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DFT Study of Hyperfine Interactions in Some Types of the Complexes

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It is well known that chemical applications of the NQR and Mössbauer spectroscopies use the sensitivity of the experimental parameters to investigate changes in the electron density at the nucleus [1]. The nuclear quadrupole constants and isomer shift are a function of both nuclear and electronic properties of the molecular systems, which are combined in such a way that independent quantitative information on both kinds of properties cannot be obtained by NQR and Mössbauer spectroscopy alone. Since the electronic properties are usually of interest and because the nuclear parameters are constant, the hyperfine parameters are most frequently used to compare the electronic properties of different molecules. The covalent effects and the shielding of one set of electrons by another also influence the electronic environment of the nucleus and may be reflected in changes in the isomer shift. On the other hand central to most simple theories of Lewis acidity is the idea that both ionic and covalent interactions play important roles in stabilizing the donor-acceptor bond [2].

In this report, we present a DFT calculations based on a microwave spectroscopic, nuclear quadrupole resonance and Mössbauer shifts of the donor-acceptor complexes formed from metal halides such as PtCl₂, PtCl₄, XeF₂, AuCl, AuCl₃, SbCl₅, SnF₄, SnCl₄, TiCl₄, SnBr₄, NbCl₅, TaCl₅, halogens and interhalogens with organic ligands. All ligands have a different basicity and softness. Therefore, it is of interest to investigate these complexes with a different acids and to compare their structural and electronic properties.

The full optimization of geometry was carried out using B3LYP achieved within the GAUSSIAN'03 program. The calculations of the complexes were carried out with all-electron DGDZVP basis set. The quadrupole coupling constants of the quadrupole atoms and the formation energy of the complexes has been broken down using the extended transition state (ETS) scheme implemented in the ADF package. We have used the OPTX exchange functional combined with PBE correlation functional with an uncontracted STO triple- ζ + polarization basis set using the frozen core approximation to treat the inner electrons. There are bases to consider, that the relativistic effects basic for such heavy atoms should be considered by the zero order regular approximation (ZORA) that is more reliable than the widely used Pauli formalism.

An analysis of the quality of the calculations that employ all-electron basis set for the halogen compounds was carried out. The ZORA method is shown to be a viable alternative for the calculation of halogen coupling constants in molecules. In addition, the ZORA model, in contrast to the pseudo-potential model, leads to realistic values of all metal nuclear quadrupole coupling constants [3].

The calculated energy terms can be identified with three main components of the chemical bond, i.e. Pauli repulsion, electrostatic attraction and covalent interaction. As a result, we receive the answer to a question about the relative contributions of covalent and electrostatic interactions to the donor-acceptor bond. If for the transition element complexes the electrostatic bonding is larger than covalent bonding while for the non-transition element complexes the tendency opposite. The obtained result will be coordinated to the conclusion on the basis of Klopman approach.

In the language of the theory of hard and soft acids and bases, the calculated energy gaps involve direct mixing of the donor and acceptor orbitals. Energy of the bonds, calculated from the general energy of molecules with ZPE corresponded as formation energy of the ETS scheme, and to experimental enthalpy of the complex formation. The obtained dependences between Mössbauer chemical shifts and populations of the central atoms pointed to another nature of the chemical shifts in transition compounds in comparison with non-transition element compounds.

Besides, the values of the valence electron charge density at the nucleus ρ_0 have been evaluated from ZORA calculations for a number of Au, Pt, Xe, Sn, Sb, I compounds in order to check the accuracy of the theoretical approach. The linear correlations between the experimental values of δ and the calculated values of ρ_0 is

obtained.

[1]. Parish R. V. Coord. Chem. Rev., 1982, V. 42, P. 1.

[2] Frenking G., Wichmann K. et al. Coord. Chem. Rev., 2003, V. 238-239, P. 55.

[3] Poleshchuk O. K., Branchadell V., Ritter R. A., Fateev A. V. Hyperfine Interactions, 2008, V. 181, No. 1-3, P. 27.

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