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PE Spectra, Group V Trihalides

The He I photoelectron spectra of the group V trihydrides and trihalides are assigned on the basis of a qualitative $D_{3h}/C_{3v}$–MO model which includes the analogous group III trihalides. Trends and irregularities across the series by varying either the central atoms or the substituents are discussed. Using experimentally fitted (PES) and optimized parametrization the new SCC–$X_a$ method yields results in excellent agreement with both measured ionisation potentials and dipole moments, especially for the heavier homologues. The electronic distribution and the trends in electronic and molecular properties are examined for the model series $ER_3$ ($E = N, Sb$; $R = H, Cl$) and $AsR_3$ ($R' = H, Hal$) within a complete SCC–$X_a$ (and EHT) population analysis. — The PE Spectrum of BiMe$_3$ is presented.

1. Introduction

Trivalent group V halides and hydrides enjoy great and lasting popularity among theoreticians in the field of chemistry since the pioneering work of Gillespie [2] in 1960. To appreciate the host of respective publications which have appeared since, would be beyond the scope of our contribution. Yet, the main interest has been restricted to model compounds such as $NH_3$, $PH_3$ or $PF_3$ [3]. Publications dealing with the electronic properties of heavier homologues containing As or Sb or even with serial changes within this group are rare [4, 3m], reflecting thus, the immense time-consumption of respective ab initio calculations or — generally — those of SCF quality. Photoelectron (PE) spectra of molecules $EH_3$ [5] and $EHal_3$ [6] excluding $SF_3$ are well documented by a

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Fig. 1. General view of the He I PE spectra of the known group V trihydrides and trihalides $ER_3$ with assignment and band correlation based on the $C_{3v}$ molecular symmetry. The spectra of $NHal_3$ [6] and $SbH_3$ [5a] are sketched from literature.
Table I. Band maxima (vertical IPs) of the known group V compounds ER₃ (E = N—>Sb; R = H, Hal) from He I PE spectra.

<table>
<thead>
<tr>
<th>Compound</th>
<th>IE₁(nₑ)</th>
<th>IE₂</th>
<th>IE₃</th>
<th>...</th>
<th>...</th>
<th>IE₆(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>10.15³/10.83⁶ a₁</td>
<td>14.98³/16.0⁵ e</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NF₃</td>
<td>13.73 a₁</td>
<td>16.15 a₂</td>
<td>16.55 e</td>
<td>17.52 e</td>
<td>19.71 a₁</td>
<td>21.14 e</td>
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<tr>
<td>NCl₃</td>
<td>10.69 a₁</td>
<td>11.66 a₂</td>
<td>12.08 e</td>
<td>13.02 e</td>
<td>15.41 a₁</td>
<td>16.70 e</td>
</tr>
<tr>
<td>PH₃</td>
<td>9.96⁵/10.59³ b a₁</td>
<td>12.64⁴/13.6³ e</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PF₃</td>
<td>12.28 a₁</td>
<td>15.89 e</td>
<td>16.29 a₂</td>
<td>17.35 e</td>
<td>18.51 a₁</td>
<td>19.31 e</td>
</tr>
<tr>
<td>PCl₃</td>
<td>10.52 a₁</td>
<td>11.71 e</td>
<td>12.01 a₂</td>
<td>12.97 e</td>
<td>14.24 a₁</td>
<td>15.22 e</td>
</tr>
<tr>
<td>PBr₃</td>
<td>10.00 a₁</td>
<td>10.67 e</td>
<td>10.87/11.18 e</td>
<td>11.85 e</td>
<td>13.09 a₁</td>
<td>14.09 e</td>
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<tr>
<td>PI₃</td>
<td>9.05 (a₁)</td>
<td>9.32/9.50/10.15 (e⁷+a₂)</td>
<td>10.43/10.55 (e)</td>
<td>11.7 (a₁)</td>
<td>12.5/12.8 (e)</td>
<td></td>
</tr>
<tr>
<td>AsH₃</td>
<td>9.89⁴/10.58⁶ b a₁</td>
<td>12.12⁴/13.0³ e</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AsF₃</td>
<td>13.00 a₁</td>
<td>15.24 (e+ₐ₂)</td>
<td>16.21 e</td>
<td>17.22 a₁</td>
<td>17.82 e</td>
<td></td>
</tr>
<tr>
<td>AsCl₃</td>
<td>10.95 a₁</td>
<td>11.75 (e+ₐ₂)</td>
<td>12.58 e</td>
<td>13.77 a₁</td>
<td>14.60 e</td>
<td>19.4 a₁</td>
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<tr>
<td>AsBr₃</td>
<td>10.31 a₁</td>
<td>10.75 e</td>
<td>11.12 a₂</td>
<td>11.65 e</td>
<td>12.83 a₁</td>
<td>13.67 e</td>
</tr>
<tr>
<td>AsI₃</td>
<td>9.23 (a₁)</td>
<td>9.47/9.55/10.23 (e⁴+a₂)</td>
<td>10.45/10.63 (e)</td>
<td>11.71 (a₁)</td>
<td>12.34/12.59 (e)</td>
<td>19.76 (a₁?)</td>
</tr>
<tr>
<td>SbH₃</td>
<td>9.51⁵/10.02³ a₁</td>
<td>11.39⁵/11.9³ e</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>SbF₃</td>
<td>12.54 a₁</td>
<td>14.68 (e+ₐ₂)</td>
<td>15.30 e</td>
<td>16.06 a₁</td>
<td>16.55 e</td>
<td></td>
</tr>
<tr>
<td>SbCl₃</td>
<td>10.73 a₁</td>
<td>11.50 a₂</td>
<td>11.62 e</td>
<td>12.28 e</td>
<td>13.20 a₁</td>
<td>13.48 e</td>
</tr>
<tr>
<td>SbBr₃</td>
<td>9.77 a₁</td>
<td>10.22 a₂</td>
<td>10.35/10.75 (e)</td>
<td>11.14 e</td>
<td>12.12 a₁</td>
<td>12.84 e</td>
</tr>
<tr>
<td>SbI₃</td>
<td>9.06 (a₁)</td>
<td>9.26/9.40/10.04 (e⁷+a₂)</td>
<td>10.19/10.40 (e)</td>
<td>11.29 (a₁)</td>
<td>11.89/12.05 (e)</td>
<td></td>
</tr>
</tbody>
</table>

