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Theoretical predictions of trends in spectroscopic properties of homonuclear dimers and volatility of the 7p elements

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Fully relativistic density functional theory electronic structure calculations were performed for homonuclear dimers of the 7p elements, 113–118 and their 6p homologs, Tl through Rn. All the dimers of the heaviest elements, with the exception of (118)², were found to be weaker bound than their lighter homologs. The difference in the dissociation energy (Dₐ) between the 6p and 7p homologs was shown to decrease from group 15 to group 17, with a reversal of the trend in group 18. A remarkable feature is a shift of the maximum in Dₑ(M₂) from group 15 in the third through sixth rows to group 16 in the seventh row. Strong relativistic effects on the 7p atomic orbitals, particularly, their large spin-orbit splitting, were shown to be responsible for these trends. Using the calculated Dₑ(M₂), the sublimation enthalpies, ΔHₘₐₜ, of macroamounts, or formation enthalpies of gaseous atoms, ΔH₂(g), of the heaviest elements were estimated using a linear correlation between these quantities in the chemical groups. The newly estimated values are in good agreement with those obtained via a linear extrapolation from the lighter homologs in the groups. © 2010 American Institute of Physics. [doi:10.1063/1.3425996]

I. INTRODUCTION

Studies of chemical properties of the heaviest elements are among the most fundamental in all of chemistry. Due to the instability of nuclei and short half lives of their isotopes, they are, however, limited to measurements of very few properties—volatility in the gas phase and complex formation in solutions.¹,² Volatility is studied with the use of the gas-phase chromatography technique, whereby single atoms or molecules are adsorbed on the surface (usually a noble metal) of detectors located along a chromatography column.³ The obtained adsorption enthalpies, ΔHₘₐₜ, are then related to the sublimation enthalpies, ΔHₘₜ, of macroamounts using a linear correlation between them.⁴ So far, such experiments with the use of gold plated detectors were performed for elements 112 (copernicium, Cn) and 114 and their lighter homologs.⁵,⁶

Presently, 7p elements such as 113 and heavier are in the focus of the experimental gas-phase studies: Several long-lived neutron-rich isotopes⁷ were discovered suitable for their chemical separation. These elements are expected to be very volatile and less reactive than their lighter 6p homologs. The reason for that is a large spin-orbit (SO) splitting of the 7p atomic orbitals (AOs) resulting in the decreasing accessibility of the 7p₁/₂ AO for bonding.⁸,⁹ Early predictions based on linear extrapolations from the lighter homologs in the chemical groups have also shown that elements 112–117 should have smaller ΔHₘₜ of formation enthalpies of gaseous atoms, ΔH₂(g), than their lighter homologs.¹⁰,¹¹

Fully relativistic band-structure calculations¹² for the solid state of Cn have, however, shown that its cohesive energy, E coh, should be larger than that of Hg, in contrast to the earlier predictions.¹¹ This case shows that linear extrapolations may not always work, and a careful analysis of the electronic structures of gaseous and solid states of the elements should be made before their use. Thus, relativistic electronic structure calculations are desirable in order to reliably predict sublimation and adsorption properties of the heaviest elements and to understand the nature of the chemical interactions and trends.

In our earlier work,¹³ we have shown that metal-metal interactions in the solid state, or adsorption energies on metal clusters, can be reliably predicted on the basis of calculations of binding energies of intermetallic dimers. Using results of the four-component (4c) density functional theory (DFT) calculations, we have shown that the difference in the M₂(Auₙ) (M=Hg and Cn; Pb and element 114; 1 ≤ n ≤ 120) binding energy between homologs does not change much with the gold cluster size and adsorption position. We have also shown¹³,¹⁴ that Dₑ(M₂) of groups 12 and 14 elements correlate with E coh or ΔHₘₜ.¹²,¹⁵

In a similar way, we will try to give here estimates of ΔHₘₜ of the 7p elements (113–117) on the basis of the calculated binding energies of their homonuclear dimers. We will do so again via a correlation between Dₑ(M₂) and known ΔHₘₜ or ΔH₂(g), in the chemical groups in order to take into account the gradual change in the macroamount structure and bonding.

