

Manifestation of substituent effects in the Auger parameter

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The Auger parameter is composed of contributions from both Auger and photoelectron energies; it is held to be a function of only extra-atomic relaxation (i.e., ligand polarization). Its correlation with the Hammett-Taft inductive substituent constant demonstrates this to be true. Further, both the Auger and photoelectron energies are also demonstrated to correlate with the same substituent constant. This fact is used to separate direct and indirect contributions to the extra-atomic relaxation.

INTRODUCTION

In an effort to avoid Auger energy-shift problems due to substrate charging, Wagner proposed¹ the use of an energy difference, reasoning that both peaks should experience the same energy shift due to substrate changing. This difference, which he defined as that between the kinetic energy of the most intense Auger peak and the kinetic energy of the most intense photoelectron peak, was termed the Auger parameter, α . Making reasonable assumptions about the constancy of certain energy components on going from the atom to the molecule,^{1,2} the Auger parameter was shown^{1,3-5} to be due entirely to extra-atomic relaxation (i.e., ligand polarization).

A problem with the definition of α is that it could be negative, depending on the relative positions of the most intense Auger and photoelectron peaks. In an effort to avoid this perceived problem, Wagner initially^{1,3} proposed the arbitrary addition of 1000 or 2000 to the negative value of α , to give a positive value; ultimately,⁴ he adopted the solution of Gaarenstroom and Winograd,⁶ who defined α' as the sum of the kinetic energy of the Auger peak (E_A) and the binding energy of the photoelectron peak (E_B). Being equal to $\alpha + h\nu$, the energy of the exciting radiation, it, too, is due entirely to extra-atomic relaxation.

Now, this dependence on extra-atomic relaxation can be demonstrated in the case of substituents well characterized in terms of their polarization contributions. One such type of characterization, already at hand, is the use of the Hammett-Taft inductive substituent constant, σ_I .⁷⁻⁹ Substituent constants are based on the demonstration⁸ that a given substituent has a similar effect on both rate and equilibrium, irrespective of the molecule on which it is placed. Taft showed⁷ that they could be separated into components, one of which (σ_I) was due only to inductive contributions. For those substituents which manifest only inductive contributions, the dependence of the Auger parameter on polarization would be demonstrated by its correlation with σ_I . While originally developed for organic systems,⁷⁻⁹ these substituent con-

stants have recently been shown^{10,11} to be equally applicable to inorganic systems.

The purpose of this paper is to demonstrate that, within certain constraints, $\Delta\alpha'$ ($=\Delta\alpha$) does, indeed, correlate with $\sum\sigma_I$. These constraints include uncertainties due to the use of several sources for any series of values, as well as errors in calibration and measurement. Quite apart from this, these correlations will demonstrate that $\Delta\alpha'$ contains both direct and indirect effects and that it is possible to separate them, so that they can be studied individually. Here, indirect refers to an event which precedes the emission of the Auger electron and has an indirect influence on it.

RESULTS

The following examples are taken from several of the compilations made by Wagner and others, and correlated with the σ_I values from the comprehensive and critical compilation of Gordon and Ford.⁹ The examples chosen are representative rather than exhaustive.

Br: the data, taken from Ref. 12, are found in Table I and plotted in Fig. 1. The correlation of $\Delta\alpha'$ with σ_I is

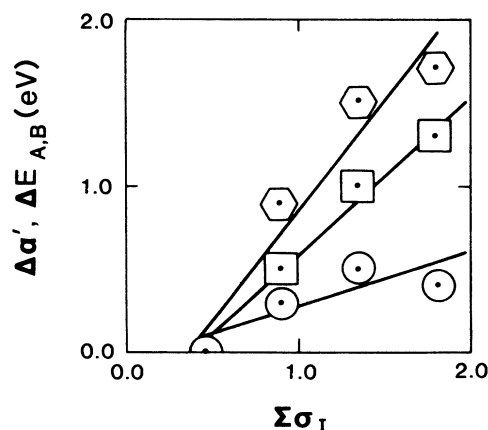


FIG. 1. A plot of the Auger parameters of Br vs $\sum\sigma_I$: ○, ΔE_B ; □, ΔE_A ; ⬡, $\Delta\alpha'$.

TABLE I. Auger parameters for Br.

Molecule	$\Delta E_B(2p)$ (eV)	$+\Delta E_A(KL_{2,3}L_{2,3})$ (eV)	$=\Delta\alpha'$ (eV)	$\sum\sigma_I^a$
CH ₃ Br	0	0	0	0.45
CH ₂ Br ₂	0.3	0.5	0.8	0.90
CHBr ₃	0.5	1.0	1.5	1.35
CBr ₄	0.4	1.3	1.7	0.80

^aEvaluated for the central C, for which more data are available.