a Adiabatic IE; b band maximum; c vertical IE.

The PE spectra given in Fig. 1 show both common and striking features which need some comment:

i) On descending the Vth group, bands show an overall more or less small low energy shift, reflecting the trend and the dominant effect of the respective E p valence shell IPs. Bands are "moving" closer to each other, because longer valence bonds are accompanied by decreasing interactions between appropriate central atomic and peripheral R₃ orbitals (the overlap between these orbitals becomes less). The same is true on going from F to I down the VIIth group maintaining the central atom (e.g. PF₃ → PI₃).

ii) On passing from N to Sb the low energy shift is less pronounced for the first bands, i.e. for the lone pair orbital ionisation energies (nₑ or IEₑ) of the central atoms which are held responsible for the donor properties of these bases. The levelling trend for the nₑ energies which is lost for the trifluorides results mainly from the geometry dependent differing E₂pₐ hybridization contributions to the orbital composition of nₑ (Table II) and was thoroughly discussed for EMe₃ and EH₃ [7]. The 4a₁ correlation

large number of discussions each presenting a partial aspect of the entire set of experimental and theoretical problems involved.

We have confined ourselves to the study of the electronic structures and properties of group V compounds with respect to serial changes upon replacing alternatively central atoms or substituents, continuing earlier work on the parent trialkyls [7]. To furnish an overall view of this class of compounds we have used He I PE data in conjunction with the time-saving SCC—Xα method [8] which will be shown filling in the gap left for the heavy homologues by other computational methods.

2. Results and Discussion

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lated by SCC—Xα energies and will be discussed below. Vertical ionisation potentials (IPs) are listed in Table I in the order of increasing binding energies.

