

Vibrational Spectroscopy Studies of the Non-Covalent Interactions Governing Photophysical Properties in Some Crystalline Difluoride Boron Complexes

L.A.Kuarton*, O.B.Ryabchenko

*(Far Eastern Federal University, Vladivostok,
Russian Federation)*

**E-mail:* kuarton.la@dvfu.ru

Boron β -diketonate complexes are used in different fields of science and industry because of their luminescent and phototransforming properties, which depend not only on structure of a complex but also on non-covalent interactions (NCI) that are mostly due to substituents and heteroatoms in the chelate ring.

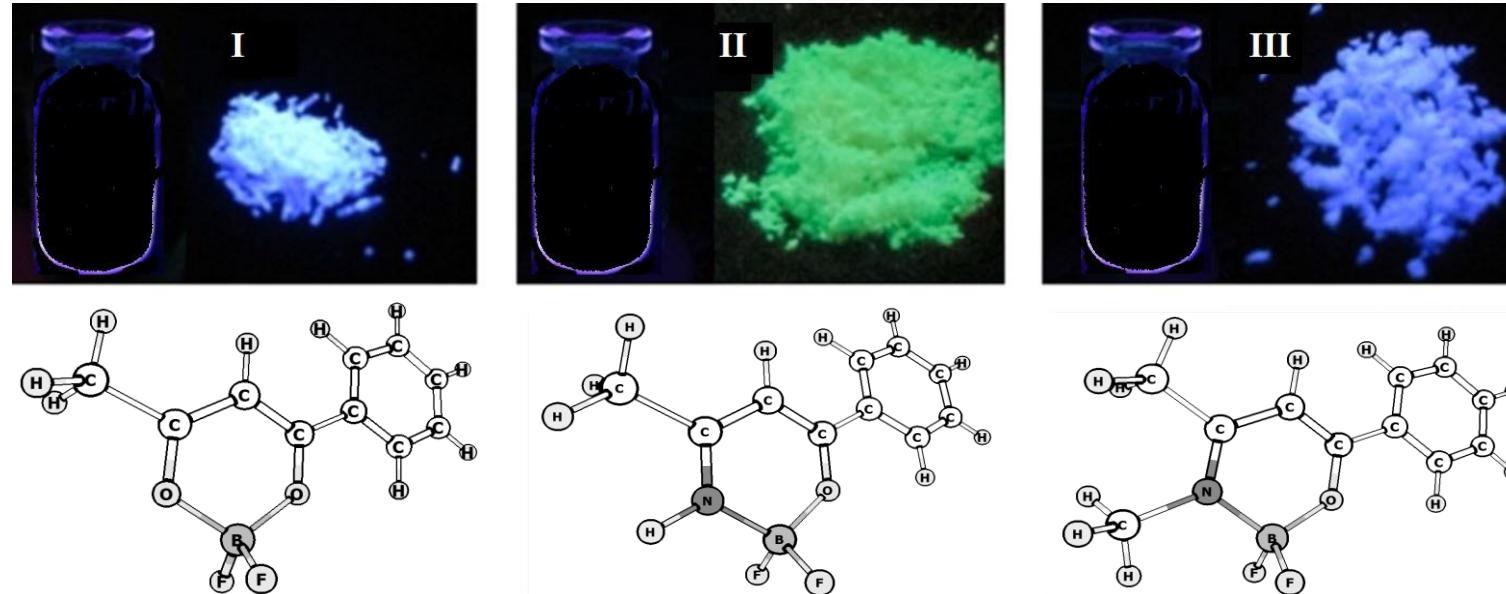


Photo from: E. V. Fedorenko, A. G. Mirochnik, A. Yu. Beloliptsev, I. V. Svistunova, G. O. Tretyakova. Design, Synthesis, and Crystallization-Induced Emission of Boron Difluorides β -Ketoimimates. - ChemPlusChem 2018, 83, 117 – 127.

Samples, Methods

Complexes were synthesized in chemical cluster FEFU.