TABLE II. Auger parameters for Si.

Molecule	$\Delta E_B(2p)$ (eV)	$+\Delta E_A(KL_{2,3}L_{2,3})$ (eV)	$=\Delta\alpha'$ (eV)	$\sum\sigma_I$
SiF ₄	0	0	0	2.08
SiCl ₄	-1.5	4.8	3.3	1.88
SiCl ₃ Me	-2.6	5.6	3.0	1.36
SiCl ₂ Me ₂	-3.1	6.5	3.4	0.84
SiClMe ₃	-4.6	7.5	2.9	0.32
SiMe ₄	-5.8	8.4	2.6	-0.20
SiMe ₃ OEt	-5.4	8.0	2.6	0.11
SiMe ₂ (OEt) ₂	-5.0	7.7	2.7	0.42
SiMe(OEt) ₃	-4.6	7.4	2.8	0.73
Si(OEt) ₄	-4.1	6.9	2.8	1.04
SiH ₄	-4.6	5.9	1.3	0

TABLE III. Auger parameters for P.

Molecule	$\Delta E_B(2p)$ (eV)	$+\Delta E_A(KLL)$ (eV)	$=\Delta\alpha'$ (eV)	$\sum\sigma_I$
PH ₃	0	0	0	0
PMe ₃	-1.1	3.3	2.2	-0.15
PCl ₃	2.8	0.4	3.2	1.41
PF ₃	4.7	-4.2	0.5	1.56
P(OMe) ₃	1.2	1.0	2.2	0.78
PCl ₂ Me	1.5	1.3	2.8	0.89
PEt ₃	-1.5	4.5	3.0	-0.15
P(CF ₃) ₃	1.7	1.2	2.9	1.26
PF ₅	0	0	0	2.60
PF ₃ O	-1.4	0.8	-0.6	2.54
PCl ₃ O	-3.3	5.2	1.9	2.39
P(OMe) ₃ O	-4.8	6.0	1.2	1.76
P(CH ₂ Cl)Cl ₂ O	-4.2	6.0	1.8	2.09

TABLE IV. Auger parameters for Cl.

Molecule	$\Delta E_B(2p_{3/2})$ (eV)	$+\Delta E_A(KL_{2,3}L_{2,3})$ (eV)	$=\Delta\alpha'$ (eV)	$\sum\sigma_I^a$
CCl ₄	0	0	0	1.88
CHCl ₃	-0.2	-0.2	-0.4	1.41
CCl ₃ F	0.2	-0.8	-0.6	1.93
CH ₂ Cl ₂	-0.4	-0.6	-1.0	0.94
CCl ₂ F ₂	0.4	-1.5	-1.1	1.98
C ₂ H ₅ Cl	-1.1	-0.3	-1.4	0.42
CClF ₃	0.8	-2.4	-1.6	2.03
CH ₃ Cl	-0.8	-1.2	-2.0	0.47

^aEvaluated for the central C, for which more data are available.

TABLE V. Auger parameters for In.

Molecule	$\Delta E_B(3d_{5/2})$ (eV)	$+\Delta E_A(M_4N_{4,5}N_{4,5})$ (eV)	$=\Delta\alpha'$ (eV)	$\Sigma\sigma_I$
InO _{0.5}	0	0	0	0.49
InO _{1.5}	-0.5	0.5	0	1.47
In(OH) ₃	0.4	-1.6	-1.2	0.75
InI ₃	1.4	-0.7	0.7	1.20
InBr ₃	1.7	-1.7	0	1.35
InCl ₃	1.6	-2.4	-0.8	1.41
InF ₃	1.9	-3.0	-2.1	1.56

clearly visible, as are those of the components, ΔE_A and ΔE_B .

Si: the data, taken from Ref. 4, are found in Table II and are plotted in Fig. 2. While the correlations are clear, there is a marked difference here, compared with the data for Br in Table I and Fig. 1: ΔE_A and ΔE_B have opposite slopes, with the sign of the slope of $\Delta\alpha'$ following that of ΔE_B , the larger of the two components.

P: the data, on both P^{III} and P^V, taken from Ref. 13, are found in Table III and Fig. 3. Again, correlations exist, with ΔE_A and ΔE_B having opposite slopes. As with the Si, $\Delta\alpha'$ appears to be slightly positive because the absolute value of the slope of ΔE_A is greater than that of ΔE_B .

Cl: the data, taken from Ref. 4, are found in Table IV and Fig. 4. Here, too, in contradistinction to the Br

correlation, the slopes of ΔE_A and ΔE_B are opposite in sign.

In: the data, taken from Ref. 4, are found in Table V and Fig. 5. While there is again correlation with σ_I , note that the slope of the $\Delta\alpha'$ correlation is, for the first time, negative.