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Fig. 2. a) Qualitative MO model for (E)R₃ systems belonging to both point groups C₃ᵥ and D₃h. The R₃ group orbitals are designated R, V, T with respect to their relative orientations. E is the baricenter of the AO energies of isolated R substituents. Explanation see text.

b) Simulation of the “composite molecule” procedure by SCC-Xₐ calculations for Cl₃, SbCl₃ and GaCl₃ to visualize the magnitudes of the through-space and through-bond interactions for the hypothetical process: E+Cl₃→ECl₃ (C₃ᵥ)→ECl₃ (D₃h). Explanations see text.
lines (Fig. 1) exhibit significant deviations from the overall trend. It is apparent that together the arsines possess higher first IPs than the parent phosphines and stibines. This originates from the relative position of As within the table of the elements: Due to the complete but poorly shielding 3d-shell the effective nuclear charge $Q_{\text{As}}$ influences particularly 4s and 4p AOs which compose $n_{\text{As}}$ (the "scandide" contraction).

Yet, the outstanding feature concerning the $n_E$ band correlation is associated with the PF$_3$ band pattern: PF$_3$ exhibits an anomalously low first IP when compared to the IE$_1$ of the EF$_3$ congeners or of the corresponding trihydrides. This is caused by the counteracting changes in s/p-hybridization going from EH$_3$ to EF$_3$ (note the reversed order of bond angles for neutral EH$_3$ and EF$_3$ (E = N, P; Fig. 4a) which cannot be explained on electronegativity grounds [2c]) stabilizing $n_{\text{PF}_3}$ but destabilizing $n_{\text{PF}_3}$ with respect to the parent IE$_1$ of EH$_3$.

An alternative explanation is furnished by the "perfluoro effect" [9]. Although this effect is, strictly speaking, only valid for planar $\pi$ systems it could partially be active for the $\pi$-type MOs of PF$_3$ and hence for the $n_{\text{PF}_3}$ lone pair MO (compare the HOMO contour plots of EF$_3$ given in Fig. 3b). Here, hyperconjugation partly counteracts the large $\sigma$-type electron withdrawal (−1) exerted by the F atoms. Hyperconjugative destabilization of $n_{\text{PF}_3}$ by F obviously does not cancel the stabilizing inductive ability of F as required by the perfluoro effect, but, might well be one of the reasons for the low energy position of the first band of PF$_3$.

Spin orbit splitting has to be considered whenever fourth and fifth row atoms are involved. There are striking similarities between the band patterns of the chlorides, bromides and even iodides (Fig. 1) which allow the qualitative band assignment on the basis of the C$_3$v MO model (Fig. 2 a, b) to be adopted instead of considering the double group C$_3$v, with its symmetry lowering; therefore, we renounced the assignment of the respective bands for EI$_3$ in detail (see also Table I), but, we agree with the proposals for EI$_3$ as found in literature [6i–k].

iii) The band group following IE$_3$ shows only a slight energy variation within the series upon exchanging the central atoms and is therefore assigned to ionizations from rather pure substituent MOs (compare to Fig. 2). These $n_R$ bands can be distinguished by a high count rate and by their narrow half widths. The band pattern can be fully explained on the basis of the qualitative MO model as depicted in Fig. 2.

iv) The high energy bands which suffer from pronounced band shifts particularly when passing from E = N to P have to be assigned to typical $\sigma_{E-R}$ type MOs*. The large gap between analogous $\sigma_{E-R}$ and $\sigma_{P,\text{AsSb}-R}$ MO energies (note the IP$_{E-H}$ trend as well) is a characteristic feature for the PE data of such species in general and is often accompanied by interchanges of $\sigma_{E-R}$ and $n_R$ (R = e.g. Me, CF$_3$, Me/Hal, etc.) correlation lines between the second and third row species (cf. N$\equiv$P or F$\equiv$Cl, etc.) [1].

v) The heavier congeners as EI$_3$ show some complex structure in the high energy region which we tentatively attribute to ionisations from s-type MOs obscured by shake up and/or autoionization states as indicated in Fig. 1. We prefer not to discuss these features in depth, since He II PE data which would help to clarify the position of the E$_3$−Hal energies are still missing.

3. The Qualitative Interaction MO Model (C$_{3v}$/D$_{3h}$)

The band pattern of the PE spectra of the title compounds and of analogous isoelectronic molecules (e.g. HSiCl$_3$) can be sufficiently rationalized within the frame of the qualitative MO model presented in Fig. 2. This model is based on the local and higher D$_{3h}$ symmetry of the planar R$_3$ fragment of ER$_3$ systems belonging to both point groups C$_3$v and D$_{3h}$ and is equally well suited to discuss the PE spectra of group III [10] and group V compounds. The procedure (known also as the "composite molecule" MO approach [11]) receives strong support from the differing spin-orbit energy splittings found for the occupied degenerate MOs of the tribromides and triiodides (4e, 3e, 2e; Fig. 1) which were shown to depend on the different orientations of the n$_R$ MOs (radial = R, horizontal = T (tangential), vertical = V; Fig. 2) [12].

