Study of thiacalexarene conformation effect on the electronic structure by X-Ray Absorption Spectroscopy and quantum chemistry methods

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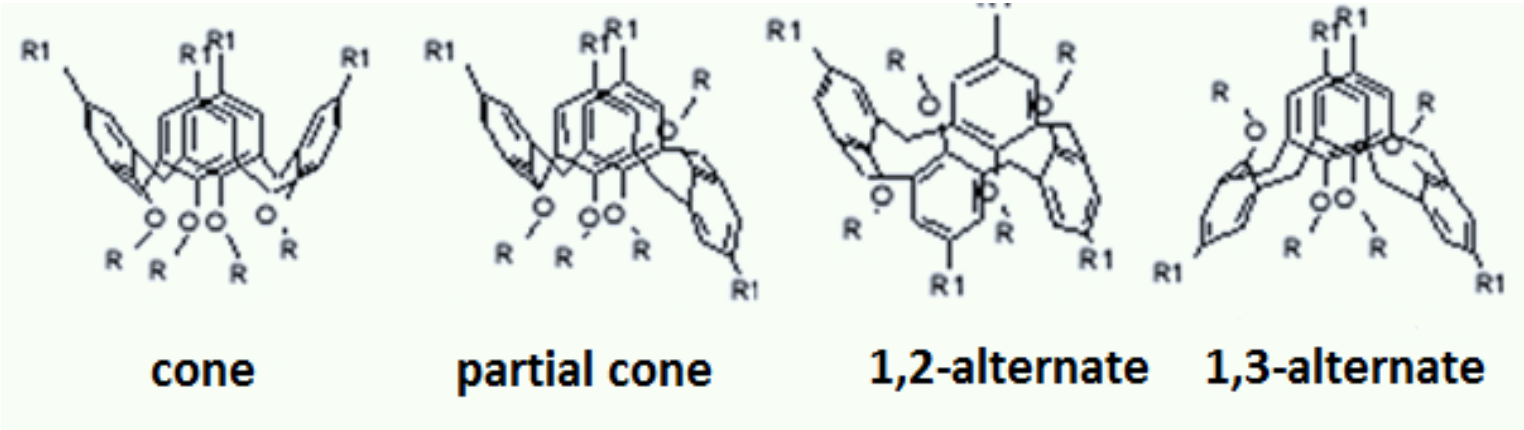
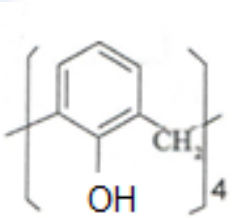
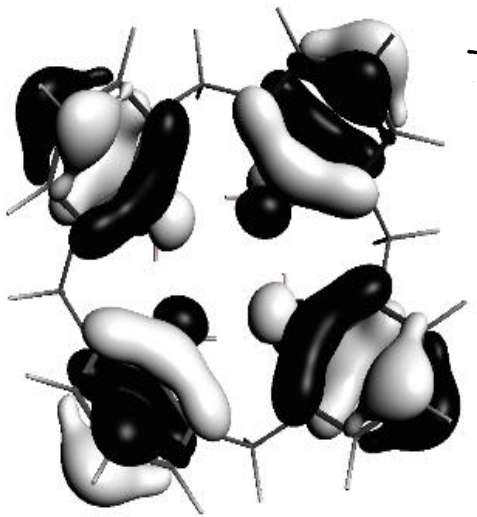
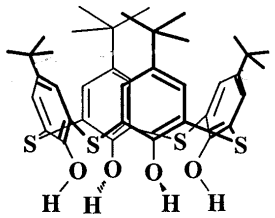
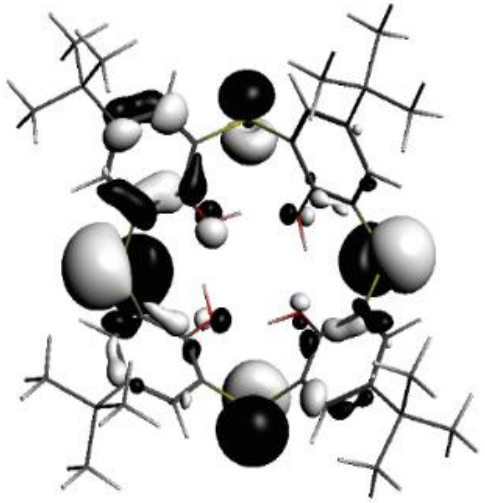


