported that the annihilation cross-section decreases as the degree of branching increases.

The connectivity parameter $^3\chi_c^v$ and to some extent $^1\chi^v$, are related to the degree of branching in a mole-

cule. The negative sign of the coefficient of $^3\chi_c^v$ explains decrease in positronium cross-section with increase in branching and accounts for steric effects in annihilation rates. The appearance of N in the general regression probably explains the role of gross size of the molecule in the annihilation process.

It is encouraging to have obtained a simple correlation which can give values of $\left\langle \sigma v \right\rangle_{av}$ within experimental accuracy for such a large sample of compounds. We have observed that the results improve considerably when the 182 compounds are divided into five broad groups of alkanes, oxygenous compounds, halogen compounds, benzenes and unsaturated compounds (Table 3). The values of cross-sections calculated according to these group regressions (Eqs. 8 to 13) are also compared with the experimental values in Table 2.

It is interesting to note that n-alkanes give an excellent one-parameter regression, i.e.,

$$\left\langle \sigma v \right\rangle_{av} = 1.9311 \ (0.0082) \ ^1\chi + 0.0137(0.0476)..\ (7)$$

$n=15; \quad r=0.9999; \quad S=0.068 \quad (4.319); \quad F_{1,13} = 55831;$ EV$=0.9997$. This can be rationalised by the fact that for n-alkanes $^3\chi_c^v$ is zero as there is no branching and there is a linear correlation between N and $^1\chi$ ($N=2.06 \ ^1\chi$).

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‡For alkenes the agreement is poor because the experimental data corresponds to cis-trans mixtures of different compositions.

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