In Fig. 2a the relative R$_3$ group orbitals and their energies are generated from the energetic baricenter (R) of the isolated substituents on allowing through-space interactions to become effective. Here, only valence orbitals with predominant $p$-character and their relative energies are taken into account. The

* The 3a$_1$-PE bands of AsF$_3$ and SbF$_3$ show vibrational fine structure confirming this assignment (see H. Walther, l.c. [1]).
model which was simulated by the SCC–Xα method expanded by Jorgensen's PSI/77 – program [13] to create electron density and MO contour plots – is selfexplanatory. The energy sequence derived for R3 and – after admitting through-bond interactions (R3+E→ER3) – for ER3 is governed by the nodal rule and the overlap of the lobes. The MO types are characterized with respect to out-of-plane (V) and in-plane contributions (T, R) continuing with the convention to symbolize eigenvectors introduced earlier [6]). R-type MOs are particularly involved in σ-type bonding and are totally changed in energy by allowing them to interact with appropriate central AOs. Under D3h and C3v symmetries they are subject to sp-hybridization which is neglected in Fig. 2a for clarity. The MO model for the hydrides EH3 is indirectly incorporated in Fig. 2 where it is covered by the respective R-section.

There are two types of MOs in Fig. 2a which need further inspection: The group MOs 1a2' and 1e' are unique in character, since they do not exhibit any contributions from the central atoms for symmetry reasons. They could therefore serve as internal inductive standards. Although – formally – only 1a2' is maintained on lowering the symmetry (D3h→C3v), the discrimination of the former degenerate orbitals (e', e''→e) is still present and is corroborated by the (final) MO types plotted in Fig. 2b. There is also strong support from the half widths of the respective PE peaks and from the comparably large spin-orbit splitting observed for the "e"-bands of the triiodides (Fig. 1) as mentioned earlier. As deduced from our calculations or as indicated experimentally for isosteric species [1] the distinction between both in-plane T and R type MOs vanishes during the hypothetical process R3+E→ER3 (C3v, D3h) allowing the low energy 4e MOs to gain appreciable σE=R bonding character (note the reversed assignment of nR and σE→R MO energies for E = P, As, Sb and R = Me, CF3 [1] in contrast to R = Hal (Fig. 1)).

Since neither through-bond nor through-space interactions nor the energy baricenter (R) are accessible from the PE spectra we have performed some model SCC–Xα calculations for SbCl3, Cl3/Sb, Cl3/Ga and GaCl3 to unravel the magnitudes of the various σ and π type interactions βRR and βER. To diminish the influence of the differing inductive contributions from the central atoms we have selected Sb and Ga for their similar electronegativities [14]. Additionally, the bond lengths are of similar magnitudes.

Fig. 2b shows that the perturbation of R3 group orbitals by E AOs is equal to zero for 1a2 (inductive effects being neglected!) – which is but subject to strong through-space interaction – and is least for 1e'' or 3e, resp. The energy shift is largest for R-type group orbitals of R3 which are consumed for bond formation. The less varied V- and T-type MOs refer to more or less pure substituent MOs; they cause the most striking feature of the PE spectra given in Fig. 1 since the respective characteristically shaped bands (1a2, 4e, 3e, (3a1)) do not change much in energy upon exchanging the central atoms (for GaCl3 cf. lit. [10]). Since interchanges of 1a2 and 4e correlation lines are not symmetryforbidden the sequence is not clearcut in cases where both energies are hidden inside a single PE band (as in AsCl3 or SbCl3). There is strong correspondence between the V- and T–PE band pattern of parent group V and group III [10] compounds as far as smaller through-space interactions βRR and the missing lone pair orbital energy are considered for the latter.

