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NON-RELATIVISTIC AND RELATIVISTIC MOLECULAR CALCULATIONS FOR THE CHALCOGEN HEXAFLUORIDES: SF_6, SeF_6, TeF_6, PoF_6

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ABSTRACT

Non-relativistic Hartree-Fock-Slater and relativistic Dirac-Slater self-consistent orbital models are applied for the analysis of the electronic structure of the chalcogen hexafluorides: SF_6, SeF_6, TeF_6 and PoF_6. The molecular eigenfunctions and eigenvalues are generated using the discrete variational method (DVM) with numerical basis functions. The results obtained for SF_6 are compared with other ab initio calculations. Information about relativistic level shifts and spin-orbit splitting has been obtained by comparison between the non-relativistic and relativistic results.

INTRODUCTION

The electronic structure of sulphur hexafluoride SF_6 has been the subject of experimental as well as theoretical investigations for some time. The main reason for this activity has been to understand the complex valence structure of this molecule (ref. 1)*. One interesting feature of the photoelectron spectra obtained with the HeI and the HeII radiation was the large difference in intensities for the observed peaks due to the dependence of the cross-section with excitation energy (refs. 2, 3). This type of behaviour has recently been analyzed more systematically by Gustafsson (ref. 4) who measured partial photoionization cross sections for the valence levels of SF_6 by utilizing synchrotron radiation. He found that the

*A review of different theoretical and experimental assignments for SF_6 is presented in ref. 1.

excitation functions for some of the peaks in the photoelectron spectra were dominated by strong resonance effects. This behaviour was interpreted as transitions from valence states of ungerade symmetry to a state of gerade symmetry above the vacuum level. The interpretation proposed by Gustafsson differs for two of the valence levels from the earlier assignments (refs. 2, 3, 5), which were mainly based on intensity considerations in the XPS and the UV spectra. The assignment proposed by Gustafsson has later been supported by theoretical calculations of photoionization cross sections using the multiple-scattering Xα-method (ref. 6). A number of theoretical ab initio and semiempirical calculations have also been performed in order to assign the peaks in the photoelectron spectra (ref. 1). The new experimental information obtained with synchrotron radiation (ref. 4) has also initiated new large scale ab initio calculations (ref. 7) for a further check of earlier results (ref. 1). These new theoretical values do not agree with the assignment proposed by Gustafsson but support the earlier assignments. There remains therefore still some problems to be solved.

The electronic structure of the heavier chalcogen hexafluorides SeF_6, TeF_6, and PoF_6 is in contradiction to SF_6 investigated very little. Only non-relativistic MSXα calculations have earlier been presented for SeF_6 and TeF_6. As a part of our current research program to perform calculations for series of molecules (refs. 8-9) in order to investigate relativistic effects, it would be interesting to study the chalcogen hexafluorides. The present paper gives a summary of this analysis while a more detailed study will be presented elsewhere.

COMPUTATIONAL METHOD

The one-electron molecular hamiltonian is in non-relativistic molecular calculations given by

$$h = -\tfrac{1}{2}\nabla^2 + V(\vec{r}) \qquad (1)$$

where $-\tfrac{1}{2}\nabla^2$ represents the kinetic energy operator and $V(\vec{r})$ the potential energy operator, which is given as a sum of Coulomb and exchange terms. This last part is in the Hartree-Fock-Slater (HFS) method given by

$$V_x(\vec{r}) = -3\alpha \left[\frac{3\rho(\vec{r})}{8\pi} \right]^{1/3} \qquad (2)$$

where α is an exchange parameter which is of the order of 0.7 for most of the atoms. $\rho(\vec{r})$ is the total molecular charge density (ref. 10). A variational method is used to find the molecular wavefunctions which are approximated by linear combinations of symmetry orbitals. The atomic orbitals which are used to build up the symmetry orbitals are generated with an atomic SCF program. The HFS and overlap matrix elements are evaluated according to the discrete variational method (refs. 11-12) and the secular equation is then solved by standard techniques. The molecular wavefunctions are analyzed according to a Mulliken population scheme in terms of the input atomic basis functions in every cycle of the self-consistent procedure. These new populations of the functions are then used to construct a new molecular charge density required to generate the molecular potential. Self-consistency is obtained when there is no change in the occupation numbers. This procedure is referred to as the discrete variational self-consistent charge method DV-SCC (ref. 13). The relativistic calculations are performed in the same way by use of the Dirac-Slater Hamiltonian (refs. 8-9).

RESULTS

The calculations were performed using the experimental equilibrium bond length R(X-F) of 2.9556 au., 3.1559 au. and 3.4394 au. for X = S, Se and Te, respectively. By a comparison of the experimental bond lengths for the lighter hexafluorides and the atomic radii of the constiuent atoms, the bond length for PoF_6 was taken as 4.15 au. The point group of these molecules is O_h.