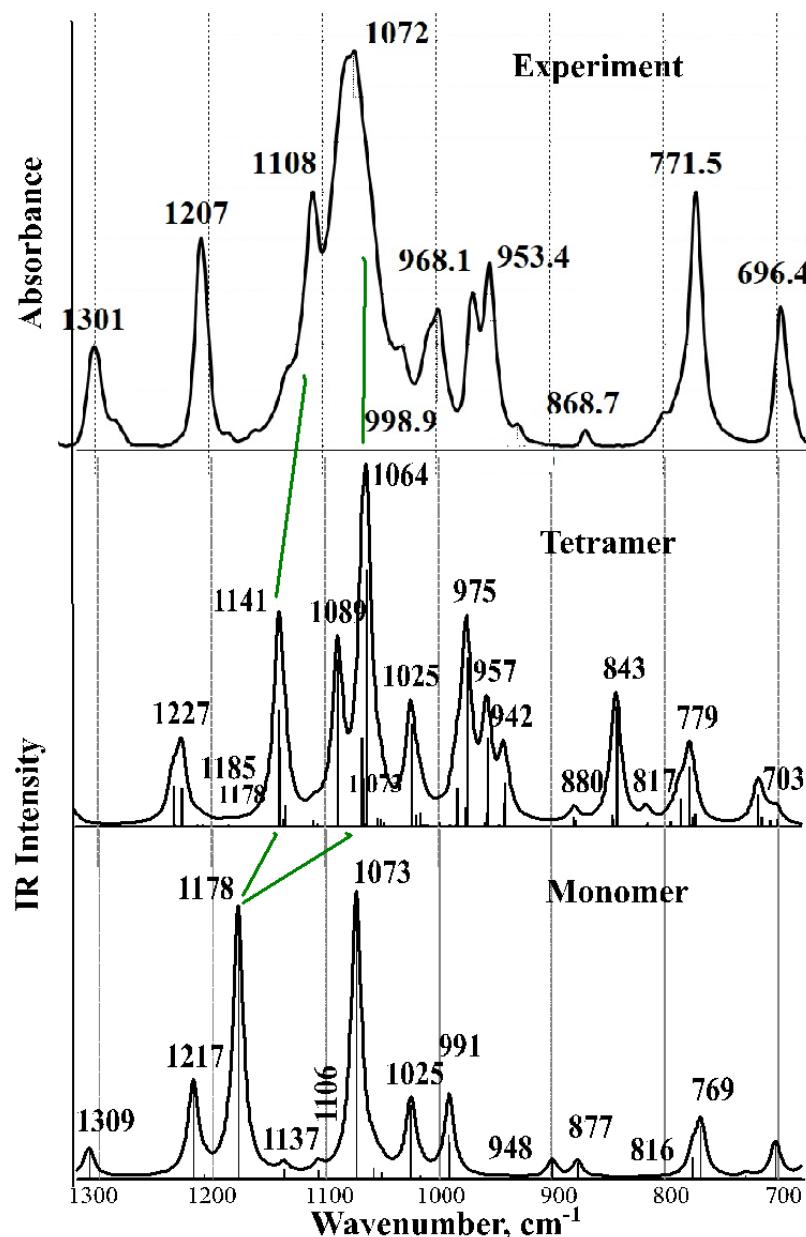
FT-IR spectra were registered by spectrometer Vertex 70. Samples were prepared by pressing in pellets with KBr.

Quantum-chemical calculations were performed by means of a program **Firefly** DFT/B3LYP method in basis set 6-311G (d, p).

Vibrational mode visualization, calculated spectrum simulation:
Chemcraft.

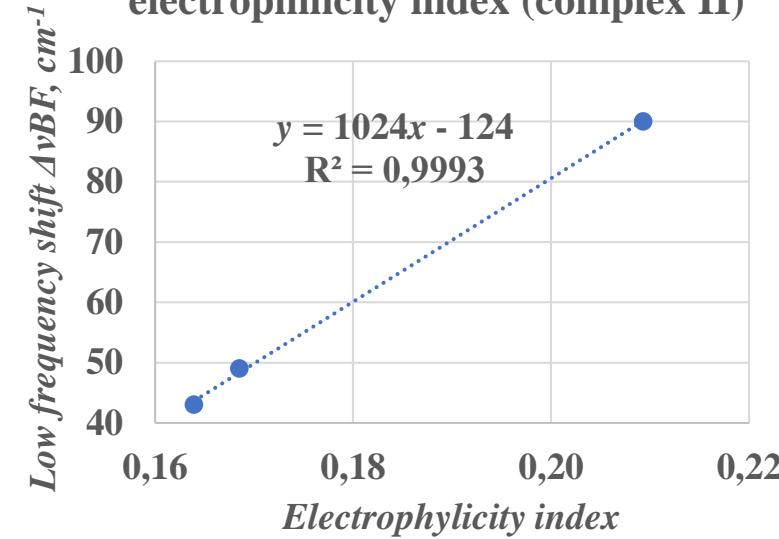
NCI visualization: **Multiwfn** and **VMD** program tools.

Tetramer model spectra are very helpful in assignment and searching for vibrational marker bands.



Measured and calculated IR spectra of the complex II in the 1320–680 cm^{-1} range.