4. The Theory

The SCC–Xα method [8] is based on a one-electron Hamiltonian which can be separated into an atomic part and the neighbour contributions to the potential according to (1)

\[ H_{ij}^{\nu\nu} = \frac{1}{2} (\epsilon_i^{\nu} + \epsilon_j^{\nu}) S_{ij}^{\nu\nu} + \frac{1}{2} (V_{ij}^{\nu\nu} + V_{ji}^{\nu\nu}) \]

(1)

where \( S_{ij}^{\nu\nu} \) is the overlap matrix. The matrix elements of the potential \( V_{ij}^{\nu\nu} \) are defined as

\[ V_{ij}^{\nu\nu} = \sum_{x=y} \int \phi_x^{\nu}(r) \phi_y^{\nu}(r - R_{xy}) \phi_x^{\nu}(r - R_{xy}) d^3r \]

(2)

where \( \phi_x^{\nu}(r) \) – taken here as a Slater-type orbital (STO) – is an atomic basisfunction of the j-th orbital centered at the ν-th atom. A reasonable atomic model potential additionally allowing the matrix elements to be calculated analytically results from a combination of the Xα-approximation with an assumed atomic charge density which is proportional to \( e^{-\eta r} \) [8]:

\[ V_{at}(r) = -\frac{2Q}{r} N \left( \frac{2e^{-\eta r}}{r} + \eta e^{-\eta r} \right) - \alpha' \eta N \frac{1}{2} e^{-\eta r} \]

(3)

Here, \( N \) stands for the number of electrons and \( Q = Z-N \) represents the effective atomic charge. The exchange parameter \( \alpha' \) is taken to equal 0.706 for all atoms [8, 15]. Consequently, the method contains three undetermined quantities which are expli-
citly the atomic ionisation potentials $\epsilon_i^+$, the Slater exponents $\zeta_i$, and the charge density exponent $\eta_i$. They are all chosen charge-dependent as defined in eq. (4–6):

\begin{align}
\epsilon_i^+ &= \epsilon_i^0 + \epsilon_i^1 Q_v + \epsilon_i^2 Q_v^2 \\
\zeta_i &= \zeta_i^0 + \zeta_i^1 Q_v \\
\eta_i &= \eta_i^0 + \eta_i^1 Q_v 
\end{align}

As has been described [16] $\epsilon_i^0$, $\zeta_i$, $\eta_i$, and $\eta_i^1$ are determined from atomic data, whereas $\eta_i^0$ are fitted to experimental molecular ionisation potentials and dipole moments. Compared with these former calculations [16] two changes have been made in the present work:

The first one concerns the calculation of the three-center integrals of eq. (7) which is the most time-consuming part of the program due to their enormously increasing numbers in larger systems:

\begin{equation}
V_{i,j,v}^{\mu
u} = \sum_{\kappa \neq \mu \nu} \int \phi^{(\mu)*}(\bar{r} - \bar{R}_{mv}) V_{\mu \nu}^{(\kappa)}(\bar{r} - \bar{R}_{mv}) \phi^{(\nu)}(\bar{r}) \, d^3 r \quad (7)
\end{equation}

Substitution of the one-center expansion of the potential

\begin{equation}
V_{\mu \nu}^{(\kappa)}(\bar{r} - \bar{R}_{mv}) = 4\pi \sum_{l,m} V_{\mu \nu}^{(\kappa)}(r,R_{mv}) Y_{lm}(\hat{r}) Y_{lm}(\hat{r}) \quad (8)
\end{equation}

with the radial parts $V_{\mu \nu}^{(\kappa)}(r,R_{mv})$ given previously [8] yields

\begin{equation}
V_{i,j,v}^{\mu
u} = 4\pi \sum_{\kappa \neq \mu \nu} \sum_{l,m} Y_{lm}(\hat{r}) \phi^{(\mu)*}(\bar{r} - \bar{R}_{mv}) \phi^{(\nu)}(\bar{r}) \, d^3 r. 
\end{equation}

Replacing now the (angular-independent) potential part $V_{\mu \nu}^{(\kappa)}$ by an average over the interval $[0, R_{mv}]$ we obtain the simple expression

\begin{equation}
V_{i,j,v}^{\mu
u} = 4\pi \sum_{l,m} B_{lm} \int \phi^{(\mu)*}(\bar{r} - \bar{R}_{mv}) Y_{lm}(\hat{r}) \phi^{(\nu)}(\bar{r}) \, d^3 r \\
B_{lm} = \sum_{\kappa \neq \mu \nu} V_{\mu \nu}^{(\kappa)}(R_{mv}) Y_{lm}^{*}(\hat{R}_{mv}). 
\end{equation}

