ON THE SEPARATION OF INITIAL AND FINAL STATE EFFECTS IN PHOTOELECTRON SPECTROSCOPY USING AN EXTENSION OF THE AUGER-PARAMETER CONCEPT

GEORG HOHLNEICHER and HARALD PULM

Lehrstuhl für Theoretische Chemie, Universität zu Köln, Greinstr. 4, 5000 Köln 41 (Federal Republic of Germany)

HANS-JOACHIM FREUND

Institut für Physikalische und Theoretische Chemie, Universität Erlangen-Nürnberg, Egerlandstr. 3, 8520 Erlangen (Federal Republic of Germany)

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ABSTRACT

First, we show that the quantity \( \Delta \beta(i) = \Delta E_A(kii) + \Delta E_B(i) - \Delta E_B(k) \) is directly related to the final state relaxation contribution \( \Delta R(i) \) of the binding energy shift \( \Delta E_B(k) \). \( \Delta E_A(kii) \) is the kinetic energy shift of the Auger transition which corresponds to the decay of a hole state with a hole in level \( k \) into a final state with two holes in level \( i \). The shift parameter \( \Delta \beta(i) \), which is based on information on two binding energies, is conceptually similar to Wagner's Auger parameter. To establish the relation between \( \Delta \beta(i) \) and \( \Delta R(i) \) one needs, however, less drastic approximations than in the case of Auger parameter shifts. The only approximation necessary is the assumption that \( \Delta R(i) \) is determined by coulomb contributions.

Secondly, we use \( \Delta \beta(i) \) to analyse the experimental data of eighteen gaseous phosphorus-containing compounds obtained by Sodhi and Cavell*. It is shown that \( \Delta R(P_{2p}) \) is strongly related to changes in the polarizability of the ligands. The initial state effects derived from our study deviate from those expected on the basis of simple electronegativity considerations.

INTRODUCTION

In spite of the highly developed methodology of modern spectroscopic methods we have only very limited possibilities to probe the local character of the electron distribution in a molecule or a solid. Most of the methods
which are useful for this purpose are either limited to special nuclei, like Mössbauer spectroscopy [2], or they have difficulties with nonlocal contributions, like most kinds of NMR spectroscopy [3]. Binding energies of inner shell electrons which became experimentally accessible by X-ray photoelectron spectroscopy [4] have therefore been extensively studied as a new source for this type of information [4]. Since an inner shell electron is highly localized at a given nucleus, its energy is expected to be strongly related to the electron distribution around this nucleus. With ab initio calculations it was indeed possible to verify a direct relation between the orbital energy of inner shell electrons and the electrostatic potential which is created by the valence electrons [5]. This relation is the basis of all kinds of "potential models". In these models, the potential is usually approximated by the "potential at the nucleus". In the "point charge approximation" the potential is constructed from charges localized at the position of the different nuclei. The point charge model is specifically attractive for chemists, since the concept of partial atomic charges which in itself is connected to the concept of electronegativity is one of the fundamental concepts in chemistry, even though its theoretical justification is still under discussion [6].

The problem in the use of binding energies as a probe for local structures in the electron distribution is connected with the fact that the binding energy is the difference between the energy of an initial and a final state. Only in the frozen orbital approximation, where all the remaining electrons are not influenced by the removal of the inner shell electron under consideration (Koopmans' theorem [7]) do we find a direct relation between orbital energy $\epsilon(i)$ and binding energy $E_B(i)$

$$E_B(i) = -\epsilon_i$$

(1)

It is only in this approximation that the binding energy is directly related to the electron distribution of the initial state. To correct for the approximations that lead to eqn. (1) the exact binding energy is usually expressed as [8]

$$E_B(i) = -\epsilon_i - R_i$$

(2)

The relaxation energy $R_i$ is the energy obtained from a gedankenexperiment where we first remove an electron from orbital $i$ keeping all orbitals frozen and then allow the whole electron system to adjust to the vacancy now present in orbital $i$. Following this picture we usually speak of a "final state relaxation effect". In most applications we use a differential form of eqn. (2)

$$\Delta E_B(i) = -\Delta \epsilon_i - \Delta R_i$$

(2a)

Equation (2a) relates changes in binding energy — the so-called binding energy shifts — to changes in orbital energies and changes in relaxation
contributions. $\Delta \varepsilon_i$ is the initial state contribution to $\Delta E_B$, and $\Delta R_i$ is the final state contribution. Binding energy shifts are therefore influenced by initial and final state effects. To derive information on the charge distribution of the initial state, it is necessary to disentangle the two contributions. Two strategies have been developed to deal with this problem.