Results of our previous 4c-DFT calculations on Cn₂ and (114)₂ are published in Refs. 13, 14, and 16. The M₂ dimers of elements 112–115 and 117 were also considered in the
framework of the 2c- and 4c-Beijing density functional (BDF) method, in different approximations.\textsuperscript{17-22} Relativistic effective core potentials single and double couple cluster (RECP CCSD) calculations were reported for Pb\textsubscript{2} and (114)\textsubscript{2}.\textsuperscript{18} The RECP were also applied to M\textsubscript{2} (M is elements 112, 114, and 118).\textsuperscript{23} Earlier, the electronic structure of (113)\textsubscript{2} was studied on the basis of \textit{ab initio} Dirac–Fock (DF) calculations.\textsuperscript{24} Results of these various calculations for M\textsubscript{2} and other small diatomic molecules of the 7p elements and their 6p homologs, e.g., MH, are critically compared in Refs. 21 and 22. A broader overview of calculations for the 7p elements is given in Refs. 25 and 26. All those calculations have shown that compounds of the 7p elements in the low oxidation states should be less stable than those of their 6p homologs.

Section II contains a description of the method used. Section III offers a short overview of atomic energy levels. Results and discussion of the molecular calculations are given in Sec. IV followed by conclusions in Sec. V.

II. METHOD OF THE CALCULATIONS

For the calculations, we have used our four-component relativistic DFT method developed within the noncollinear spin-polarized formalism.\textsuperscript{27} In this approximation, the total energy is given by the following expression:

\[
E = \sum_{i} n_{i} \left( \langle \phi_{i} | \hat{H} | \phi_{i} \rangle + \int \rho \hat{V}_{\mathrm{NG}} d^{3}r + \frac{1}{2} \int \rho \hat{V}_{\mathrm{H}} d^{3}r + E_{\mathrm{xc}}[\rho, \bar{m}] \right) + \sum_{p \neq q} \frac{Z_{p} Z_{q}}{|\vec{R}_{p} - \vec{R}_{q}|},
\]

(1)

with the density \( \rho \) and magnetization \( \bar{m} \) expressed as

\[
\rho(\vec{r}) = \sum_{i=1}^{M} n_{i} \phi_{i}^{\ast}(\vec{r}) \phi_{i}(\vec{r})
\]

and

\[
\bar{m}(\vec{r}) = -\mu_{B} \sum_{i=1}^{M} n_{i} \phi_{i}^{\ast}(\vec{r}) \beta \Sigma \phi_{i}(\vec{r}).
\]

(2)

(3)

Here, \( n_{i} \) are the electronic occupation numbers, \( \vec{r} \) and \( \vec{R}_{q} \) are the electronic and nuclear coordinates, respectively, and \( \mu_{B} \) is the Bohr magneton. The index \( i \) runs over all occupied molecular orbitals (MOs) \( M \), which are four-component Dirac spinors. The four-component spin operator \( \Sigma = (\Sigma_{x}, \Sigma_{y}, \Sigma_{z}) \) is built from the two-component Pauli matrices \( \vec{\sigma} \). The Dirac kinetic operator has the form

\[
\hat{t} = c \vec{\alpha} \cdot \vec{p} + c^{2}(\beta - I),
\]

(4)

where \( \vec{\alpha} = (\alpha_{x}, \alpha_{y}, \alpha_{z}) \) and \( \beta \) are the four-component Dirac matrices in the standard representation, and \( I \) is the four-component unit matrix.

\( \hat{V}_{\mathrm{NG}} \) represents the potential energy of the interaction of the electrons with the nuclei

\[
\hat{V}_{\mathrm{NG}} = \sum_{p} \frac{Z_{p}}{|\vec{r} - \vec{R}_{p}|},
\]

(5)

where the index \( p \) runs over all nuclei in the molecular system and \( \hat{V}_{\mathrm{H}} \) is the electronic Hartree potential,

\[
\hat{V}_{\mathrm{H}}(\vec{r}) = \int \rho(\vec{r}) \left( \frac{\hat{p}(\vec{r})}{|\vec{r} - \vec{p}|} \right) d^{3}r.
\]

(6)

Application of the variational principle with the constraint of conservation of the number of electrons leads to the single particle Kohn–Sham equations in a noncollinear formulation

\[
\left\{ \hat{r} + \hat{V}_{\mathrm{NG}} + \hat{V}_{\mathrm{H}} + \frac{\delta E_{\mathrm{xc}}[\rho, \bar{m}]}{\delta \rho} - \mu_{B} \beta \Sigma \frac{\delta E_{\mathrm{xc}}[\rho, \bar{m}]}{\delta \bar{m}} \right\} \phi_{i} = \epsilon_{i} \phi_{i}, \quad i = 1, \ldots, M'.
\]

(7)

Here \( \hat{V}_{\mathrm{H}} \) is the Hartree potential from a model density and \( M' \geq M \) is the number of MOs. The noncollinear formulation allows the magnetization density to point in any direction at any point of the system under consideration. (A collinear spin orientation can also be treated with this method.)

