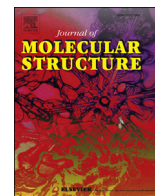




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Electronic structure and spectroscopic properties of mixed sodium actinide oxides Na_2AnO_4 (An = U, Np, Pu, Am)

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Dedicated to Prof. Georgiy V. Girichev on the Occasion of his 70th birthday.

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ABSTRACT

Multireference relativistic post-HF and DFT calculations have been performed on four Na_2AnO_4 (An = U, Np, Pu, Am) molecules. Beyond the electronic characteristics of the ground and excited electronic states, the molecular geometries and vibrational frequencies have been determined.

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1. Introduction

In order to reduce the radioactive waste of nuclear reactors, the reactors under recent development are planned to operate in a closed fuel cycle, in which the highly radioactive minor actinides are re-used for energy generation. One of the new designs is the Sodium cooled Fast Reactor (SFR). The main advantages of the sodium melt as coolant are the high heat capacity resulting in a high margin to overheating and the high boiling point ($T = 1156\text{ K}$) being well above the reactor's planned operating temperature (around 850 K).

The nuclear reactors have to obey to very high safety standards, therefore possible accidents have to be carefully explored. Such an accident can be the breach of the fuel clad, in which case the sodium coolant and fuel can react with each other forming mixed sodium actinide oxides. Beside U and Pu (components of the MOX fuel) the most relevant actinides in these fuels are Np and Am. From the Na-An-O systems the An = U and Pu ones have been studied extensively in the literature. The published properties include the crystal structures [1,2], thermodynamic [3–5], magnetic [6,7], and spectroscopic properties of the solids [8–10]. In the solid phase

numerous compositions were reported: Na_3UO_4 , NaUO_3 , Na_2UO_4 , Na_4UO_5 , $\text{Na}_2\text{U}_2\text{O}_7$, $\text{Na}_6\text{U}_7\text{O}_{24}$ [1], $\text{Na}_2\text{Np}_2\text{O}_7$, Na_2NpO_4 , Na_4NpO_5 , Na_5NpO_6 , Na_3NpO_4 or Na_4NpO_4 [11,12] and Na_2PuO_3 , Na_3PuO_4 , Na_4PuO_4 , Na_6PuO_5 , $\text{Na}_4\text{Pu}_2\text{O}_5$, Na_6PuO_6 , Na_4PuO_5 [1,2,12,13]. For the gaseous phase scarce data indicate the possible appearance of Na_2NpO_4 as evaporation product on the basis of mass spectrometric measurements [14].

In the present paper we are dealing with Na_2AnO_4 species, which can form in the vapour at severe accident situations. In order to simulate their formation and behaviour, the knowledge of their thermodynamic characteristics is required. These data can be calculated from reliable structural and spectroscopic parameters obtained conveniently by means of advanced quantum chemical calculations [15–20]. In the following we present the electronic structure of the four Na_2AnO_4 (An = U, Np, Pu, Am) molecules determined by relativistic multireference calculations as well as some other structural and spectroscopic properties of the ground electronic states determined by B3LYP density functional theory (DFT) calculations.

2. Computational details

The calculations were performed using the software MOLCAS

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8.0 [21]. The complete active space (CAS) SCF method [22] was used to generate molecular orbitals and reference functions for subsequent multiconfigurational second-order perturbation theory calculations of the dynamic correlation energy (CASPT2) [23,24]. The Douglas-Kroll-Hess Hamiltonian was used in the CASSCF calculations in order to take into account scalar relativistic effects.

All electron basis sets of atomic natural orbital type, developed for relativistic calculations (ANO-RCC) with the Douglas-Kroll-Hess Hamiltonian [25,26] were used for all the atoms. For the actinides a primitive set of 26s23p17d13f5g3h basis functions was contracted to 9s8p6d5f2g1h [27] achieving TZP quality. Analogous contracted basis sets were applied for O (14s9p4d3f2g/4s3p2d1f) [28] and for Na (17s12p5d4f2g/5s4p2d1f) [29].

To determine the optimal size of the active space, preliminary state-averaged calculations using five roots (i.e. considering five electronic states in CASSCF) were performed in C1 symmetry with various number of inactive electrons. We found for all the four actinides that only two 2-electron orbitals had populations below 1.96 e, hence only these two orbitals were included beyond the unpaired An valence electrons in the active spaces [30]. Accordingly, in the subsequent calculations the active spaces contained 4, 5, 6, 7 electrons on 16 orbitals for the U, Np, Pu, and Am derivatives, respectively.