The remaining integral is a two-center integral; it should be emphasized that the $\kappa$-dependence is now removed from the integrand so that the number of integrals to be computed actually increases just as fast as the corresponding number of two-center integrals. Furthermore, it has been shown [17] that this approximation generally causes changes of less than 5% even for dipole moments and electric field gradients compared to the exact expression (7), the reason being the preservation of the full angular dependence. This conclusion can be drawn from the results of analogous calculations using an angular averaged approximation instead of (9) where the complete radial part is retained. In this case, dipole moments even may have the wrong sign and the ordering of energy levels is changed in several cases.

Secondly, the iterative process turns out to be self-consistent with regard to the occupation numbers $x_{nl}$ of the constituent AOs instead of the effective charges $Q_v$, yielding more stable results for subsequently computed spectroscopic data. It is thus necessary, as is typical for self-consistent charge methods, to define an appropriate form of population analysis. We have adapted here a weighted form according to

\begin{equation}
x_i^w = 2a_i^w \sum_{\kappa \neq \lambda \mu \nu} S_{i\kappa}^{w} P_{\mu \nu}^{w}/(a_i^w + a_{\lambda}^w) \\
a_i^w = \frac{1}{c_i} \sum_{m,n=-1}^{l} x_{nm} \frac{1}{2l+1} 
\end{equation}

which we found to be more reliable than the Mulliken population analysis whenever strong polarity is to be considered or atoms with largely deviating atomic sizes are involved.

The most striking examples in this respect are the halides H–Hal where the application of the Mulliken population analysis results in Cl being almost neutral while Br and I become positively charged ($Q_{Br} = +0.034e$, $Q_I = +0.108e$). That this is no artefact of the SCC–Xa parametrization procedure may be concluded from an earlier ab initio calculation on HBr [18] where the Mulliken population analysis again results in a positive charge of 0.023 e on bromine. These unreasonable results are avoided by our technique; only iodine in HI is calculated to be slightly positive with $Q_I = +0.014e$.

The SCC–Xa parameters used here have been optimized for $E_2/E_4$ and Hal–Hal' by fitting the calculated IPs to the experimental ones obtained from UV–PES ($E_2/E_4 = (N)$, $P$, $As$ [19a], $Sb_2/Sb_4$ [19b]; H–Hal and Hal$_2$ [20]). The universal applicability and the quality of the SCC–Xa procedure especially for P and As compounds are demonstrated in Table II where eigenvalues and HOMO AO compositions are summarized for a range of these group V bases. Figures 4a to 4c comprise a survey of related experimental and calculated properties using SCC–Xa (Fig. 4b) and EHT methods (Fig. 4c; the latter with and without charge-dependence).
Table II. Listing of the SCC—X_a eigenvalues of the occupied MOs for EX_3 group V trihalides and the percentual AO compositions of the respective HOMOs (4a_i).

<table>
<thead>
<tr>
<th>ER_3</th>
<th>1a_i</th>
<th>1e</th>
<th>2a_i</th>
<th>2e</th>
<th>3a_i</th>
<th>3e</th>
<th>4e</th>
<th>1a_2</th>
<th>4a_i</th>
<th>%-HOMO-composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF_3</td>
<td>44.95</td>
<td>39.98</td>
<td>25.67</td>
<td>21.48</td>
<td>20.35</td>
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5. On the Electronic Origin of Selected Molecular Properties — an Illustrated Attempt to Relate Experimental and Calculated Data