The relativistic local density approximation for \( E_{\mathrm{xc}} \) is used to achieve self-consistency. For nonlocal corrections, added perturbatively, the relativistic form (Ref. 28) of Becke’s generalized gradient approximation for exchange (B88) (Ref. 29) and of Perdew’s (P86) (Ref. 30) functional for correlation is used. Many other functionals, such as PW91, PBE, TPSS, etc., are also implemented in the method, although we will focus our discussion on the B88/P86 results to be able to compare them with the published ones.

In the calculations, optimized numerical basis functions were used with an overall basis error in the total energy below 0.01 eV. The basis sets consist of the minimal sets of AOs plus some optimized “atomic-like” functions (similar basis sets were used in Refs. 13, 14, 16, and 27). For example, the basis set for element 117 is \( \{ \text{[Rn]}5f_{5/2}5f_{7/2}6d_{3/2}6d_{5/2}7p_{1/2}7p_{3/2}7d_{3/2}7d_{5/2}8s_{1/2}8p_{3/2}5g_{7/2}5g_{9/2}6f_{5/2}6f_{7/2} \} \). The MO composition was studied with the use of the Mulliken population analyses.\textsuperscript{31}

III. ATOMIC PROPERTIES AND TRENDS

Atomic data are always useful when analyzing trends in the calculated molecular properties. Figures 1(a) and 1(b) show DF binding energies and maxima of the radial charge density, \( R_{\max} \), of the valence electrons of the 6p and 7p elements, as well as of the 6s AO of H\textsubscript{2} and the 6d\textsubscript{5/2} AO of Cn.\textsuperscript{32} One can see that increasing SO splitting, as well as increasing relativistic stabilization of the np\textsubscript{1/2} and destabilization of the np\textsubscript{3/2} AOs in the groups and rows (the latter is also partially an orbital effect), results in the fact that the 7p\textsubscript{1/2} AOs go in energy and spatial extension beyond the 6p\textsubscript{3/2} AOs. As a consequence, the following trends can be expected: An increase in the inertness of the elements in groups 13 and 14 (due to the stabilization of the np\textsubscript{1/2} AO) and a relative decrease in it in groups 15–18 (due to the destabilization on the np\textsubscript{3/2} AOs).
These trends in the energies, as well as in $R_{\text{max}}$ of the valence orbitals (the contraction of the np$_{1/2}$ AO and expansion of the np$_{3/2}$ AOs) will influence trends in $D_e(M_2)$ and $\Delta H_{\text{sub}}$, as will be shown below.

IV. RESULTS OF THE CALCULATIONS AND DISCUSSION

A. Electronic structures and spectroscopic properties of $M_2$ (M=Hg through Rn and elements 112–118)

The calculated $D_e$ and equilibrium bond lengths, $R_e$, of $M_2$ (M=elements 113–118 and their homologs Tl through Rn) in comparison with experimental values and some other, preferentially DFT calculations, are given in Table I. Hg$_2$ and Cn$_2$ are also listed there for comparison: A discussion of their electronic structures and comparison with results of various calculations can be found in earlier works.\textsuperscript{13,14,16,33} [A comparison with the RECP CCSD(T) results\textsuperscript{23} for Cn$_2$ and (114)$_2$ is not given in Table I since the latter suffer from basis set errors, as discussed in Ref. 14]. We will focus here on the discussion of the electronic structures of the dimers of the 7p elements, while those of their lighter homologs are discussed in detail elsewhere.\textsuperscript{17,18,22} The obtained $D_e$ and $R_e$ of the $M_2$ species, where $M$ are elements Hg/112 through Rn/118, are also depicted in Figs. 2 and 3, respectively.

The calculated spectroscopic properties of Tl$_2$ and (113)$_2$, Pb$_2$ and (114)$_2$, Bi$_2$ and (115)$_2$, as well as of At$_2$ and (117)$_2$ in this work agree very well with those of the $2c\cdot2e$ [SO zero-order regular approximation (SO-ZORA)] and 4c-BDF and calculations,\textsuperscript{17–22} as well as with the experiment (see Table I).

