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Additivity of Atomic Static Polarizabilities and Dispersion Coefficients

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A new empirical method is proposed to evaluate the average molecular polarizabilities assuming the additivity of atomic static polarizability. Atomic static polarizability for each atom in a particular valence state is obtained. Calculated molecular polarizabilities of 94 non-halogenated compounds and of the bases in nucleic acids show the excellent agreement with experimental data.

To check the further validity of this method, dispersion coefficients for CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, n-C_5H_{12}, n-C_6H_{14}, n-C_7H_{16}, n-C_8H_{18}, H_2, H_2O and NH_3 are obtained from a sum of atomic terms using a London-type formula, and are compared with the accurate values of dipole oscillator strength distribution (DOSD) method. The results show the excellent agreement between theory and experiment.

Key words: Atomic static polarizabilities – Dispersion coefficients.

1. Introduction

It is generally known that the molecular polarizability cannot be expressed simply as a sum of atomic polarizabilities, and a polarizability must be assigned to each atom depending on the atoms bonded to it [1].

Recently, an empirical method to calculate the average molecular polarizability by a square of a sum of atomic hybrid components has been given [2] and good results are obtained.

In present work, a new empirical approach is proposed to obtain the molecular polarizabilities from the atomic polarizabilities. To check the further validity of

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this method, dispersion coefficients for several molecules are also calculated and compared with the accurate results of dipole oscillator strength distribution (DOSD) method [3–5].

2. Atomic Static Polarizability

Considering a molecule as being made up of N atoms, each of which acts as a point particle located at the nucleus and responds to a uniform electric field, the total induced dipole moment of the molecule $\vec{\mu}_{\mathrm{mol}}$ can be expressed as a sum of the atomic induced dipole moments $\vec{\mu}_i$'s such as

$$\vec{\mu}_{\mathrm{mol}} = \sum_i^N \vec{\mu}_i. \tag{1}$$

Then, the average static polarizability of the molecule can be written simply as a sum of the atomic polarizabilities;

$$\bar{\alpha}_{\mathrm{mol}} = \sum_i^N \bar{\alpha}_i \tag{2}$$

Table 1. Optimum atomic static polarizabilities and ionization potentials

Atom	Valence state[a]	$\bar{\alpha}_i$[d]	I_i[g]
C	tetetete (C1)	1.064	14.57
	trtrtrπ(C2)[b]	1.382	11.22
	trtrtrπ(C3)[b]	1.230	11.22
	trtrtrπ(C4)[c]	1.529	11.22
	didi$\pi\pi$(C5)	1.279	11.24
N	te^{2}tetete(N1)	1.094	14.31
	trtrtrπ^2(N2)	1.090	12.25
	tr^{2}trtrπ(N3)	1.030	14.51
	di^{2}di$\pi\pi$(N4)	0.852	14.47
O	te^{2}te^{2}tete(O1)	0.664	18.40
	tr^{2}tr^{2}trπ(O2)	0.460	17.25
	tr^{2}trtrπ^2(O3)	0.422	14.97
	te^{2}te^{2}te^{2}te(O4)	1.791[e]	6.31
H	σ(H)	0.386	13.61
P	teteteteπ(P)	1.743[f]	12.09

[a] te = tetrahedral, tr = trigonal, di = diagonal, σ = sigma and π = π orbital; each valence state is designated in parenthesis.

[b] C2 corresponds to aliphatic carbon atom; C3 to aromatic one.

[c] C4 corresponds to carbon atom in condensed hydrocarbons.

[d] Optimum atomic static polarizabilities, units in Å^3.

[e] Obtained from the refractive index data of KH_2PO_4 in Ref. [6].

[f] Obtained from $(CH_3)_3PO_4$ data in Ref. [7].

[g] Experimental ionization potentials, units in eV, taken from Ref. [8], except H and P from Ref. [9].

where $\bar{\alpha}_i$ is the effective atomic polarizability of each atom depending on the atoms bonded to it.

In present work, the values of $\bar{\alpha}_i$ are obtained from the experimental polarizabilities of homologous molecules. For example, from the molecular polarizabilities of 12 saturated hydrocarbons from CH_4 to n-$C_{12}H_{26}$, the values $\bar{\alpha}_H = 0.386$ Å^3 and $\bar{\alpha}_{C1} = 1.064$ Å^3 for hydrogen and carbon atoms in the tetrahedral valence state are optimized, where the subscript denoting the valence state of each atom is illustrated in footnotes of Table 1.