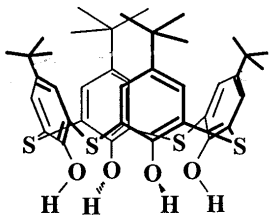
The HOMO structure of CA and TCA

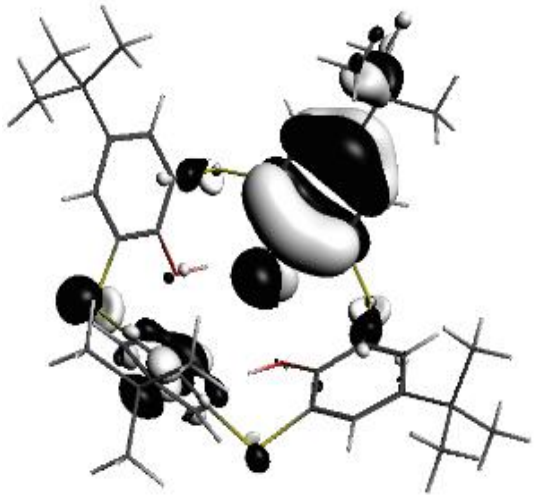












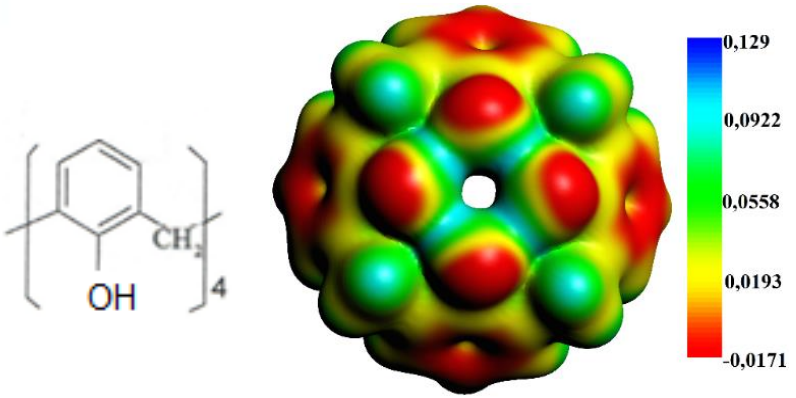
HOMO(112A) -9,445 eV
63,43(C2pπ)+17,31(O2pπ)
chalice π-system

HOMO(192A) -9.504 eV
3,49%(C2pπ)+0%(O2p)+75,58%(S2pnσ)
sulfur lone pair

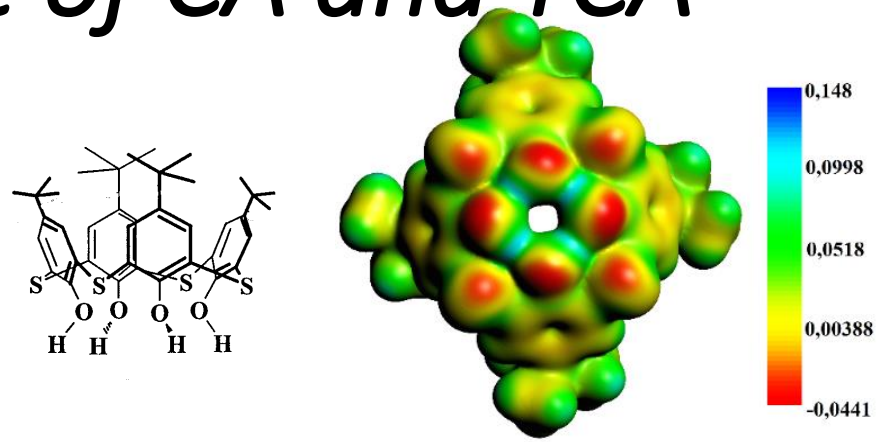
HOMO-15(187A) -9.738 eV
61,04%(C2pπ)+ 10,74% (O2pπ)+ 4,96%(S2pπ)
chalice π-system

In previous studies, valence X-ray emission spectra of TCAs were studied, and the electronic structure of molecules was calculated. According to the results of quantum chemical calculations, it was revealed that the HOMO of the simplest CA consists mainly of carbon contributions that forming a chalice of the CA molecule. The HOMO TCA consists of the contributions of a 3p lone pair of bridging sulfur atoms, and the molecular orbitals responsible for the carbon π-system lie deeper (HOMO-15).