For Tl$_2$ and (113)$_2$, three lowest lying electronic states, $0_{g}^+$, $0_{u}^-$, and $1_u$, arise from the [$(1/2)_{2}$(1/2)$_{3}^{2}$] configuration. Our DFT and BDF (Ref. 17) calculations have found the $1_u$ ground state as the lowest both for Tl$_2$ and (113)$_2$. We have, however, obtained a slightly different result for $D_e$(Tl$_2$) than the BDF calculations, closer to the experimental value. In our calculations, the np$_{1/2}$ and np$_{3/2}$ AOs were treated orthogonal to each other, as is foreseen methodically. (In the case of nonorthogonality of the np$_{1/2}$ and np$_{3/2}$ AOs of Tl, a larger value of 0.58 eV was obtained).

The BDF (Ref. 17) and Kramers’ restricted configuration interaction\textsuperscript{37} (KRCl) calculations found the $0_{u}^-$ state in Tl$_2$ as the second excited, while in our calculations, the second ex-
<table>
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<th>Molecule</th>
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<th>$w_e$</th>
<th>$D_e$</th>
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<td>0.062</td>
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</table>

$^a$4c-DFT calculations (Ref. 16).
$^b$4c-BDF PBESIC calculations (Ref. 33).
$^c$Reference 34.
$^d$4c-BDF BP functional; the PBESCC functional data are in the brackets (Ref. 17).
$^e$Reference 35, $R_e$(Tl$_2$) was questioned in Ref. 36 where $w_e$=39 cm$^{-1}$ was reported.
$^f$BDF calculations (Ref. 17) and KRCI results (Ref. 37) give the 0$^+$ state as second excited.
$^g$4c-DFT calculations (Ref. 14).
$^h$4c-BDF calculations (Ref. 18).
cited state is $0^+_g$ as in the $(113)_2$ molecule. The $0^+_g$ state was found at 0.266 eV. The order of the states in $(113)_2$ agrees in both types of the DFT calculations. [Out of the other types of calculations on $\text{Te}_2$, the best is, obviously, SO-ECP CI (Ref. 37) giving $R_c=3.05$ Å, $\omega_c=79$ cm$^{-1}$, and $D_e=0.38$ eV].

All the calculations show that bonding in $\text{Te}_2$ and $(113)_2$ is weak as a result of the np$_{3/2}$ electrons not being able to form a full $\sigma$-bond. $D_e([113]_2)$ is much smaller than $D_e(\text{Te}_2)$ since the 7p$_{1/2}$ AO is more stabilized than the 6p$_{1/2}$ AO and there is very little mixing with the 7p$_{3/2}$ AOs. Earlier, the DFT calculations$^{24}$ have also shown that $(113)_2$ should be weakly bound because the 7p$_{1/2}$ electrons cannot yield a full $\sigma$ bond.

Bonding in $\text{M}_2$ increases from $\text{Te}_2$ to $\text{Pb}_2$ because the number of bonding electrons increases from two to four (both the 6p$_{1/2}$ and 6p$_{3/2}$ AOs take part in the bond formation). An increase in $D_e$ is much smaller from $(113)_2$ to $(144)_2$ because the latter is almost a closed-shell system due to the large stabilization of the 7p$_{1/2}$ AOs and a very weak mixing with the 7p$_{3/2}$ AOs [see, e.g., Fig. 4(b) for $(115)_2$, as a similar case]. (See also discussions in Refs. 13 and 14.)

Further on, in $\text{Bi}_2$ and $(115)_2$, the np$_{3/2}$ electrons become active. They form a 3/2u ($\pi_u$)-bonding MO so that $D_e$ is larger than those of $\text{Pb}_2$ and $(114)_2$, respectively [Figs. 4(a) and 4(b) and Table II]. $(115)_2$ is, however, much weaker bound than $\text{Bi}_2$ due to the same reason as $(114)_2$ with respect to $\text{Pb}_2$: The 7p$_{1/2}$ AOs are too stabilized so that they form almost an independent system of bonding and antibonding MOs. This is demonstrated in Fig. 5(b), where the MO energies of $(115)_2$ are shown as a function of the interatomic distance $R$. One can see that the 1/2u ($\sigma_u$) MO of $(115)_2$ is partially antibonding at $R_e$, i.e., its energy increases with decreasing $R$, while that of Bi is typically bonding (its energy decreases with $R$) [Fig. 5(a)]. Such a behavior of the $\sigma_u$ MO is typical of all the 7p element dimers. Thus, there is a little 7p$_{1/2}$-7p$_{3/2}$ AO mixing in $(115)_2$ in difference to the larger 6p$_{1/2}$-6p$_{3/2}$ AO mixing in $\text{Bi}_2$, which makes the bond weaker.

Our highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gaps are 1.075 eV for $\text{Bi}_2$ and 0.406 eV for $(115)_2$, being also very close to the BDF values$^{17}$ of 1.05 and 0.40 eV, respectively.