(i) The development of such models as the relaxed potential model (RPM) or the transition state model (TSM) which take relaxation into account. Comparison of the resulting binding energies with those predicted in the frozen orbital approximation then allows separation of initial and final state effects. A recent survey of these models has been given by Sodhi and Cavell [1].

(ii) The search for combinations of experimentally accessible quantities which depend only on initial or only on final state effects.

Following (ii), Wagner [9a,b] has proposed the relation

$$\Delta \alpha(i) = \Delta[E_B(i) + E_A] = 2\Delta R_i$$

which has been widely used. $\Delta \alpha$ is the so-called “Auger parameter shift”. It is the sum of a binding energy $\Delta E_B(i)$ as observed in photoemission and the kinetic energy shift of an Auger signal ($\Delta E_A$), both measured with respect to a certain standard. A great advantage in the use of $\Delta \alpha$ is its applicability to insulating solid samples: when we obtain $\Delta E_B(i)$ and $\Delta E_A$ from the same sample under the same measurement conditions both values are affected equally by sample charging. Since $\alpha$ is derived from the difference of two kinetic energies ($E_B(i) = h\nu - E_{kin}^P(i)$), the influence of sample charging cancels out and $\Delta \alpha$ values can be compared for charged samples.

The problem connected with the application of eqn. (3) results from a basic approximation used in its derivation. It is assumed that the binding energies of all inner shells shift by an equal amount with changes in the chemical environment or, as it is usually called, the “chemical state” of the atom considered. From the recent results of Sodhi and Cavell [1] it is, however, obvious that this assumption is not justified in general. We therefore propose a new relation

$$\Delta \beta(i) = \Delta[2E_B(i) - E_B(k) + E_A(kii)] = 2\Delta R_i$$

which should provide better experimental estimates for relaxation contributions. Since we no longer assume all inner shell orbital energies shift by the same amount it is necessary to specify the Auger process in eqn. (4): $k$ refers to the primary hole, i.e., the initial state for the Auger decay, while $i$ denotes the level which carries the holes in the final state of the Auger process. With this specification the relaxation contribution $\Delta R_i$ is well defined and only refers to a given level $i$. The derivation of eqn. (4) is discussed in the next section. We then apply eqn. (4) to the experimental data given by Sodhi and Cavell [1] and compare the results derived from this equation to those obtained with other methods.
THEORETICAL FRAMEWORK

For the following we denote inner shell orbitals by $i, j, \ldots$ and not by the usual X-ray labels $K, L, \ldots$. In the limit of complete relaxation \[lo\] the energy of an Auger transition is given by

$$E_A(kij, X) = -E_{i^*j^*}(X) + E_{k^*}$$

$E_{k^*}$ is the energy of a state with a hole in orbital $k$. Correspondingly, $E_{i^*j^*}$ is the energy of a state with a hole in $i$ and a second hole in $j$. $X$ denotes the specific state which results from the open shell interaction of the two vacancies. Denoting the ground state energy of the initial system which has no vacancies by $E_0$, we obtain for the initial state of the Auger decay

$$E_{k^*} = E_0 + E_B(k)$$

$E_B(k)$ is the binding energy of the $k$ electron which can be measured in photoemission. Similarly, the energy of the final state of the Auger transition can be expressed as

$$E_{i^*j^*}(X) = E_0 + E_B(i) + E_B(ji^*, X) = E_0 + E_B(j) + E_B(ij^*, X)$$

Here $E_B(ji^*, X)$ is the energy necessary to remove an electron from orbital $j$ of a system which already has a vacancy in orbital $i$. From eqns. (6) and (7) we obtain the following expression for the kinetic energy of the electron emitted in an Auger process

$$E_A(kij, X) = E_B(k) - E_B(i) - E_B(ji^*, X)$$

Expressing the binding energies as in eqn. (2) yields

$$E_A(kij, X) = -\epsilon_k - R_k + \epsilon_i + R_i + \epsilon_j(i^*) + R_j(i^*, X)$$

$$= -\epsilon_k - R_k + \epsilon_j + R_j + \epsilon_i(j^*) + R_i(j^*, X)$$

$\epsilon_j(i^*)$ is the energy of orbital $j$ in a system which has already lost an electron from another core orbital $i$. Correspondingly, $R_j(i^*)$ is the relaxation energy for a state which already had a vacancy in orbital $i$ and from which a second electron is then removed from orbital $j$.