Similar correlations were found for all the elements evaluated, a random sampling of 16 out of a total of some 25 such tabulations which lend themselves to this type of correlation. Of these, only Na and Zn showed $\Delta\alpha'$ correlations with negative slopes.

The use of a substituent constant to account for Auger or photoelectron chemical shifts is not new. Indeed, Lindberg and Hedman¹⁴ assumed the additivity of substituent chemical shifts to define ligand electronegativities, $\chi(j)$. These were redetermined by Bahl *et al.* for a series

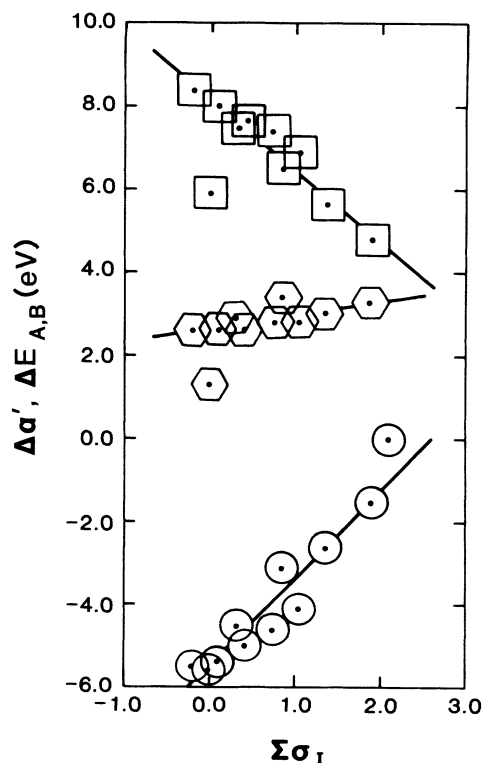


FIG. 2. A plot of the Auger parameters of Si vs $\Sigma\sigma_I$: \circ , ΔE_B ; \square , ΔE_A ; \hexagon , $\Delta\alpha'$.

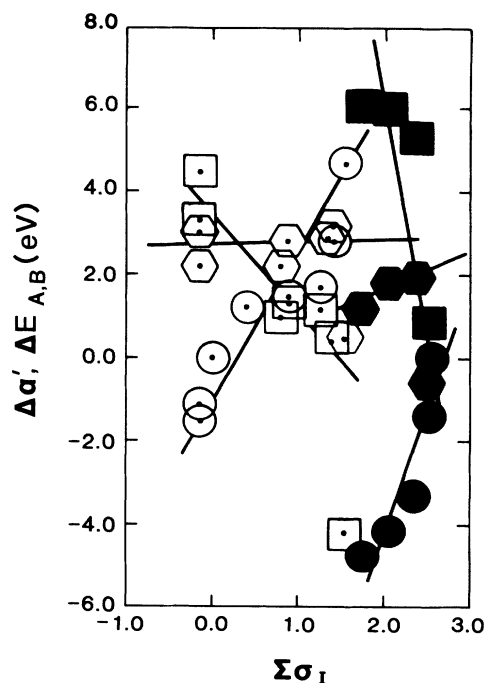


FIG. 3. A plot of the Auger parameters of P vs $\Sigma\sigma_I$: \circ , ΔE_B ; \square , ΔE_A ; \hexagon , $\Delta\alpha'$. The open symbols are for P^{III} and the solid symbols are for P^V.

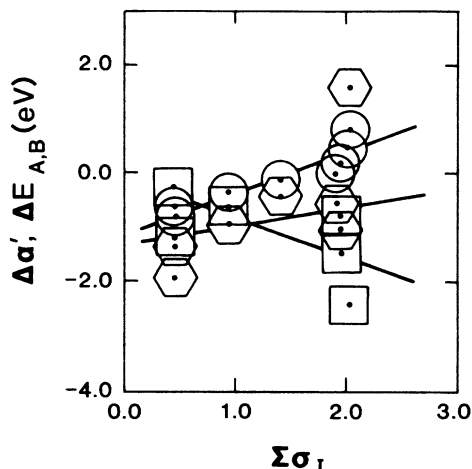


FIG. 4. A plot of the Auger parameters of Cl vs $\Sigma\sigma_I$: \circ , ΔE_B ; \square , ΔE_A ; \diamond , $\Delta\alpha'$.

of As compounds¹⁵ and a similar series of Te compounds.¹⁶ Many of the substituents have corresponding σ_I values. These are listed in Table VI and are plotted in Fig. 6. While it is clear that correlations do exist, these correlations appear to be element dependent, necessitating a different set of $\chi(j)$ values for each element.