The value $\bar{\alpha}_{C2} = 1.382$ Å^3 is obtained from the average polarizabilities of four unsaturated aliphatic hydrocarbons such as ethylene, 2-pentene, 1-hexene and 1-heptene. From the molecular polarizabilities of five aromatic hydrocarbons including toluene, *p*-xylene, mesitylene, durene and benzene, the value $\bar{\alpha}_{C3} = 1.230$ Å^3 is obtained. The value $\bar{\alpha}_{C4} = 1.529$ Å^3 for carbon atom in condensed ring systems is obtained from 15 condensed hydrocarbons. And the value $\bar{\alpha}_{C5} = 1.279$ Å^3 obtained from acetylene is used for carbon atom in *sp*-hybrid states. Similarly, the values of $\bar{\alpha}_i$ for nitrogen, oxygen and phosphorus atoms in various valence states are determined.

Table 2. Average molecular polarizabilities of aliphatic hydrocarbons[a]

Molecules	This work	Miller et al.[b]	Yoffe[c]	Expl.[d]
methane	2.61	2.60	2.69	2.60
ethane	4.44	4.44	4.60	4.47
propane	6.28	6.29	6.50	6.29
butane	8.12	8.14	8.41	8.12
pentane	9.95	9.98	10.31	9.95
hexane	11.79	11.83	12.22	11.78
heptane	13.62	13.68	14.12	13.61
octane	15.46	15.52	16.03	15.44
nonane	17.30	17.37	17.93	17.35
decane	19.13	19.22	19.84	19.10
undecane	20.97	21.06	21.74	21.04
dodecane	22.80	22.91	23.65	22.75
ethylene	4.31	4.23	4.30	4.26
2-pentene	9.82	9.76	10.01	9.84
1-hexene	11.65	11.60	11.92	11.65
1-heptene	13.49	13.45	13.82	13.51
acethylene	3.33	3.33	3.38	3.33
1-heptyne	12.51	12.57	12.90	12.87
average percent error[e]	0.38	0.50	2.87	

[a] Units in Å^3.

[b] Ref. [2].

[c] Obtained from the parameters of Ref. [2] using Eq. (10) in Ref. [10].

[d] Experimental data taken from the indicated references in Ref. [2].

[e] The average percent error is obtained from the average of $100 \times |\bar{\alpha}_{cal.} - \bar{\alpha}_{exp.}|/\bar{\alpha}_{exp.}$.

The optimum values of $\bar{\alpha}_i$ and the notation for each valence state are listed in Table 1. In Tables 2–6, the average molecular polarizabilities calculated from the atomic polarizabilities by Eq. (2) are compared with the experimental values and also with the calculated values of Miller's [2]. In addition, the molecular polarizabilities obtained from a sum of atomic polarizabilities by Yoffe and Maggiora [10] are compared in these Tables. In each Table, the average percent error is shown respectively.

In Table 2, the average molecular polarizabilities of aliphatic hydrocarbons are listed, and our results agree to experimental values within approximately 0.4%, whereas Miller's results [2] give a comparable values to ours, but Yoffe's results yield errors up to 2.9%. Our results for the compounds containing nitrogen atom in various valence states in Table 3 agree to the experimental values within 1.72%, which are comparable to Miller's values (1.78%), but much lower than Yoffe's values (4.42%). In Table 4, the results for the compounds containing oxygen and phosphorous atoms are given. Our values differ from the experimental values by only 1.4%, whereas the average percent errors in Miller's and

Table 3. Average molecular polarizabilities of compounds containing nitrogen[a]

Molecules	This work	Miller et al.	Yoffe	Expl.
isopropylamine	7.76	7.80	8.08	7.77
diethylamine	9.60	9.65	9.98	9.61
triethylamine	13.27	13.34	13.79	13.38
tri-*n*-propylamine	18.78	18.88	19.51	18.87
hydrazine	3.73	3.78	3.93	3.46
N,N-dimethylhydrazine	7.40	7.47	7.74	7.21
aniline	11.69	11.49	12.09	11.58
N-methylaniline	13.53	13.34	14.00	13.50
N,N-dimethylaniline	15.36	15.19	15.90	15.40
N-ethylaniline	15.36	15.19	15.91	15.32
N,N-diethylaniline	19.03	18.88	19.71	19.01
Pyrrole	7.94	8.03	8.26	7.94
Pyridine	9.11	9.47	9.68	9.18
Quinoline	14.80	15.65	16.70	15.70
Hydrogen Cyanide	2.61	2.59	2.66	2.59
p-cyanotoluene	13.89	14.05	14.30	13.90
3-aminobutyronitrile	9.51	9.63	9.68	9.17
3-dimethylaminobutyronitrile	13.18	13.32	13.49	12.87
pyrazole	7.35	7.15	7.38	7.23
1-methylpyrazole	9.19	8.99	9.28	8.99
1,5-dimethylpyrazole	11.03	10.83	11.19	10.72
1-ethyl-5-methylpyrazole	12.86	12.67	13.09	12.50
p-nitrotoluene	14.49	13.97	14.52	14.10
nitrobenzene	12.66	12.14	12.61	12.92
p-toluidine	13.01	13.34	14.13	13.47
average percent error	1.72	1.78	4.42	

[a] Refer to footnotes in Table 2.