The electronic structures of the title molecules were investigated using D_{2h} symmetry, in which the eight symmetry species of the point group were treated separately. For the lowest-energy symmetry species (within 20 kJ/mol) geometry optimizations were performed in order to ensure the ground electronic states and the respective global minimum geometries of the four title compounds. The vertical excited electronic states were calculated on the optimized geometries of the ground electronic states. Beyond the ground-state spin multiplicities (1, 2, 3, 4 for the U, Np, Pu and Am compounds, respectively) the neighbouring spin multiplicities were also probed.

Spin-orbit (SO) effects were taken into account by using the complete active space state interaction (CASSI) method [31], which allows CASSCF wave functions for different electronic states to interact under the influence of a spin-orbit Hamiltonian. Dynamic electron correlation is taken into account using the CASPT2 energies as spin-orbit free (SF) energies in the spin-orbit Hamiltonian (SO-CASPT2). The above described multireference methods and the ANO-RCC basis set were successfully applied in a number of studies on actinide-containing systems [32–53].

The DFT calculations were carried out with the Gaussian 09 code [54]. Our main DFT method was the B3LYP exchange–correlation functional [55,56] which provided previously very good

performance for both actinide oxides [47,57,58] and mixed alkali transition metal oxides [20]. A few test calculations were performed with PBE0 [59,60], B2PLYP [61], MP2 [62] and CCSD(T) [63–65] theories. For the actinides the small-core quasi-relativistic pseudopotentials of the Stuttgart-Cologne group (ECP60MWB [66,67] and the 14s13p10d8f6g valence basis set contracted to 10s9p5d4f3g (ECP60MWB_SEG basis) [67]) was used, while for O and Na the aug-cc-pVTZ all-electron basis set [68]. Because the goal of these calculations was to get the ground-state spectroscopic properties, only the ground state spin multiplicities were calculated. The ground-state characters of the results were confirmed by applying the STABLE keyword of Gaussian 09, which checks for eventual lower-energy solutions of the wavefunction. The geometry optimizations were followed by the frequency calculations confirming the minimum characters of the obtained geometries. The anharmonic frequencies were calculated by evaluation of the quartic force field by means of numerical derivation (Freq = Anharmonic keyword in Gaussian 09). The assignment of the fundamentals was done on the basis of visual observation by means of the GaussView software [69], facilitating the recognition of their main vibrational components. The study of the bonding properties was based on atomic charges and orbital populations obtained by natural bond orbital analysis [70] using the NBO5.9 [71] code.

3. Results and discussion

3.1. Electronic structure

The electronic structure of the Na_2AnO_4 species was investigated on the double bidentate $\text{NaO}_2\text{AnO}_2\text{Na}$ coordination structure, characteristic on hexavalent alkali transition metal mixed oxides [20,72–76]. However, the D_{2d} geometry formed by the transition metal compounds proved to be a saddle-point for actinides according to our calculations. The minimum structure for all the four Na_2AnO_4 molecules is the planar D_{2h} one (presented in Fig. 1), hence we optimized these structures at the SF CASPT2 level. The optimized geometries of the ground electronic states (except where noted) were used to evaluate the characteristics of the electronic structures.

The lowest-energy electronic states of Na_2UO_4 from SF- and SO-CASPT2 calculations are given in Table 1. In agreement with general experience on closed-shell hexavalent uranium-containing molecules [15,77–79], the ground state of Na_2UO_4 is 1A_g . This SF state forms exclusively the SO ground state. We note that contributions from another configurations (also in most low-lying excited states)

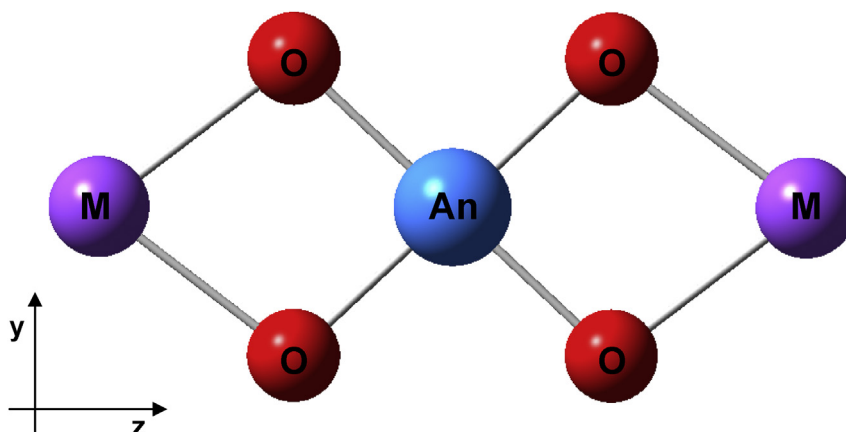


Fig. 1. The D_{2h} minimum structure of the investigated molecules.

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