Different theoretical ionization potentials for SF_6 in the valence region are presented in Fig. 1 and compared with the corresponding experimental values. Hartree-Fock (HF) ionization energies as obtained by von Niessen et al. (ref. 7) are shown in the first column. These values corrected for correlation and reorganization effects (many-body effects (MB)) are shown in column 2. This represents the most accurate result available today. Ionization energies calculated with free-electron-like exchange potentials are presented in the next columns by using the transition state procedure (ref. 10). Using this approach, binding energy shifts due to the non-validity of Koopmans' theorem for local potentials, as well as the relaxation energy, are included in the evaluated eigenvalues. The values in Fig. 1 column 3 have been calculated by Rösch et al. (ref. 14) using the MSXα-method with the exchange parameter values α given by Schwartz (ref. 15). The molecular

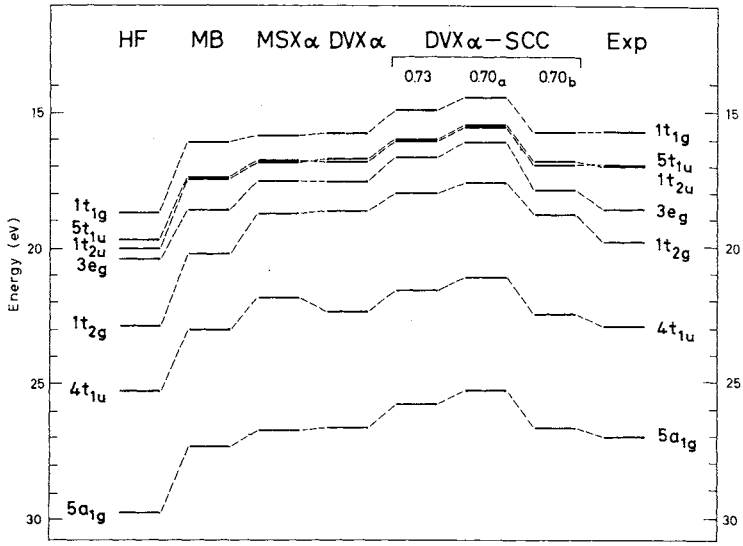

Fig. 1. Theoretical ionization energies for SF_6 evaluated with different models and the experimental values are compared. The notation of the different methods is described in the text.

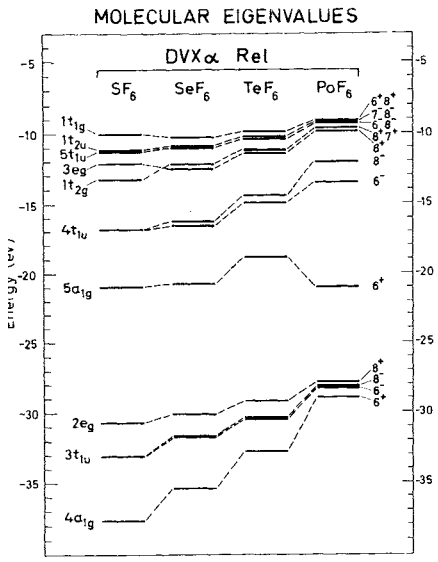

Fig. 2. Relativistic molecular eigenvalues for the valence levels of SF_6, SeF_6, TeF_6 and PoF_6. The notation 6^-, 8^- etc for the relativistic levels is a shorthand for γ_6, γ_8 etc.

potential is in the MSXα-calculation spherically averaged in the atomic spheres surrounding the atoms in the molecule and the potential is then kept constant in the interstitial regions. A better description of the molecular potential can be obtained by using the so called Discrete Variational Method (DVM) (ref. 12) in the evaluation of the molecular matrix elements. In this method an accurate expansion of the molecular density and potential is obtained by a set of auxiliary functions centered on the nuclei in the atoms. Results obtained in such a way by Gutzev and Levin (ref. 16) are presented in column 4 using an exchange parameter $\alpha = \frac{1}{7}(6\alpha_F + \alpha_S) = 0.735$. Results obtained in this work with the SCC-method by use of numerical basis functions are presented in the next column for the exchange parameter $\alpha = 0.73$ and 0.70, respectively. These ionization energies have been obtained by using a minimal numerical basis set consisting of sulphur 1s, 2s, 2p, 3s, 3p and fluorine 1s, 2s, 2p. The values in the next column have been calculated with an extended basis by also including 3d, 4s, 4p,4d and 4f on the sulphur atom. The experimental ionization energies as obtained in XPS- and UV-spectroscopy are given to the right in the figure (refs. 5, 17,18). The assignment of these peaks has been obtained from intensity arguments of the photoelectronspectra. The recent photoionization cross section measurements by Gustafsson give the same ordering as given in the figure except that the second peak should be composed of $5t_u + 3e_g$ and the third peak should be $1t_{2u}$. All the theoretical calculations presented, give the same level-ordering for all the levels except for some changes in the very close $1t_{2u}$ and $5t_{1u}$ levels. The spacing between the levels is also rather similar to the experimental values although the absolute values are somewhat different. The ionization energies evaluated with free electron like potentials are in rather good agreement with the more sophisticated many-body calculations.

Relativistic molecular eigenvalues as evaluated with the DVXα method for SF_6, SeF_6, TeF_6 and PoF_6 are shown in Fig. 2. These results have been obtained with a minimal basis set. We notice the trends of narrower valence F-2s bands with higher Z for the central atom. This is mainly due to a larger bond distance between the central atom and the fluorines with increasing atomic number. There is also an indication of more loosely bound levels for the heavier molecules. This behaviour follows the general trends of the atomic eigenvalues for the valence ns and np levels of S, Se, Te and Po. Transition state calculations have also been performed for the last occupied level of these molecules with the results 14.5 eV, 14.5 eV, 13.8 eV and 12.7 eV, for

SF_6, SeF_6, TeF_6 and PoF_6, respectively.

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