Yoffe's results are 2.02% and 7.90%, respectively. Finally, in Tables 5 and 6, the average polarizabilities of benzene derivatives and condensed hydrocarbons are reported. The average percent errors in our results are much smaller than either Miller's or Yoffe's results.

For 94 non-halogenated compounds shown in Tables 2–6, the total average percent error amounts only to 1.58% in our work, but to 1.91% and 5.39% in Miller's and Yoffe's works, respectively.

In Table 7, the values of average polarizabilities for the bases in nucleic acids including adenine, guanine, thymine, cytosine and uracil are presented to test the further applicability of the present method to the calculation of molecular polarizabilities of biological molecules. The results show better agreement with experimental results than any other works.

Table 4. Average molecular polarizabilities of compounds containing oxygen and phosphorus[a]

Molecules	This work	Miller et al.	Yoffe	Expl.
water	1.44	1.47	1.62	1.45
methanol	3.27	3.28	3.53	3.26
ethanol	5.11	5.11	5.43	5.07
1-propanol	6.94	6.95	7.34	6.77
glycol	5.77	5.85	6.26	5.71
dimethyl ether	5.11	5.11	5.43	5.16
diethyl ether	8.78	8.79	9.24	8.73
n-propyl methyl ether	8.78	8.79	9.24	8.86
furan	7.23	7.23	7.85	7.23
n-propyl ethyl ether	10.62	10.63	11.15	10.68
di-*n*-propyl ether	12.45	12.48	13.05	12.55
acetone	6.29	6.33	6.70	6.40
methyl ethyl ketone	8.12	8.17	8.60	8.19
diethyl ketone	9.96	10.01	10.51	9.93
diisopropyl ketone	13.63	13.70	14.32	13.53
methyl propyl ketone	9.96	10.01	10.52	9.93
n-propionaldehyde	6.29	6.33	6.71	6.35
n-butyraldehyde	8.12	8.17	8.62	8.18
formic acid	3.28	3.47	3.72	3.32
acetic acid	5.12	5.26	5.62	5.15
propionic acid	6.95	7.07	7.55	6.96
butyric acid	8.79	8.89	9.45	8.58
methyl butyrate	10.62	10.72	11.36	10.41
methyl propionate	8.79	8.89	9.44	8.79
methyl acetate	6.95	7.07	7.53	6.81
formamide	4.09	3.85	4.21	3.88
acetamide	5.92	5.66	6.11	5.39
benzamide	13.02	13.38	13.94	12.75
trimethyl phosphate	10.86	9.55	12.53	10.86[b]
average percent error	1.40	2.02	7.90	

[a] Refer to footnotes in Table 2.

[b] Taken from Ref. [7].

Table 5. Average molecular polarizabilities of benzene derivatives[a]

Molecules	This work	Miller et al.	Yoffe	Expl.
toluene	11.53	12.25	12.43	11.83
p-xylene	13.37	14.10	14.33	13.70
mesitylene	15.20	15.94	16.24	15.38
durene	17.04	17.79	18.14	17.40
benzene	9.70	10.40	10.52	10.39
p-cyanotoluene	13.89	14.05	14.30	13.90
benzamide	13.02	13.38	13.94	12.75
hexamethyl benzene	20.72	21.48	21.95	20.81
p-nitrotoluene	14.49	13.97	14.52	14.10
nitrobenzene	12.66	12.14	12.61	12.92
p-toluidine	13.01	13.34	14.13	13.47
average percent error	2.15	2.69	4.43	

[a] Refer to footnotes in Table 2.

Table 6. Average molecular polarizabilities of condensed hydrocarbons[a]

Molecules	This work	Miller et al.	Yoffe	Expl.
naphthalene	18.38	18.09	18.24	17.48
anthracene	25.27	25.79	26.05	25.93
phenanthrene	25.27	25.79	26.05	24.70
naphthacene	32.15	33.51	33.85	32.27
1,2-benzanthracene	32.15	33.51	33.85	32.86
chrysene	32.15	33.51	33.85	33.06
1,2:5,6-dibenzanthracene	39.04	41.22	41.65	41.31
acenaphthene	21.28	21.01	22.89	20.61
pyrene	28.32	30.05	30.37	29.34
fluorene	23.27	21.15	24.47	21.69
anthraquinone	24.48	25.86	26.79	24.46
2,3-benzfluorene	30.16	28.81	32.27	30.21
acridine	24.38	24.80	25.16	25.49
coronene	41.33	46.32	46.81	42.50
phenazine	23.50	23.82	24.27	23.42
average percent error	2.83	3.10	5.35	

[a] Refer to footnotes in Table 2.