The HOMO structure of CA and TCA



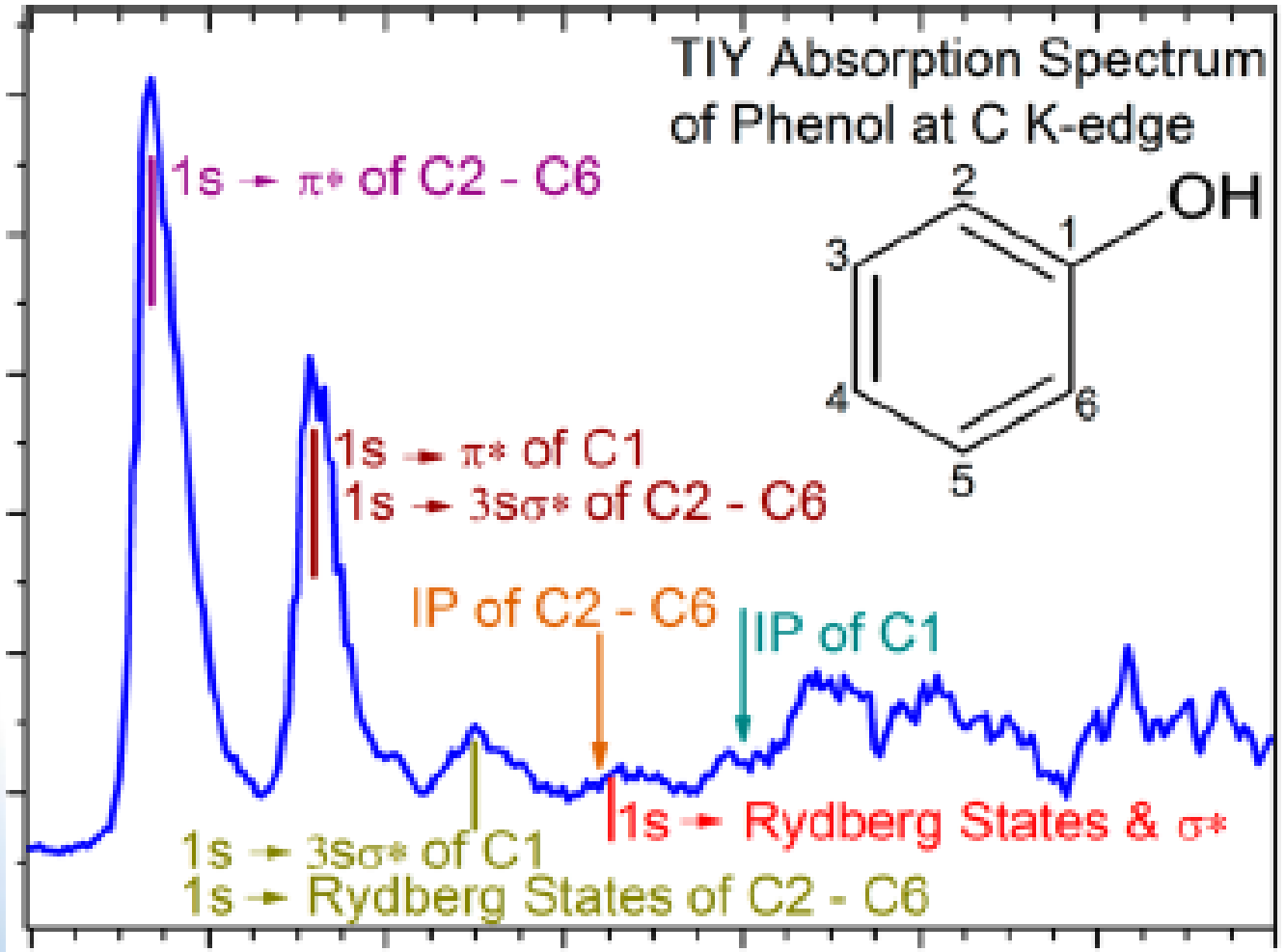
Electrostatic distribution maps of CA



Electrostatic distribution maps of TCA

As a result, we can conclude that the π-system of carbon, which forms a calixarene bowl along with donor oxygen and sulfur atoms, also plays an important role in the donor-acceptor properties of the molecules under consideration. In this regard, the influence of the molecule conformation on the π-system of CA and TCA molecules, as well as the effect of macrocycle formation on the