

Relativistic molecular calculations of superheavy molecules (*)

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Résumé. — On étudie la structure électronique des hexafluorures des métaux 6d superlourds au moyen de calculs relativistes Dirac-Slater moléculaires. Les résultats théoriques sont comparés aux calculs et aux expériences effectués sur les séries homologues 4d et 5d. La structure électronique est dominée par le fort couplage spin-orbite qui, pour les éléments superlourds, est du même ordre de grandeur que le champ cristallin pour les électrons de valence. Des valeurs des énergies d'ionisation ont été calculées par la méthode de l'état de transition.

Abstract. — Relativistic molecular calculations within the Dirac-Slater scheme have been used in a study of the electronic structure of 6d-metal superheavy hexafluorides. The theoretical results are compared with calculations and measurements of the homolog 4d- and 5d-metal hexafluorides. Large spin-orbit splitting dominates the electronic structure and even has the same order of magnitude as the crystal-field splitting for the valence electrons for the superheavy molecules. Ionization energies have been calculated using a transition state procedure.

1. **Introduction.** — In recent years a number of atomic calculations have been carried out in the region of superheavy elements. With sophisticated interpretations of these results one was able to get a first idea of the physical and chemical properties of the still unknown superheavy elements. These results have been reviewed by Hermann [1] and Fricke [2]. Many authors [1-3] also have emphasized that further development in this field is dependent on realistic (which in this case means relativistic) calculations for molecules containing superheavy elements. A better knowledge of their chemical and physical properties is the condition for the successful extraction and identification of possibly artificially generated superheavy atoms. Preliminary results are given in this work for (E106) F₆ and its 4d and 5d elements analogs MoF₆ and WF₆ for comparison. We also compare it with the recently presented results [4] for (E110) F₆ the analog of the 5d element PtF₆.

The calculation procedure which is based on the relativistic self-consistent Dirac-Slater model has been reviewed in earlier works and is therefore not presented here [5, 6].

2. **Results.** — In figure 1 we present the outer electron structure resulting from relativistic calculations of (E106) F₆, WF₆ and MoF₆ as well as a non-relativistic calculation of MoF₆. The composition and relative ordering of the molecular levels depends on the relative level positions for the consti-

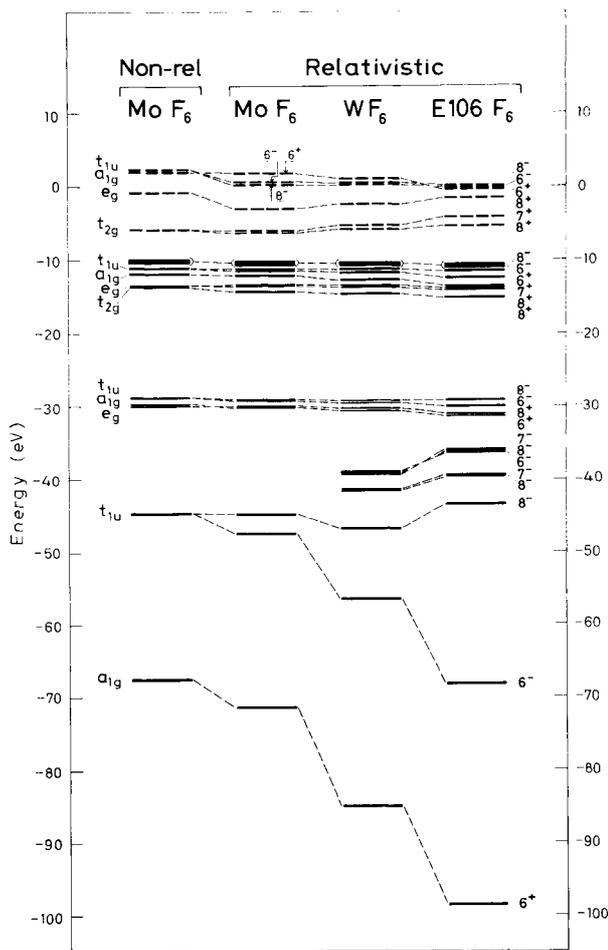


Fig. 1. — Energy eigenvalues of the outer electrons for MoF₆, WF₆ and (E106) F₆. Non-relativistic calculation of MoF₆ also included.

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tuent atoms, the crystal-field splitting and covalency effects. The experimental bond length of

$$R_{\text{Mo-F}} = 1.82 \text{ \AA}, \quad R_{\text{W-F}} = 1.83 \text{ \AA}$$

have been used; $R_{\text{E106-F}}$ was estimated as 1.84 Å. Extended calculations [4] of (E110) F_6 have shown, that the positions of the levels are very insensitive to changes even of 0.1 Å of the relative distance between the metal and the fluor atoms. The splitting of the non-relativistic levels into the relativistic ones has been indicated by using the compatibility relations between the single and double groups.

The main influence on the position of the levels already is given by the position of the atomic levels [7]. The lowest a_g and t_u levels shown in figure 1 mainly can be described by a ns respectively np level of the heavy atom. The large spin-orbit splitting into the 6^- and 8^- states can easily be seen. The next levels mainly originate from the f levels of the central atom and from the atomic fluor $2s$ level.

For the valence electron levels at about -10 eV,

a more detailed analysis shows that there is a reordering of the valence levels for (E106) F_6 , so that a γ_8^- level becomes the last occupied states, whereas in all lighter systems this is a γ_8^+ level.

The first excited states for these molecules (dashed levels in Fig. 1) are the crystal-field split t_{2g} and e_g molecular levels derived from the nd atomic level. Experimentally the t_{2g} spin-orbit splitting for the $5d$ metal hexafluorides has been measured to be ≈ 0.6 eV [8], which is in good agreement with the relativistic result of (0.5 ± 0.1) eV. The corresponding spin-orbit splitting for (E106) F_6 is ≈ 1.2 eV. First ionization energies have been calculated by performing transition state calculations for the last occupied valence level with the results 14.4 eV, 14.5 eV and 14.4 eV for the MoF_6 , WF_6 and (E106) F_6 , respectively. This should be compared with the experimental values of 15.1 eV, 15.5 eV for MoF_6 and WF_6 . Assuming the same discrepancy for (E106) F_6 we predict its first ionization energy to be 15.4 eV.

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