3. Dispersion Coefficient

Since the intermolecular interaction is assumed to be a sum of atom–atom contributions, the molecular dispersion coefficient can be expressed by adding the atomic dispersion terms [10] such as

$$C_6(A, B) = \sum_i \sum_j C_6(i, j) \tag{3}$$

Table 7. Molecular static polarizabilities of the bases in nucleic acids[a]

Bases	This work	Miller et al.[b]	Seprödi et al.[c] (ZDO method)	Adams et al.[d] (IEHT method)	Expl.[e]
Adenine	13.35	12.75	17.47	8.12	13.11
Guanine	13.87	–	16.03	8.17	–
Thymine	11.40	11.48	25.42	7.15	11.23
Cytosine	10.52	10.27	25.43	6.30	10.33
Uracil	9.56	–	–	–	–

[a] Units in Å^3.
[b] Ref. [2].
[c] Ref. [11].
[d] Ref. [12].
[e] Ref. [13].

Table 8. Comparison of dispersion coefficients[a]

Molecules	This work	Slater–Kirkwood[b]	London[e]	Yoffe[g]	DOSD's[i]
CH_4	71.4	101.7[c]	63.7[c]	76.2[h]	77.4[j]
C_2H_6	208.4	277.9[d]	168.2	246.5[h]	288.1
C_3H_8	416.9	547.5	323.1	446.3	459.0
n-C_4H_{10}	697.1	908.9	511.9	747.0	757.7
n-C_5H_{12}	1048.9	1362.1	744.3	1124.6	1138.3
n-C_6H_{14}	1472.4	1905.4	1021.4	1579.2	1583.5
n-C_7H_{16}	1967.4	2360.5	1345.5	2110.7	2106.3
n-C_8H_{18}	2534.1	3265.6	1663.8[f]	2719.3	2701.5
H_2	6.1	8.0[c]	7.5[c]	6.3[h]	7.2[j]
H_2O	24.2	42.4[c]	19.3[c]	31.3[h]	27.0[j]
NH_3	53.1	78.8[c]	34.8[c]	58.3[h]	53.2[j]

[a] Units in $\text{eV} \cdot \text{Å}^6$.
[b] Calculated by using data in Ref. [5].
[c] Ref. [10].
[d] Ref. [15].
[e] Calculated by using data in Refs. [5] and [16].
[f] Calculated by using data in Refs. [5] and [17].
[g] Calculated by Eqs. (13) and (14) in Ref. [10].
[h] Refs. [10] and [15].
[i] Ref. [5].
[j] Refs. [3] and [4].

where i and j are the atoms in particular valence states of the molecules A and B, respectively. According to the London approximation [14], $C_6(i, j)$ can be written as

$$C_6(i, j) = \frac{3}{2} \frac{\bar{\alpha}_i \bar{\alpha}_j I_i I_j}{I_i + I_j} \tag{4}$$

where $\bar{\alpha}$ and I are the atomic static polarizability and the ionization potential, respectively.

Using Eqs. (3) and (4) with data in Table 1, we evaluated dispersion coefficients of several saturated hydrocarbons, H_2, H_2O and NH_3 for which the accurate values are known. The results are given in Table 8, and compared with the Slater–Kirkwood values [4, 10, 15], the molecular London values [4, 10, 16], the atomic London values obtained from Yoffe's work [10] and the results of dipole oscillator strength distributions (DOSD) method of Meath et al. [3–5].

Our results show satisfactory agreement with the accurate values of DOSD method. However, Yoffe's values are always larger than ours, and these larger values may be due to the overestimated atomic polarizabilities as shown in Tables 2–6. Our excellent theoretical values for the molecular polarizabilities and the dispersion coefficients indicate that our assumption on the additivity of the atomic polarizabilities in particular valence states may be reasonable.

4. Conclusion

A new empirical method is proposed to evaluate the molecular polarizabilities from the atomic polarizabilities in a particular valence state, and the excellent agreement with experimental data are obtained with the simple method.

Yoffe et al. [10] pointed out that good polarizability values do not necessarily guarantee good results of dispersion coefficients, however, reasonable values of dispersion coefficients are also obtained from a sum of the atomic contributions using a London-type formula.

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