Equation (9) is widely used in connection with RPM and TSM applications (see ref. 1 and references given therein). For our purpose eqn. (9) is not suitable, since $\epsilon_j(i^*)$ is not directly related to the initial state without vacancies. Therefore, eqn. (9) is not appropriate to separate initial and final state effects. Instead of eqn. (9) we use a different description for the final state of the Auger transition, a description already discussed by Shirley [11]

$$E_{i^*j^*}(X) = E_0 - \epsilon_i - \epsilon_j - R_{ij} + F(ij, X)$$

In this case we describe the final state of the Auger process in such a way
that we remove an electron from orbital $i$ and another electron from orbital $j$ within the frozen orbital approximation. By $F(ij, X)$ we take into account the interaction between the two open shells which leads to the specific state $X$. Finally we consider the adjustment of the remaining electrons to the two holes. This adjustment yields a relaxation energy $R_{ij}$. From eqn. (10) we obtain the following expression for the kinetic energy of the Auger electron

$$E_A(kij, X) = -e_k + e_i + e_j - R_k + R_{ij} - F(ij, X)$$  \hspace{1cm} (11)$$

All three orbital energies now refer to the initial state of the system. We proceed by selecting a special Auger process, namely one for which the two holes in the final state are in the same orbital $i$, and combine the corresponding Auger kinetic energy with the binding energies $E_B(k)$ and $E_B(i)$. This yields

$$\beta(i, X) = E_A(kii, X) + 2E_B(i) - E_B(k) = -2R_i + R_{ii} - F(ii, X)$$  \hspace{1cm} (12)$$

With

$$E_B(i, k) = 2E_B(i) - E_B(k)$$  \hspace{1cm} (13)$$

we find

$$\beta(i, X) = E_A(kii, X) + E_R(i, k)$$  \hspace{1cm} (14)$$

For $\beta$ we have dropped the index $k$ since $\beta$ no longer depends on $k$. Similarly to $\alpha$, $\beta(i, X)$ does not depend on sample charging as long as the Auger kinetic energy and the two binding energies are derived from the same sample under the same experimental conditions. In terms of energy differences we obtain

$$\Delta\beta(i, X) = \Delta E_A(kii, X) + 2\Delta E_B(i) - \Delta E_B(k)$$

$$\Delta F(ii, X) = -2\Delta R_i + \Delta R_{ii} - \Delta F(ii, X)$$  \hspace{1cm} (15)$$

$\Delta F(ii, X)$ can be neglected if the Auger transition only involves inner shell electrons. $F(ik, X)$ determines the splitting and the intensity distribution within a given Auger multiplet. For Auger transitions which do not involve valence electrons, changes in the chemical state lead usually only to a shift of the multiplet as a whole and not to changes in the multiplet structure. This shows that changes in the $F(ik, X)$ have to be small. The same argument has been used by Wagner [9a,b] and by Aitken et al. [12] in their derivation of eqn. (3). The argument, however, is no longer applicable when valence electrons take part in the Auger transition. In this case the multiplet structure often shows pronounced chemical state dependence [13]. Neglecting $\Delta F(ii, X)$ we obtain

$$\Delta\beta(i) = -2\Delta R_i + \Delta R_{ii}$$  \hspace{1cm} (16)$$

We have dropped the state symbol $X$ since eqn. (16) applies only to cases
where the Auger kinetic energy shift does not depend on the specific state from which the shift is derived.