DISCUSSION

As Figs. 1–5 clearly demonstrate, not only is α' a function of $\Sigma\sigma_I$, so, too, are ΔE_A and ΔE_B . Because σ_I is a property of the ligand only, $\Delta\alpha'$ is confirmed as being due only to polarization effects (as are ΔE_A and ΔE_B). Now, it may be shown^{16–19} that the Auger energy

$$E_A(XYZ) = E_B(X) - E_B(Y) - E_B(Z) - E(hh) + E_A(r), \quad (1)$$

where $E_B(i)$ refers to the binding energy of an electron in the i th atomic level, $E(hh)$ is the hole-hole interaction energy in the final state and $E_A(r)$ is the sum of reorgani-

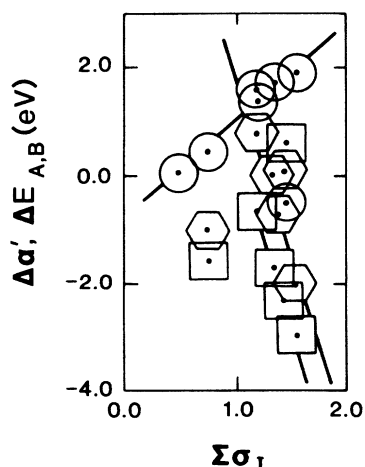


FIG. 5. A plot of the Auger parameters in In vs $\Sigma\sigma_I$: \circ , ΔE_B ; \square , ΔE_A ; \diamond , $\Delta\alpha'$.

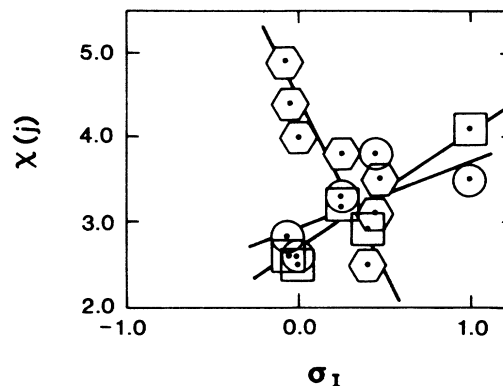


FIG. 6. A plot of ligand electronegativities vs σ_I : \circ , Ref. 14; \square , Ref. 15; \diamond , Ref. 16.

zation energies of the XY and Z transitions. In our case, where only the ligand is being changed, one may write that

$$\Delta E_A = \Delta E_A(r) = \Delta E_A(r)^{XY} + \Delta E_A(r)^Z. \quad (2)$$

Similarly, for the photoemission process,

$$\Delta E_B = \Delta E_B(r). \quad (3)$$

It should be noted, in Tables I–V, that $\Delta E_A(r)^Z = \Delta E_B(r)$, so that

$$\Delta\alpha' = \Delta E_A(r)^{XY} + 2\Delta E_A(r)^Z. \quad (4)$$

That is, $\Delta\alpha'$ reflects a particular sum of $\Delta E(r)$ values, all of which are proportional to $\Sigma\sigma_I$ (i.e., all of which are influenced by ligand polarization). Due to the fact that they represent rather deep core orbitals, none has energy values low enough to be disregarded.²⁰

Another parameter of interest would be, say, α'' , the difference in E_A and E_B , so that

$$\Delta\alpha'' = \Delta E_A(r) - \Delta E_B(r) = \Delta E_A(r)^{XY}. \quad (5)$$

While not plotted, they are always more negative in slope than a plot of ΔE_A versus $\Sigma\sigma_I$. Thus, while $\Delta E_B [= \Delta E_B(r) = \Delta E_A(r)^Z]$ is always positive in slope, $\Delta\alpha'' = \Delta E_A(r)^{XY}$ is sometimes negative (see Figs. 2, 3, and 5). Clearly, then, ΔE_B represents a direct effect and $\Delta\alpha''$, an indirect effect, in the sense that $\Delta E(r)^{XY}$ is the energy of

TABLE VI. Ligand electronegativities.

Substituent	$\chi(j)$			σ_I
	Ref. 14	Ref. 15	Ref. 16	
Cl			3.5	0.47
Br	3.8	3.8	3.1	0.45
I		2.9	2.6	0.40
OH	3.2	3.3	3.8	0.25
=O	3.5	4.1	3.9	0.98
<i>t</i> -Bu		2.6	4.9	-0.07
Me	2.8	2.5	4.4	-0.05
ϕ	2.6	2.5	4.0	0

a rearrangement which precedes the emission of the Auger electron and has an indirect influence on it.

CONCLUSIONS

The Auger parameter α' , defined as the sum of the kinetic energy of an Auger peak and the binding energy of a photoelectron peak, is shown to contain polarization contributions from both XY and Z Auger transitions. These contributions are shown to be separable. Each of them, as well as α' , is shown to correlate with σ_I , a measurement of extra-atomic relaxation.

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