There is evidence from nonspecialist chemical literature [14] that the ER_3 bases belong to those molecules that are discussed most frequently. Their bonding properties and reactivities comprising their donor/acceptor qualities, inversion barriers, hybridization states, d-orbital contributions or dipole moment trends, etc., have called up theoreticians since
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A)

\[
\begin{align*}
& \text{H}_3\text{N} \quad \mu = 1.47 \text{ D} \quad \angle \text{HNH} = 107.2^\circ \quad \text{N} = 1.015 \text{ Å} \\
& \text{F}_2\text{N} \quad \mu = 0.2 \text{ D} \quad \angle \text{FNF} = 102.5^\circ \quad \text{N} = 1.37 \text{ Å} \\
& \text{Cl}_2\text{N} \quad \mu = 0.60 \text{ (0.39) D} \quad \angle \text{ClNC1} = 107.9^\circ \quad \text{N} = 1.76 \text{ Å} \\
& \text{Cl}_2\text{P} \quad \mu = 0.78 \text{ D} \quad \angle \text{PC1} = 100.1^\circ \quad \text{P} = 2.04 \text{ Å}
\end{align*}
\]

\[a = \text{Atomic electronegativities [27]; } b = \text{bond energies (kcal/mole) [14]; } c = \text{inductive substituent effects [28].}\]

B)

\[
\begin{align*}
& \text{H}_3\text{N} \quad \mu = 1.42 \text{ D} \\
& \text{F}_2\text{N} \quad \mu = -0.19 \text{ D} \\
& \text{Cl}_2\text{N} \quad \mu = 0.45 \text{ D} \\
& \text{Cl}_2\text{P} \quad \mu = 1.22 \text{ D} \\
& \text{Cl}_2\text{Sb} \quad \mu = 2.70 \text{ D}
\end{align*}
\]

\[a = \text{Effective atomic charges; } b = \text{overlap charges.}\]
their discovery or postulation. Pauling, Lewis and VSEPR models [2, 14] are closely associated with these compounds as are Walsh diagrams [21, 7, 2b] or Pearson’s HSAB concept, cf. [14], or even bent bond pictures [22]. As far as thermodynamics do not account for their molecular properties — e.g. as for the explosive natures of NCl₃ or NI₃ — and as far as properties do not refer to virtual orbitals — e.g. as to the π-acceptor quality of PF₃ [14] — the electronic distribution in such series should indirectly or directly reflect their chemical behaviour.

To illustrate what happens to the electronic distributions of the ER₃ molecules on exchanging the central atoms (E = N → Sb, Ga) or the ligands (R = H, F → I), resp., total valence electron density plots excluding d orbitals appear to be most instructive allowing the periodicity of substituent effects and the influence of varying atomic sizes, electronegativities and polarizabilities to be assessed. Cross-sectional electron density plots with the basal plane passing through E, R₁ and 1/2 R₂ R₃ are presented in Fig. 3a for the model series NH₃, NCl₃, PCl₃, AsCl₃ and SbCl₃ as well as for AsH₃, AsF₃, AsCl₃, AsBr₃, and AsI₃. GaCl₃ — void of a central atomic lone pair MO — is included here for comparison. In Fig. 3b valence MO wavefunction contour maps are given for the lone pair MOs of both series to see whether certain atomic properties can be traced back to a single MO which in our case is the HOMO, the most important one concerning reactivity and basicity as is generally assumed. 

The total valence electron densities of both series show a characteristic tendency to delocalization going towards the heavier homologues — note the drastic change between first or second row, resp., and third row atoms (NCl₃ → PCl₃ or AsF₃ → AsCl₃) in Fig. 3a. The apparent delocalization on descending the series AsR₃ may be interpreted quite similar to the nephelauxetic effect [14] known from transition metal halide complexes. The electron densities are obviously governed by the relative electronegativities decreasing with growing atomic number. The same is true for the atomic effective charges Q_eff given in Fig. 4b and 4c. They are nearly balanced in the case of NCl₃ and are responsible for the unpolar N−Cl bond and partially for its small dipole moment.

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<th>N</th>
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<th>Cl</th>
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*a = Formal charges calculated within an iterative EHMO method; b = overlap charges calculated within an iterative EHMO method; c = bond orders [23] calculated within the noniterative EHMO procedure.