We now make use of the assumption that differences in relaxation energies are dominated by classical coulomb contributions. With this assumption the relaxation contribution $\Delta R_{ii}$ for a system with two vacancies in the inner shell orbital $i$ is four times as large as the relaxation contribution $\Delta R_i$ for a system with only a single vacancy in this orbital

$$\Delta R_{ii} = 4\Delta R_i$$

(17)

Using this approximation we immediately obtain eqn. (4) from eqn. (16). The classical model, in which screening is assumed to be quadratically dependent on the charge, has been successfully used by Mott and co-workers [14] in connection with energetic considerations on sodium halides. It is also inherent in all derivations of eqn. (3). An interesting experimental confirmation for the applicability of this approximation has been found by Kaindl and co-workers [15] from the study of rare gas adsorbates on transition metal surfaces. For these adsorbates initial state effects are considered to be small since rare gas atoms are only weakly bound to transition metal surfaces. Application of eqn. (17) together with the approximation $\Delta R_i = \Delta R_k, k$ leads to the prediction that in the case of negligible initial state contributions the Auger kinetic energy shift is three times as large and of opposite sign as the binding energy shift. The experimental ratio found for Xe NOO and Xe 4d is indeed approximately $-3$ [15], in spite of the fact that the Xe NOO process includes valence electrons.

Combination of eqns. (2a) and (4) finally leads to

$$\Delta \epsilon_i = - \left[\Delta E_B(i) + \Delta \beta(i)/2\right]$$

Thus, by using $\Delta \beta$ as an experimentally derived estimate for $\Delta R$ we are able to resolve the pure initial state effect $\Delta \epsilon$. Equation (18), however, is only applicable in cases where the binding energies $\Delta E_B$ refer to the vacuum level. This is usually not true for solid samples. For these samples the binding energies are normally given with respect to the Fermi level. Since the Fermi energy $\epsilon_F$ is different for different samples it is necessary to include the change in Fermi energies

$$\Delta \epsilon_i = - \left[\Delta E_B(i) + \Delta \beta(i)/2\right] + \Delta \epsilon_F$$

(19)

With the usual approximation in which $-\Delta \epsilon_F$ is set equal to the difference in the corresponding work functions ($\Delta \phi$) we find

$$\Delta \epsilon_i = - \left[\Delta E_B(i) + \Delta \beta(i)/2\right] - \Delta \phi$$

(20)

Independently measured work functions can only be used for samples which are sufficiently conducting. For a non-conducting sample the Fermi energy itself depends on experimental conditions, specifically the number of defects created by X-ray irradiation and the density of low energy electrons...
which are present in the vicinity of the sample surface. For non-conducting materials it is therefore necessary to measure $\phi$ under the same experimental conditions as $E_B(i)$. In principle $\phi$ can be obtained from the low energy cutoff on the photoelectron distribution [16].

To conclude this section we would like to connect the present analysis with the traditional analysis in terms of Wagner's Auger parameter, $\alpha$, which is defined as

$$\alpha(kij, X, I) = E_A(kij, X) + E_B(I)$$

Equation (21) indicates that the Auger parameter introduced by Wagner is defined for any arbitrary combination of an Auger transition $E_A(kij)$ and a binding energy $E_B(I)$. For these arbitrary combinations eqn. (3), however, does not generally hold. As Thomas pointed out in ref. 9d, the application of eqn. (3) implies $i = j$ and $l = k$ or $l = i$. With this restriction we obtain from eqns. (2), (11) and (15)

$$\alpha(kii, X) = E_A(kii, X) + E_B(i)$$

$$= -\epsilon_k + \epsilon_i - R_k - R_i + R_{ii} + F(ii, X)$$

Auger parameters found in the literature do not always fulfill the above-mentioned conditions. Often, the selection of Auger transition and binding energy depends on what is easily obtainable experimentally. In contrast, $\beta$ is uniquely defined: the Auger process has to be $kii$ and the two binding energies are strictly connected to the initial and final state of the Auger transition.