electron density distribution in cyclic CA and TCA molecules, is of interest. The HOMO structure are correlated with the donor ability of the molecules, and the LUMO with the acceptor. Therefore, the task was to study LUMO molecules. CK-edge NEXAFS spectra were recorded at the Berlin Elektronenspeicher ring für Synchrotronstrahlung (BESSY II, Helmholtz-Zentrum Berlin, Berlin, Germany) using radiation from the Russian-German beamline (RGBL).

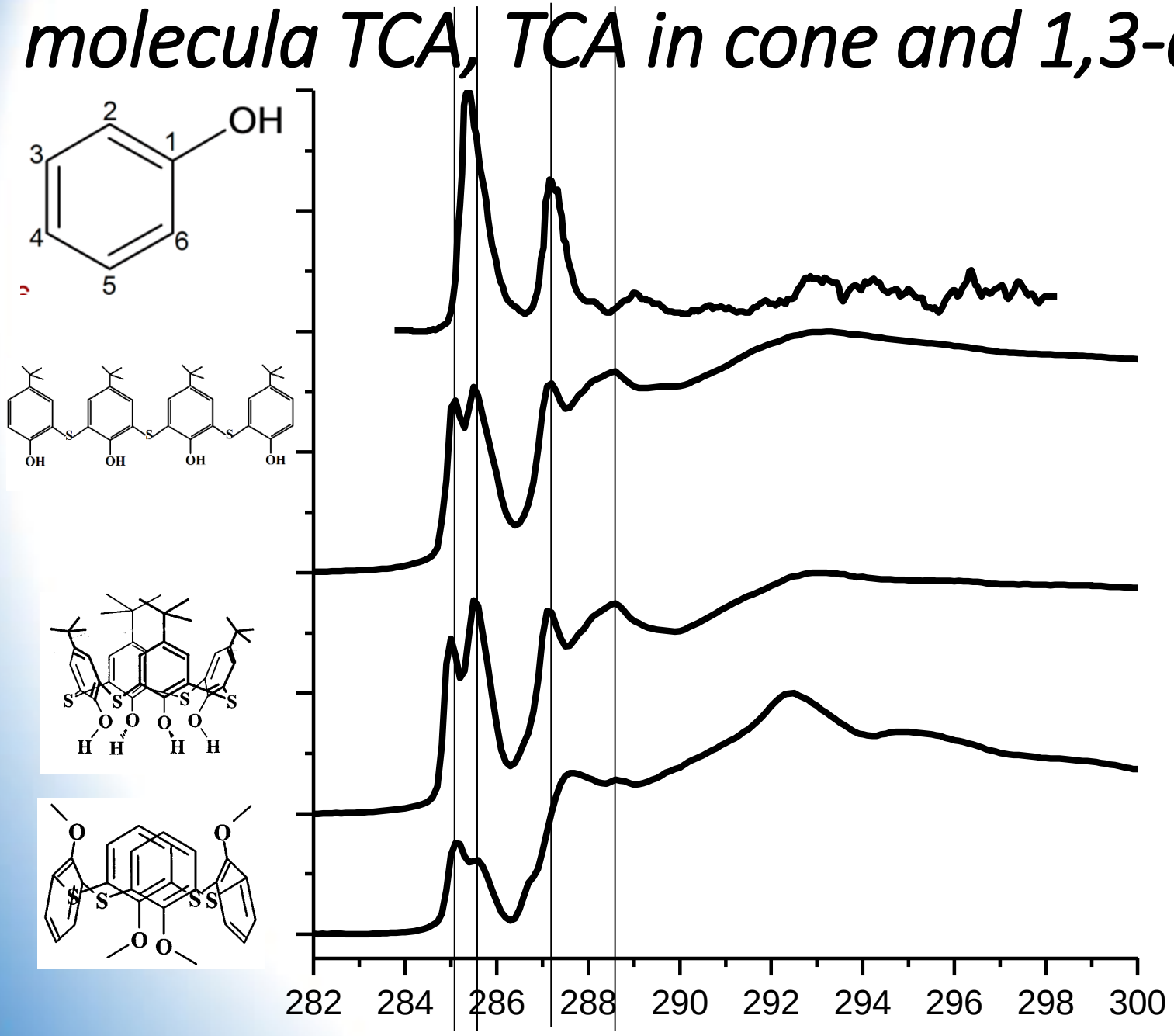
Experimental carbon K-Edge absorption of phenol