In group 16, $D_e(\text{Po}_2)>D_e([116]_2)$, as in the previous groups. One can see (Fig. 2), however, that the maximum in $D_e(\text{M}_2)$ of the 7p elements comes at group 16, while that of

![Diagram](image)

**TABLE II.** The MO composition (Mulliken gross population) of $\text{Bi}_2$ and $(115)_2$.

<table>
<thead>
<tr>
<th>$D_e$ (eV)</th>
<th>MO</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.219</td>
<td>1/2u ($\sigma_u^*$)</td>
<td>0.234[6p$<em>{3/2}$]+0.234[6p$</em>{1/2}$]+0.129[6s$_{3/2}$]</td>
</tr>
<tr>
<td>-2.922</td>
<td>3/2u ($\pi_u^*$)</td>
<td>0.496[6p$<em>{3/2}$]+0.496[6p$</em>{1/2}$]+0.002[6d$_{3/2}$]</td>
</tr>
<tr>
<td>-3.816</td>
<td>1/2u ($\sigma_u^*$)</td>
<td>0.336[6p$<em>{3/2}$]+0.336[6p$</em>{1/2}$]+0.151[6s$_{1/2}$]</td>
</tr>
<tr>
<td>-4.891</td>
<td>3/2u ($\pi_u^*$)</td>
<td>0.496[6p$<em>{3/2}$]+0.496[6p$</em>{1/2}$]+0.002[6d$_{3/2}$]</td>
</tr>
<tr>
<td>-6.229</td>
<td>1/2u ($\sigma_u^*$)</td>
<td>0.413[6p$<em>{3/2}$]+0.413[6p$</em>{1/2}$]+0.079[6s$_{3/2}$]</td>
</tr>
<tr>
<td>-6.552</td>
<td>1/2u ($\sigma_u^*$)</td>
<td>0.349[6p$<em>{3/2}$]+0.349[6p$</em>{1/2}$]+0.094[6p$_{3/2}$]</td>
</tr>
</tbody>
</table>

$^a$Partially antibonding.

$^b$HOMO.

$^c$Partially bonding.
the $6p$ elements comes at group 15. $D_e(M)$ of the $p$-elements of the third through fifth rows also exhibit a maximum at group 15. This difference can be explained by the large SO effects on the $7p$ AOs. Thus, for example, in the dimers of the $6p$ elements, as in the lighter homologs, both the $np_{1/2}$ and $np_{3/2}$ AOs take part in the bond formation so that the maximum number of bonding electrons, six (one $np_{1/2}$ and two $np_{3/2}$ from each atom) and none in the antibonding MOs, comes at Bi$_2$. In the dimers of the $7p$ elements, the $7p_{1/2}$ AOs form an almost closed shell [Fig. 4(b)] so that the $7p_{3/2}$ AOs form an independent system of bonding and antibonding MOs. The maximum number of bonding electrons, four (two $7p_{3/2}$ ones from each atom) in the bonding MOs and none in the antibonding MOs, comes at (116)$_2$. In this way, $D_e$(Bi$_2$) $>$ $D_e$(Po$_2$), while $D_e$[(115)$_2$] $<$ $D_e$[(116)$_2$].

Further on, in At$_2$ and (117)$_2$, the HOMO has a considerably antibonding $3/2^*(\pi^*)$ character [Figs. 6(a) and 6(b)]. Beside the $2c$- and $4c$-DFT calculations, our results for At$_2$ agree also very well with the Dirac–Coulomb (DC) CCSD(T) ones, $^{33}$ see Table I. A detailed comparison of various, mostly DFT calculations for At$_2$ and (117)$_2$ is given in Refs. 19–21. Since the number of the antibonding electrons in At$_2$ and (117)$_2$ is larger than that in Po$_2$ and (116)$_2$, respectively, they are weaker bound than the latter. Again, $D_e$(At$_2$) is larger than $D_e$[(117)$_2$] although the difference between them is much smaller than that between Bi$_2$ and (115)$_2$, and between Po$_2$ and (116)$_2$.