The Auger parameter shift $\Delta \alpha$ is given by

$$\Delta \alpha(kii) = \Delta E_A(kii) + \Delta E_B(i)$$

$$= -\Delta \epsilon_k + \Delta \epsilon_i - \Delta R_k - \Delta R_i + \Delta R_{ii}$$

In contrast to $\Delta \beta$, $\Delta \alpha$ depends on several relaxation contributions, namely $\Delta R_i$, $\Delta R_{ii}$ and $\Delta R_k$, and in addition on the initial state contributions $\Delta \epsilon_k$ and $\Delta \epsilon_i$. Only if the two inner shell ionizations exhibit the same chemical state dependence in the initial ($\Delta \epsilon_i = \Delta \epsilon_k$) and in the final ($\Delta R_i = \Delta R_k$) state, do $\Delta \alpha$ and $\Delta \beta$ become equivalent. These are the approximations introduced in all derivations of eqn. (3) [9]. Since we can express $\Delta \alpha$ as

$$\Delta \alpha(kii) = \Delta E_B(k) - \Delta E_B(i) - 2\Delta R_i + \Delta R_{ii}$$

it is obvious that the equivalence of $\Delta \alpha$ and $\Delta \beta$ demands $\Delta E_B(i) = \Delta E_B(k)$. As stated in the Introduction, such an equality is usually not observed. It is difficult to judge how much of the difference $\Delta E_B(k) - \Delta E_B(i)$ results from initial and how much from final state effects. Theoretical calculations indicate that the chemical state dependence of $\epsilon_k - \epsilon_i$ is indeed small [4]. The difference in relaxation contributions, however, does not seem to be negligible. For example, for Mg compared to Mg$^{+}$ one finds $\Delta R_{2p} = 2.5$ eV and $\Delta R_{1s} = 3.0$ eV [17].
AN APPLICATION

To derive $\beta(i, X)$ (eqn. (12)) for a given sample we need the following experimental data:

(i) the Auger kinetic energy $E_A(kii, X)$. Complete relaxation conditions must be fulfilled and the structure of the Auger multiplet must be unaffected by variations in the chemical state,

(ii) the binding energy $E_B(i)$, and

(iii) the binding energy $E_B(k)$.

For solids, all three energies should be obtained from the same sample under the same experimental conditions to avoid any possible shift of the reference level. To evaluate initial state effects (eqn. (20)) it is also necessary to measure the work function $\phi_s$ of the sample. The latter complication is avoided when the sample is studied in the gas phase. For a first application we therefore looked for gas phase data.

A set of data which provides all necessary energies has recently been published by Sodhi and Cave [1]. In this study P 1s and P 2p binding energies and P $KL_{2,3}L_{2,3}$, $1D_2$ Auger energies have been measured in the gas phase for eighteen phosphorus compounds. The observed energy shifts with respect to PH$_3$ are listed in Table 1. The numbering of the compounds is as in ref. 1. From the data of Sodhi and Cave we calculated $\Delta E_B(1s, 2p)$ according to eqn. (13) and $\Delta R_{2p}$ according to eqn. (4). From the measured binding energy shifts $\Delta E_B(2p)$ and finally from $\Delta R_{2p}$ we obtained $\Delta\epsilon_{2p}$ (eqn. (2)). In addition to these data, we show in Table 1 the $\Delta R_{2p}$ values which are derived from the Auger parameter shift $\Delta\alpha$ (eqn. (3)) and the values calculated by Sodhi and Cave [1]. If necessary, these $\Delta R$ values are indicated by a subscript $\alpha$ or SC.

In Fig. 1 we have plotted $\Delta E_A(KL_{2,3}L_{2,3})$ vs. $\Delta E_B(1s, 2p)$. This plot is similar to a chemical state plot as introduced by Wagner [9a,b]. In Fig. 1 $\Delta\beta$ corresponds to the vertical distance of the data points from the indicated $45^\circ$-line going through the data point of the reference compound. For all compounds lying above this line $\Delta\beta$, and therefore $\Delta R$, is positive, indicating a larger final state relaxation as in the reference compound. It is obvious from Fig. 1 that for most of the investigated phosphorus compounds the final state relaxation is larger than for PH$_3$. This is not surprising. Only for PF$_3$ and OPF$_3$ do we find slightly negative relaxation contributions.