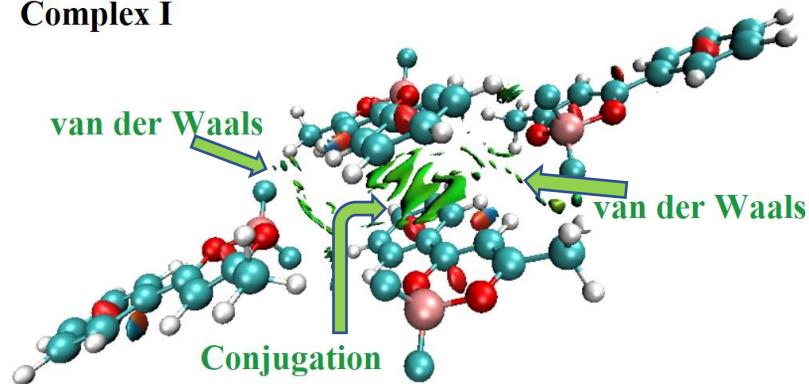
The minor of the νBF shifts vs electrophilicity index (complex II)



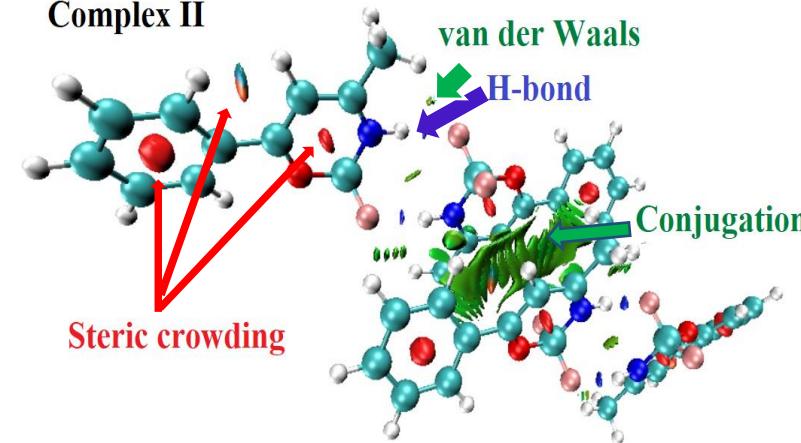
νBF band in each monomer spectrum is splitted in related tetramer spectrum to two (complexes **I** and **II**) or to three components (complex **III**) that is consistent with the types of the NCI (on the next slide).

The minor νBF shift value is likely correlated to the one of quantum-chemical descriptors whereas the greater shift does not show any correlations.

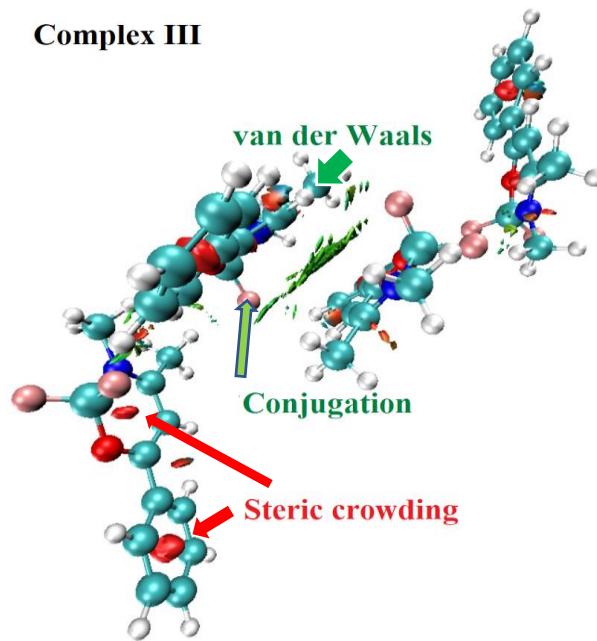
Complex I



Complex II



Complex III



NCI isosurfaces for the tetramer model give useful assistance in revealing marker IR-bands and discriminating their spectral shifts.

For example, besides dual H-bonds in the compound **II**, there is the green isosurface indicating direct **vdW** interaction between the nitrogen atoms of the neighboring molecules that may help to explain the considerable high frequency γ NH band shift.

Conclusions

1. Basing on normal mode calculations of the complexes **I**, **II**, **III** detailed assignment of IR bands has been performed in a range 4000-400 cm⁻¹. Models of monomer and tetramer fragments have been in use.
2. Marker bands showing different sensitivity to non-covalent interactions were found.
3. As an example stretching modes vBF have been considered; under interactions their bands exhibit both frequency shifts and splittings.
4. Frequency shifts are related to the types of intermolecular interactions, which have been represented as isosurfaces.
5. A probable correlation of the frequency shift vs electrophilicity index may be verified in further investigations for longer sequences of relative compounds.

Thank you for your attention