Finally, in Rn$_2$ and (118)$_2$, closed shells, the MOs con-
tain four bonding and four antibonding np$_{3/2}$ electrons so that bonding is predominantly of dispersive nature. We obtained Rn$_2$ unbound for the B88/P86 functional, which is known to underestimate van der Waals interactions, although (118)$_2$ was obtained bound (Table I). The PBE functional, more suitable in this case, gives $D_e$(Rn$_2$)=0.024 eV and $D_e$[(118)$_2$]=0.053 eV. The ECP CCSD(T) calculations$^{23}$ (Table I) have also shown that (118)$_2$ is more bound than Rn$_2$. Stronger bonding in the 118-dimer is due to the larger polarizability of element 118 (46.3 a.u.) in comparison with Rn (35.04 a.u.), as was shown by our DC-CCSD calculations. The MO population analysis in (118)$_2$ has indicated that no 8s(118) AOs take part in the bond formation. The 8s(118) AOs form the first LUMO lying 5.1 eV higher in energy.

Thus, a remarkable feature of the results of the calculations is a decrease in the $D_e$(M$_2$) difference between the 6p and 7p homologs from group 15 to group 17 and a reversal of the trend in group 18. This can be explained by the fact that the contribution of the np$_{1/2}$ AOs, which are more different than the np$_{3/2}$ AOs for the 6p and 7p homologs [Fig. 1(a)], becomes less pronounced toward the end of the rows (compare Figs. 4 and 6). Thus, bonding becomes defined by the destabilized and acting in the opposite direction np$_{3/2}$ AOs that are more similar for the two rows than the np$_{1/2}$ AOs. In group 18, the larger polarizability of the heaviest elements makes the trend reversed.

The RECP CCSD(T) calculations for MH (M=the 6p and 7p elements)$^{45,46}$ reveal similar trends in $D_e$ (both in the rows and groups), as those shown in Fig. 2, with the exception that the difference in $D_e$ between the homologs stays about the same in groups 15–17. The maximum in $D_e$(MH)
The 7p elements should decrease from group 13 to group 15. The 113–H bond was found to be the shortest. 22,45,46 Values show similar trend, except for TlH/113H, where the element 115 was calculated and corrected by the difference with experimental energies.

In both rows was found at group 16, PoH and 116H, because both molecules have the same number of extra bonding electrons.

Bond lengths in all the 7p homonuclear dimers were found to be larger than those of the 6p homologs since $R_{\text{max}}(7p_{3/2}) > R_{\text{max}}(6p_{3/2})$ (Fig. 3). The RECP CCSD $R_e(MH)$ values show similar trend, except for TH/113H, where the 113–H bond was found to be the shortest. 22,45,46 $R_e(M_2)$ of the 7p elements should decrease from group 13 to group 15 and then increase further to group 18. This behavior—with a minimum at group 15—is typical of the p-elements in the third through sixth rows. This is explained by the following. The decrease in $R_e(M_2)$ from group 13 to group 14 is due to a decrease in $R_{\text{max}}(np_{1/2})$ and an increase in the number of bonding electrons [Fig. 1(b)]. Further on, in Bi2 and (115)2, two np3/2 AOs with much larger $R_{\text{max}}$ than that of the np1/2 AOs of Pb and (114)2, respectively, form a bonding 3/2u-HOMO [Fig. 1(b)]. Since this MO is only of a $\pi$ character, a further decrease in $R_e$ is observed due to the further contraction of the np3/2 AOs contributing to the $\sigma$ bonding (the 1/2g and 1/2u MOs). (The multiconfiguration nature of

$\Delta H_f$, $D_e$, eV as a function of Z. The filled symbols are experimental values (Ref. 15), open ones: calculated here. The dashed line for $\Delta H_f(g)$ is a linear extrapolation with Z, and that for $D_e$ is predicted “experimental” value using the calculated one. The star is the predicted here $\Delta H_f(115)$ using the correlation between $\Delta H_f(g)$ and $D_e$ (see Fig. 12).

$\Delta H_f$, $D_e$, eV as a function of Z. The filled symbols are experimental values (Ref. 15), open ones: calculated here. The dashed line for $\Delta H_f(g)$ is a linear extrapolation with Z, and that for $D_e$ is predicted “experimental” value using the calculated one. The star is the predicted here $\Delta H_f(116)$ using the correlation between $\Delta H_f(g)$ and $D_e$ (see Fig. 14).

Correlations between formation enthalpies $\Delta H_f$ and dissociation energies $D_e(M_2)$ of group 15 elements (a correlation including P, dashed line, gives $\Delta H_f(115)=1.7$ eV, while that without P, solid line, gives $\Delta H_f(115)=1.45$ eV). ($D_e$ for P–Bi are experimental values, while that for element 115 was calculated and corrected by the difference with experiment for the lighter homologs, see Table I).