On average our $\Delta R$ values are somewhat smaller than those derived from $\Delta\alpha$ (cf. Table 1). This results from the fact that $\Delta E_B(i, 2p)$ is smaller than $\Delta E_B(2p)$ which in itself is a result of the more pronounced binding energy shift of P 1s as compared to P 2p. The difference between these two shifts has already been discussed by Sodhi and Cavell [1] who noted that $\Delta E_B(1s)$ and $\Delta E_B(2p)$ are nearly linearly dependent. Due to this linear dependence our $\Delta R$ values indicate approximately the same trends as the $\Delta R_\alpha$ values. The remaining differences are discussed below. The deviations between our
# Experimental Energy Shifts (eV) $\Delta E_B(1s)$, $\Delta E_B(2p)$ and $\Delta E_A(KL_{2,3}; L_{2,3}; D_{2})$, and Initial ($\Delta \epsilon_{2p}$) and Final ($\Delta \epsilon_{2p}$) State Contributions Derived from These Data by Different Methods

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<td>2p</td>
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*($1s, 2p) = 2E_B(2p) - E_B(1s)$.*
Fig. 1. Plot of the Auger kinetic energy shift \( \Delta E_{A}^{*}(KL_{2,3}L_{2,3},{}^{1}D_{2}) \) vs. \( 2\Delta E_{B}(i) - \Delta E_{B}(k) \). PH\(_3\) is used as the reference compound. The different compounds are indicated by the numbering given in Table 1. \( \Delta \beta \) is the vertical distance from the indicated 45°-line. All compounds appearing above this line have a positive \( \Delta \beta \) indicating stronger relaxation than in the reference compound.

Values and the calculated values of Sodhi and Cavell (\( \Delta R_{SC} \)) are not very large (\( \leq 1.5 \) eV) but scattered. Since we do not know how much of this scattering is caused by approximations in the calculational procedure applied by Sodhi and Cavell (CNDO/2) we do not want to discuss these deviations in more detail.

To interpret our data (\( \Delta R \) and \( \Delta \epsilon \)) we follow the ideas outlined by Aitken et al. [12]. First we consider the final state relaxation. An increase in \( \Delta R \) tells us that the positive charge at the photoionized atom is more efficiently screened. Since this screening can be connected to the polarizability of the surroundings, changes in \( \Delta R \) with variation of the ligands can be interpreted as being due to differences in the polarizability of the ligands. We have to bear in mind, however, that contributions from different ligands most likely will not be additive.

Let us now look at some of the compounds in detail. From a comparison of PF\(_3\) and PH\(_3\) we find that F is slightly less polarizable than H. However, in PF\(_5\) \( \Delta R \) is nearly zero. The larger number of substituents compensates for the somewhat lower polarizability, a behaviour which has already been
proposed by Wagner [9a,b]. This is a first hint to the above-mentioned non-additivity. In contrast to our result, which is in accordance with the calculated values from ref. 12, the $\Delta R_\alpha$ values predict fluorine to be similarly (from PF$_3$) or even slightly more (from PF$_5$) polarizable when compared to hydrogen. Aitken et al. [12] also find a slightly positive $\Delta R_\alpha$ for F compared to H.

From trivalent phosphorus compounds we obtain the following order for increasing polarizability

\[ F < H < OCH_3 < CH_3 < Cl \approx CF_3 \approx C_2H_5 \]

The figures give $\Delta R$ per ligand relative to H. For F, H, CH$_3$ and Cl the same order was derived by Perry and Jolly [18] who pointed out that this order is consistent with optically determined polarizabilities.

If $\Delta R_\alpha$ is used instead of $\Delta R$ to establish a polarizability series from trivalent phosphorous compounds the following order is obtained

\[ H \approx F < OCH_3 = CH_3 < CF_3 \approx C_2H_5 \approx Cl \]

The values have the same meaning as above. The equivalence of methyl and methoxy is a little surprising in this series. For ligands for which the polarizabilities are not too different the individual contributions seem to be fairly additive (Table 2). This is, however, no longer true if the number of ligands varies, as with PF$_5$ compared to PF$_3$, and for compounds containing multiple bonds (Table 3). The relaxation contribution of OPX$_3$ is increased with respect to PX$_3$ for the unpolarizable X = F but slightly decreased for the well polarizable X = Cl, with X = OCH$_3$ in between as expected from the polarizability series. The overall influence of oxygen is quite small, contrary to the report by Bahl and co-workers [19] for tellurium compounds. These authors find a polarizability series with O = Cl but