Phenol is the main fragment repeating in CA. The experimental carbon K-edge absorption of phenol was taken from the literature. It can be seen from the CK-edge of phenol that there are 2 maxima corresponding to π-orbitals of carbon in phenol, the first corresponds to the contributions of π-orbitals with 2-6 carbons, and the second corresponds to CO-carbon.

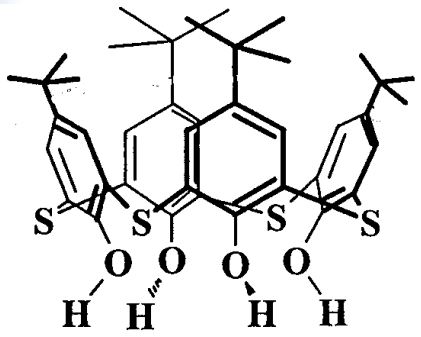
[1] Yi-Shiue Lin, Kun-Ta Lu, Yuan T. Lee, Chien-Ming Tseng, Chi-Kung Ni, and Chen-Lin Liu «Near-Edge X-ray Absorption Fine Structure Spectra and Site-Selective Dissociation of Phenol» // J. Phys. Chem. A 2014, 118, 1601−1609

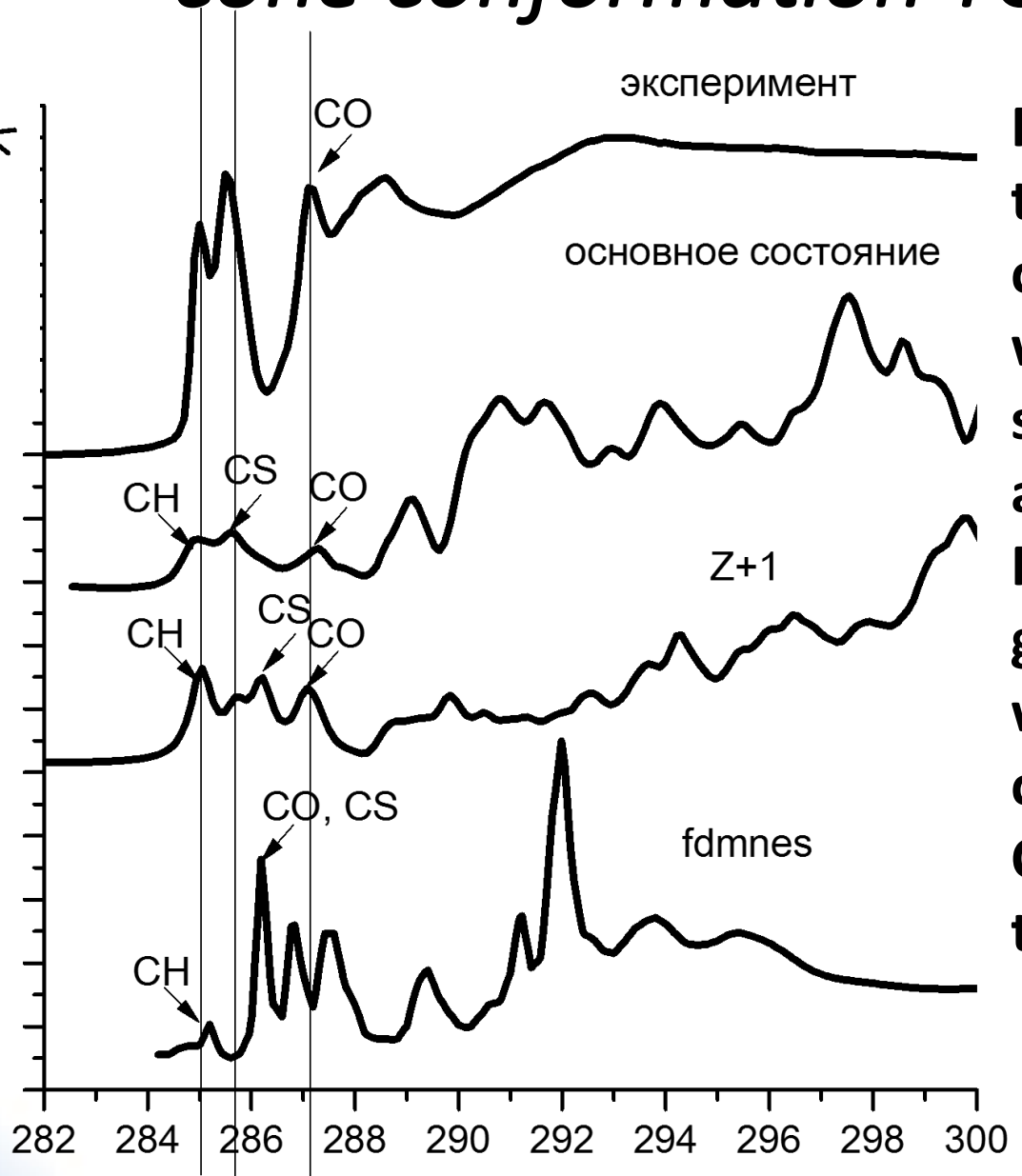
Experimental carbon K-Edge absorption of phenol, acyclic molecula TCA, TCA in cone and 1,3-alternate conformations



It can be seen from the spectra that in the spectrum region corresponding to the contributions of π-orbitals with 2-6 carbon atoms in phenol, there are 2 peaks in the TCA. The intensity ratio of these peaks practically does not change with the formation of the macrocycle. Meanwhile, a redistribution of peak intensities occurs during the transition of the TCA molecule from cone conformation to 1,3-alternate conformation.

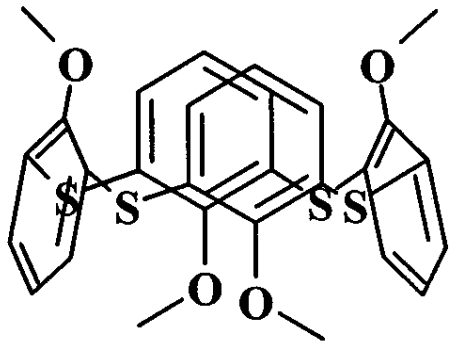
Experimental and theoretical CK-edge absorption of cone conformation TCA molecula