Correlation between formation enthalpies $\Delta H_f(g)$ and dissociation energies $D_e(M_2)$ of group 16 elements (the values for S–Po are experimental, while for element 116, these are calculated and corrected by the difference with experiment for the lighter homologs, see Table I).
the Bi atomic wave function was shown by the \textit{ab initio} multiconfiguration Dirac–Fock–Coulomb calculations\cite{17}. In the next dimers, Po\textsubscript{2}/(116)\textsubscript{2} and At\textsubscript{2}/(117)\textsubscript{2}, electrons are populating antibonding MOs, which makes the bonds longer, as in the lighter homologs. The trend in the \(w_e\) values (Fig. 7) follows the one in the \(D_e\) values.

### B. Estimates of the sublimation enthalpies

It is reasonable to expect that M-M bonding in a dimer is a first indication about M-M bonding in the solid state. In Ref. 14 (see Fig. 5 there), we have, indeed, shown that in group 14, \(D_e(M_2)\) changes in the same way as \(\Delta H_f(g)\) with \(Z\) so that a perfect linear correlation between them occurs (Fig. 8). This correlation gives \(\Delta H_f(114) = 70.3\) kJ/mol in agreement with the value obtained via a linear extrapolation from the lighter homologs in the group\cite{10,11}. The decrease in \(D_e(M_2)\) and \(\Delta H_f\) in group 14 was shown to be caused by the gradual stabilization of the np\textsubscript{1} AO\cite{13,14}.

As in group 14, \(D_e(M_2)\) and \(\Delta H_f(g)\) of the group 13 elements (Al through Tl) decrease in a similar way with \(Z\) (Fig. 9) so that a good linear correlation between these values occurs (Fig. 10). This gives \(\Delta H_f(113) = 144.7\) kJ/mol which is very close to the value (138.1 kJ/mol) obtained via a linear extrapolation from the lighter homologs in the group\cite{10,11}. The trend to a decrease in \(D_e(M_2)\) and \(\Delta H_f(g)\) with \(Z\) is caused, as in group 14, by the gradual stabilization of the np\textsubscript{1/2} AO in the group.

Group 15 is more problematic: The standard state of its elements changes from nonmetals (P) to heavier metals (Bi) with a different type of bonding and crystal structure being a result of the interplay between the np\textsubscript{1/2} and np\textsubscript{3/2} AOs. Figure 11 demonstrates different slopes of the \(D_e(M_2)\) and \(\Delta H_f(g)\) plots as a function of \(Z\) so that they even cross at Bi: \(\Delta H_f(g)\) becomes larger than \(D_e(M_2)\) with an increase in the metallic character in the group, as in groups 13 and 14. This gives a loose correlation between \(D_e(M_2)\) and \(\Delta H_f(g)\) (Fig. 12) although \(\Delta H_f(115) = 1.7\) eV can be obtained on its basis as a rough estimate. A much better correlation without P (Fig. 12) gives \(\Delta H_f(115) = 1.45\) eV. The value is close to that predicted via a linear extrapolation from the lighter homologs in the group (1.52 eV).

### Table III. Formation enthalpies of gaseous elements, \(\Delta H_f(g)\), or sublimation enthalpies of macroamounts, \(\Delta H_{sub}\) (in kJ/mol).

<table>
<thead>
<tr>
<th>Method</th>
<th>E113</th>
<th>E114</th>
<th>E115</th>
<th>E116</th>
<th>E117</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extrapolation$^a$</td>
<td>138.1</td>
<td>70.3</td>
<td>146.4</td>
<td>92.1</td>
<td>83.7</td>
</tr>
<tr>
<td>Correlation$^b$</td>
<td>144.7</td>
<td>70.4</td>
<td>152 ± 12</td>
<td>101.3</td>
<td>91.7</td>
</tr>
</tbody>
</table>

$^a$References 10 and 11.

$^b$This work.

---

**FIG. 15.** Formation enthalpies \(\Delta H_f(g)\) (rhomboids) and dissociation energies \(D_e(M_2)\) (triangles) of group 17 elements as a function of \(Z\). The filled symbols are experimental values (Ref. 15), open ones: calculated. The dashed line for \(\Delta H_f(g)\) is a linear extrapolation with \(Z\), and that for \(D_e\) is predicted experimental values using the calculated \(D_e\). The star is the predicted here \(\Delta H_f(117)\) using the correlation between \(\Delta H_f(g)\) and \(D_e\) (see Fig. 16).

**FIG. 16.** Correlation between formation enthalpies \(\Delta H_f(g)\) and dissociation energies \(D_e(M_2)\) of group 17 elements (experimental values for Cl through I and calculated ones, corrected by the difference with experiment for the lighter homolog, for At and element 117, see Table I).