TABLE 2

ADDITIVITY OF RELAXATION CONTRIBUTIONS$^a$

<table>
<thead>
<tr>
<th></th>
<th>$\Delta R$</th>
<th>$\Delta R_\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc.$^a$</td>
<td>Found</td>
</tr>
<tr>
<td>CH$_3$PCl$_2$</td>
<td>PCl$_3$ - Cl + CH$_3$</td>
<td>1.20</td>
</tr>
<tr>
<td>(CH$_3$O)$_3$PScl</td>
<td>(CH$_3$O)$_3$PS - OCH$_3$ + Cl</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>Cl$_2$PS - 2Cl + OCH$_3$</td>
<td>1.34</td>
</tr>
<tr>
<td>CH$_3$PSCl$_2$</td>
<td>Cl$_3$PS - Cl + CH$_3$</td>
<td>1.60</td>
</tr>
</tbody>
</table>

$^a$Calc: calculated from the compound shown and the increments given in the text.
TABLE 3
DIFFERENCES IN RELAXATION CONTRIBUTIONS FOR OXYGEN- AND SULPHUR-CONTAINING COMPOUNDS

<table>
<thead>
<tr>
<th>X</th>
<th>F</th>
<th>OCH₃</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔR(OPX₃) − ΔR(PX₃)</td>
<td>0.19</td>
<td>0.12</td>
<td>−0.05</td>
</tr>
<tr>
<td>ΔR(SPX₃) − ΔR(PX₃)</td>
<td>0.89</td>
<td>0.44</td>
<td>0.11</td>
</tr>
</tbody>
</table>

this is not in accordance with the fact that oxygen should be "hard" in the sense of Pearson [20]. In contrast to oxygen, the influence of S is quite large and even more dependent on the other ligands. Since S is "soft" it contributes strongly to the total relaxation when X is a hard unpolarizable ligand like F, but it contributes only weakly when X itself is soft like Cl. Such strong deviations from additivity should not be restricted to compounds containing multiple bonds. They also should appear for compounds like PF₂Cl or PF₂CH₃. It will be interesting to find out from an increasing amount of experimental data available how far experimentally determined relaxation contributions can be used to quantify Pearson’s idea of hard and soft ligands [20].

We now turn to initial state effects Δε. From the PX₃ compounds we derive the following order

H = Alkyl < OCH₃ < CF₃ < Cl < F

0.0 0.66 1.04 1.38 1.47

The numbers give Δε per ligand.

In spite of the pronounced electronegativity difference between F and Cl, their initial state effect is quite similar. This has already been noted by Aitken et al. [12] for F and Cl and also for Br. When the polarizability effect is separated the three halogens become nearly equal. Their electronegativity differences are therefore mainly due to their different polarizabilities. In accordance with ref. 12 a similar effect is found for alkyl groups. The electron-releasing effect of the alkyl groups is due only to polarizability effects. There is nearly no initial state effect compared to H and the negative binding energy shift observed for P(CH₃)₃ and P(C₂H₅)₃ compared to PH₃ results solely from relaxation contributions.

We now consider the additivity of initial state effects. In Table 4 we have calculated the initial state effects Δε from the above-given increments and an increment of 1.35 for oxygen and sulphur. The initial state effect seems to be fairly additive even in cases where the polarizability effect is not. As F and Cl, and O and S have about the same initial state effect, the initial state effect seems to be similar for second and third row elements. However, the third row elements are more polarizable. Since the initial state effects
TABLE 4
ADDITIVITY OF INITIAL STATE EFFECTS$^a$

<table>
<thead>
<tr>
<th></th>
<th>$-\Delta\epsilon$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc.$^a$</td>
<td>Found</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PF$_5$</td>
<td>7.35</td>
<td>7.42</td>
</tr>
<tr>
<td>OPF$_3$</td>
<td>5.76</td>
<td>5.77</td>
</tr>
<tr>
<td>SPF$_3$</td>
<td>5.76</td>
<td>5.71</td>
</tr>
<tr>
<td>(CH$_3$O)$_3$PO</td>
<td>3.33</td>
<td>3.46</td>
</tr>
<tr>
<td>(CH$_3$O)$_3$PS</td>
<td>3.33</td>
<td>3.63</td>
</tr>
<tr>
<td>OPCI$_3$</td>
<td>5.49</td>
<td>5.31</td>
</tr>
<tr>
<td>SPCI$_3$</td>
<td>5.49</td>
<td>5.31</td>
</tr>
<tr>
<td>CH$_3$PCI$_2$</td>
<td>2.76</td>
<td>2.78</td>
</tr>
<tr>
<td>(CH$_3$O)$_2$PSCI</td>
<td>4.05</td>
<td>4.24</td>
</tr>
<tr>
<td>CH$_3$PSCI$_2$</td>
<td>4.11</td>
<td>4.30</td>
</tr>
</tbody>
</table>