Fig. 4. A) A selection of atomic and molecular properties including atomic electronegativities, experimental bond energies and dipole moments, inductive substituent effects and structural data for representative group V hydrides and halides; B) effective atomic charges, bond and interatomic overlap charges as well as dipole moments for selected group V trihydrides and trihalides ER₃ as calculated by the SCC–Xₐ procedure; C) EHMO effective charges, overlap populations and dipole moments for ER₃ molecules (from the iterative version, cf. cit. [8]) as well as bond orders (from the noniterative procedure, cf. cit. [23]).
The bond order as calculated within the non-iterative EHT procedure [23] amounts to 0.98 and is in excellent agreement with the bond order of 1 as claimed by Pauling [24] for the N—Cl bond of NC13. There is obviously no connection between experimental bond energies [14, 25] (Fig. 4a) and calculated properties such as EHT-bond orders [23b] or SCC—Xα overlap charges $q_{\nu\mu} = 2\Sigma P_{\nu\mu} S_{\nu\mu}$ for the polar trihalides (in contrast to the trihydrides).

Two variations may be distinguished along the HOMO series of ER3 in Fig. 3b: With respect to the bonding character between E and Cl one might note that the HOMO (not the bond itself!) of NC13 is predominantly \(\pi\)-antibonding in character while AsC13 and SbCl3 are better described as hybrids of weak \(\sigma\)-bonding and antibonding \(\pi^*\) states (cf. the increasing \(s\)-contribution to the HOMO in going from NC13 to AsC13, Table II). With respect to the variations of \(\psi\) with \(r\) parallel to the threefold molecular axis, \(i.e.,\) the gradient of \(\psi\), there is strong parallelism to the acid-base behaviour of these compounds if one correlates $\partial \psi / \partial r$ with the hardness of the bases presented here (hardness obviously decreases from NC13 to SbCl3). One obtains thus a simple quantum mechanical picture of the HSAB principle [14]. There is evidence that gas phase basicities (avoiding solvation effects) correlate with the IE1 of the group V bases [26]. Unfortunately, proton affinities are rare for fourth and fifth period compounds. Recent measurements show that proton affinities parallel both trends of IE1 by varying either E or R [14, 26].

The trends and the large changes of \(\sigma\)- and \(\pi\)-character of the E—R bond within the HOMO-eigenvectors of the group V trihalides depending on the electronegativity difference of the constituent atoms E and R as claimed by Gimarc [4b] could not be reproduced by our computational methods. The same is true for the relative AO composition deduced here for these species with respect to the difference of E and R atomic electronegativities [1, 4b, 27].

6. Experimental

The trihalides of phosphorus, arsenic and antimony are partly commercial samples (Fluka GmbH; Riedel-de Haën AG; AsBr3: Serva GmbH; AsI3: Preussag) or were prepared and purified by known methods [29]. The He I PE spectra were recorded on PS 16 (Perkin Elmer) and UPG 200 spectrometers (Leybold-Heraeus GmbH) and were calibrated with argon. SCC—Xα and EHT calculations were performed on a TR 440 computer (Rechenzentrum der Freien und Hansestadt Hamburg).

This work was supported by the Deutsche Forschungsgemeinschaft. The kind help of Ms. Heike Brandstätter who measured the spectra and serviced the UPG spectrometer is gratefully acknowledged. S. E. and H. W. thank Prof. H. tom Dieck for helpful discussions and steady support.

Appendix

Two papers dealing with PE data of group V trihalides appeared after this report had been submitted. The first [30] dedicated to the whole EHAl3 series may be regarded as a mere appreciation of a modified SCF—Xα-multiple scattering method and hinges on the agreement between calculated and experimental IPs. Properties other than the IP ordering of the trihalides have not been mentioned. However, the contribution of Novak and Potts [31] on the PE spectra of BiHal3 including SbF3 is closely related to the data presented here and prompts us to disclose our PES results on BiMe3. Trimethyl bismuthane is the last member of the group V trimethyl series which are known to PE spectroscopists for E = N—Sb so far [7]; their electronic and PE spectroscopic properties have been discussed here referring to the model series of the lighter trihydrides. The PE spectrum of BiMe3 given in Fig. 5 shows one characteristic feature, namely, the strong spin-orbit splitting of ca. 0.9 eV found for the $\sigma_{Bi—CH}$ ionization energy (IE2: 4e with respect to C3 v). The energy position of the $n_{Bi}$ (IE1) band centered at 8.44 eV fits well into the scheme of the nearly constant $n_E$ IPs recorded for the EMe3 analogues [7].

![Fig. 5. He I PE spectrum of BiMe3 with qualitative assignment (numbers referring to band maxima).](image-url)