**FIG. 17.** Formation enthalpies of the 6p (triangles) and 7p elements (the squares are the present results, while rhomboids connected by a dashed line are those obtained via a linear extrapolation from the lighter homologs in the groups).
Group 16 is similar to group 15, i.e., the standard state of the elements changes from nonmetals to metals. The behavior of $D_e(M_2)$ and $\Delta H_f(g)$ as a function of $Z$ is shown in Fig. 13 demonstrating a steady decrease with $Z$. A correlation between $D_e(M_2)$ and $\Delta H_f(g)$ is shown in Fig. 14. For this correlation, $\Delta H_f(Po)$ was taken as 144.5 kJ/mol, an average of various measurements ranging from 139.4 to 146 kJ/mol (see a compilation in Ref. 47). [We can cite here two of them, of 144.4 kJ/mol (Ref. 48) and 145.7 kJ/mol (Ref. 49)]. This average fits very well the plot in Fig. 14 so that the $\Delta H_f(g)$ and $D_e(M_2)$ data are consistent. This good correlation gives $\Delta H_f(116)=101.3$ kJ/mol. Thus, we do not see why all the measurements of $\Delta H_f(Po)$ should be revisited, as is suggested in Ref. 47. The calculated there, with the use of Eq. 29, $\Delta H_f(Po)$ of 164–199 eV is, obviously, overestimated.

Finally, Fig. 15 shows $D_e(M_2)$ and $\Delta H_f(g)$ for group 17 elements as a function of $Z$. The standard state changes there from gaseous for Cl to solid for At. Though, there is no experimental value of $D_e(At_2)$, it is obvious that the $D_e(M_2)$ and $\Delta H_f(g)$ lines should cross at At, as in group 15. Notwithstanding this fact, there is a good correlation between $D_e(M_2)$ and $\Delta H_f(g)$ (Fig. 16) giving $\Delta H_f(117)=0.95$ eV (91.7 kJ/mol). This value is also very close to the one obtained via a linear extrapolation in group 17.

The obtained here $\Delta H_f(g)$ of the 7p elements and those predicted via a linear extrapolation in the groups are summarized in Table III and shown in Fig. 17. One can see that the difference in $\Delta H_f(g)$ between the 7p and 6p homologs decreases from group 15 to group 17, as that in $D_e(M_2)$, in line with the trends in the respective chemical groups. $\Delta H_f(114)$ should be the smallest in the 7p series due to the strong relativistic effects on the np1/2 electron shell, although in line with the trend in group 14.

Thus, no unexpected trends in $\Delta H_f(g)$ are established here on the basis of the relativistic calculations for the $M_2$ dimers: The energies and $R_{\text{max}}$ of the np1/2 and np3/2 AOs change smoothly in the groups (even though in the opposite directions) causing a smooth change in the macroamont properties. Solid state calculation may be valuable to check these conclusions.

V. CONCLUSIONS

Results of the calculations of the spectroscopic properties of the homonuclear dimers of the 6p and 7p elements have shown that the heaviest species, except of (118)2, are weaker bound than their 6p homologs. The reason for that is a large SO splitting of the 7p AOs resulting in the decreasing accessibility of the 7p1/2 AO for bonding.

It was also shown that the difference in $D_e(M_2)$ between the 6p and 7p homologs decreases from group 15 to group 17 and becomes even reversed in group 18 due to the same reason. Element 118 should be stronger bound to itself than Rn.

The calculations revealed a different trend in $D_e(M_2)$ of the 7p elements in comparison with the lighter homologs of the third through sixth rows: The maximum in the seventh row comes at group 16, while in the previous rows, at group 15. This is explained by the larger SO splitting of the 7p AOs and formation of an almost independent system (without the 7p1/2 AO admixing) of bonding and antibonding MOs of the 7p3/2 AO character. The bond lengths were found to be larger in all the dimers of the 7p element. The maximum in $R_e(M_2)$ comes at group 15 compounds in all the series of the p-elements.

Using our calculated $D_e(M_2)$, $\Delta H_f(g)$ were estimated for the heaviest elements 113–117 using a linear correlation between these quantities in the chemical groups. The new values are in good agreement with those obtained via a linear extrapolation in the chemical groups. Thus, elements 113–117 are expected to be more volatile (as a sublimation process) than their lighter homologs although the difference in $\Delta H_f(g)$ between the homologs decreases with the group number. Solid state calculations for the heaviest elements may be valuable to confirm the predicted trends.

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