$^a$Calc: calculated from the increments given in the text.

of O and S do not depend very much on the nature of the other ligands we can include these two atoms in the above-given series which was, at least in the case of sulphur, not possible for the polarizability series.

\[ H = \text{Alkyl} < \text{OCH}_3 < \text{CF}_3 < \text{O} = \text{S} \approx \text{Cl} < \text{F} \]

Finally, we compare our $\Delta\epsilon$ values to the results of a potential model [5]. In the point charge approximation the orbital energy $\epsilon_i$ of an inner shell orbital $i$ can be expressed as

\[ \epsilon_i = k_{Ai}q_A + V(q_B) + \epsilon_i^0 \]  

(23)

$q_A$ is the charge at the photoionized atom, $V(q_B)$ is the electrostatic potential at nucleus A created by the charges $q_B$ on the other atoms. $k_{Ai}$ is a parameter depending on the atom and the orbital under consideration. Theoretical values for $k_{Ai}$ can be derived from Mann's tabulation of atomic integrals [21] (this yields $k_{P_{2p}} = 14.32$ for the free phosphorus atom) or from the approximation [4]

\[ k = \frac{\xi}{n} \]

where $\xi$ is the Slater exponent and $n$ the principal quantum number of the valence shell of the photoionized atom. The latter yields $k_p = 15.35$ independent of the inner shell being considered.

Since we have separated initial and final state effects by using $1/2\Delta\beta(2p)$
as an experimentally derived estimate for the final state relaxation, the $\Delta \varepsilon$ values given in Table 1 have to be considered as solely due to initial state effects. We therefore have to correlate our $\Delta \varepsilon$ values directly with initial state charges. The correlation obtained for the CNDO/2 charges and off-atom potentials $V(q_B)$ calculated by Sodhi and Cavell [1] is shown in Fig. 2. The correlation is highly satisfactory (correlation coefficient 0.999). From the slope we obtain $k_{2p} = 13.24$, a value somewhat smaller than the above-mentioned theoretical value but in close agreement with that Sodhi and Cavell found from their analysis.

CONCLUSIONS

From the above-discussed reexamination of the experimental data of Sodhi and Cavell [1] we are able to draw the following conclusions.

(i) The quantity $\Delta \beta(i) = \Delta E_A (k_{II}) + 2 \Delta E_B (i) - \Delta E_B (k)$ is a better approximation to final state relaxation effects than the Auger parameter shift, $\Delta \alpha$, since it takes into account a possible difference in the chemical state dependence of different inner shells. $\Delta \beta(i)$ only depends on relaxation contributions connected with orbital $i$.

(ii) For the phosphorus compounds studied in ref. 1 the results obtained from $\Delta \beta$ are not very different from those obtained from $\Delta \alpha$. This is mainly due to the fact that relaxation contributions are relatively small for these compounds ($\Delta R < 2$ eV).
(iii) The contribution of different substituents to the total relaxation follows the usual assumption on group polarizabilities. Substituents which are "hard" in Pearson's definition [20] contribute little and those which are "soft" contribute much to $\Delta R$. The contribution of different substituents are, however, not generally additive.

(iv) Initial state effects do not follow electronegativities. F and Cl as well as O and S behave similarly, which may also be true for other second and third row elements. The initial state contributions of different substituents are fairly additive.

As mentioned earlier, the applicability of $\Delta \beta$ as an experimental estimate of final state relaxation contributions is not restricted to molecules in the gas phase. Applications to ternary Zintl phases [22] and technical catalysts [23] have just been completed. However, the analysis cannot be applied in a straightforward manner to systems with second row atoms, since for these atoms the Auger decay always involves valence electrons. This limitation also holds for the application of the Auger parameter shift, $\Delta \alpha$.

ACKNOWLEDGEMENTS

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