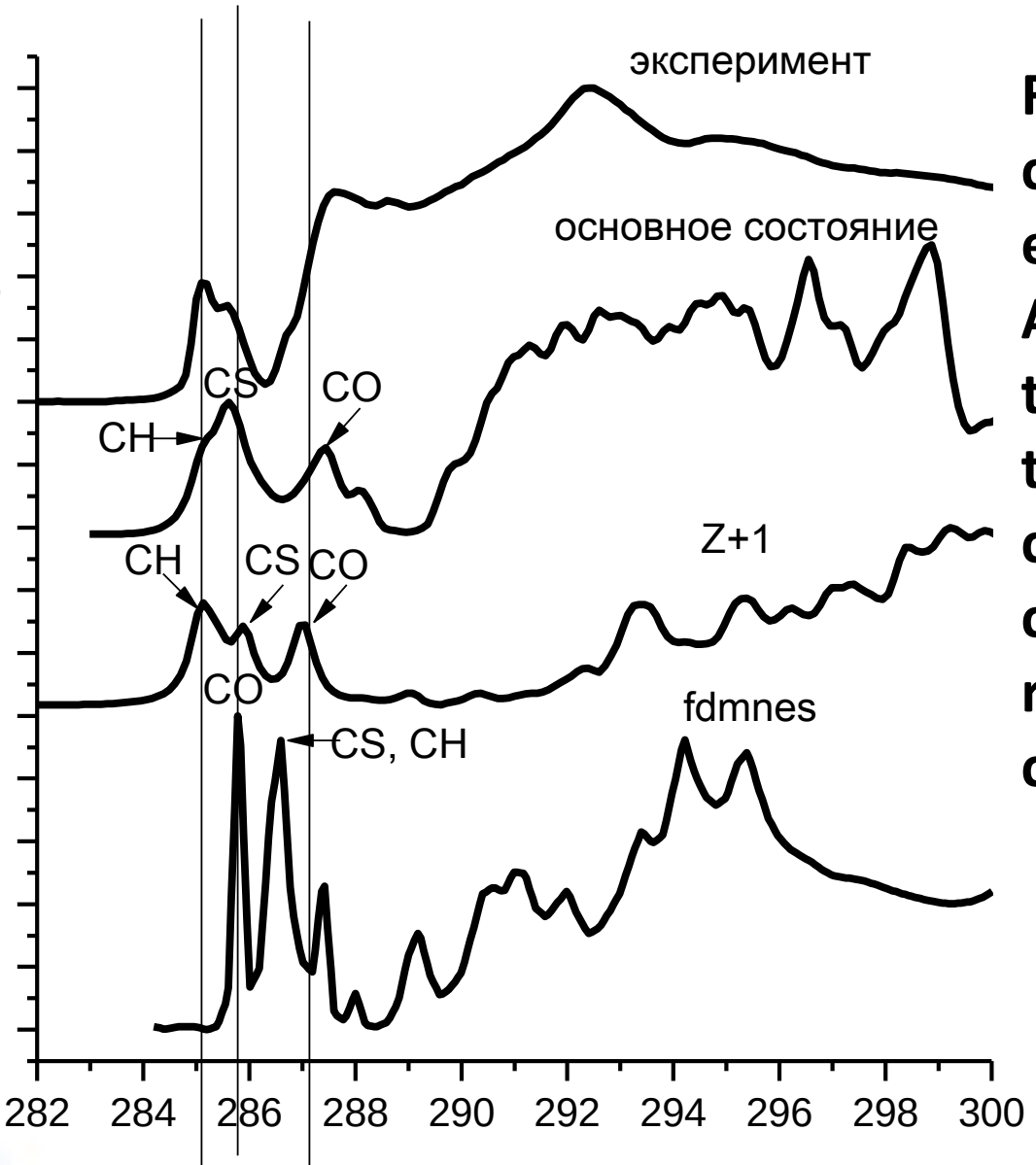




For a more detailed analysis, theoretical absorption spectra of TCA cone and 1,3-alternate molecules were constructed using the ground state of the molecule, Z+1 model, and in the Fdmnes software package. From the approximation of the ground state and the Z + 1 model, it was found that the first peak corresponds to 2p contributions of CH-carbons, and the second CS, and the third CO.

Experimental and theoretical CK-edge absorption of 1,3-alternate *conformation TCA molecula*





For the TCA molecule in 1,3-alternate conformation model Z+1 repeats the experimental spectrum more clearly. Analysis of experimental and theoretical data shows that upon the transition of TCA molecules from cone conformation to 1,3-alternate conformation, the electron density is redistributed between CS and CH carbons.

Conclusions

Analysis of experimental and theoretical data shows:

- the LUMO of the studied TCA molecules were constructed with the participation of 2p AO carbon atoms of CH, CS, CO fragments constituent TCA;
- conversion of cone conformation to 1,3-alternate conformation leads to electron density redistribution and to increase of the C2p-AO contribution of C-H fragments in LUMO.

Our gratitude to **A. Okotrub, L. G. Bushlusheva** and **A.A. Makarova** for the obtained absorption spectra

This work was supported by the bilateral Program “Russian-Germany Laboratory at BESSY II” in the part of CK-edge NEXAFS measurements.