

DFT Study of Hyperfine Interactions in Some Types of the Complexes

**Oleg Poleshchuk, Natalya Khramova,
Alexander Fateev**

***Tomsk State Pedagogical University,
Russia***

Geometry optimization

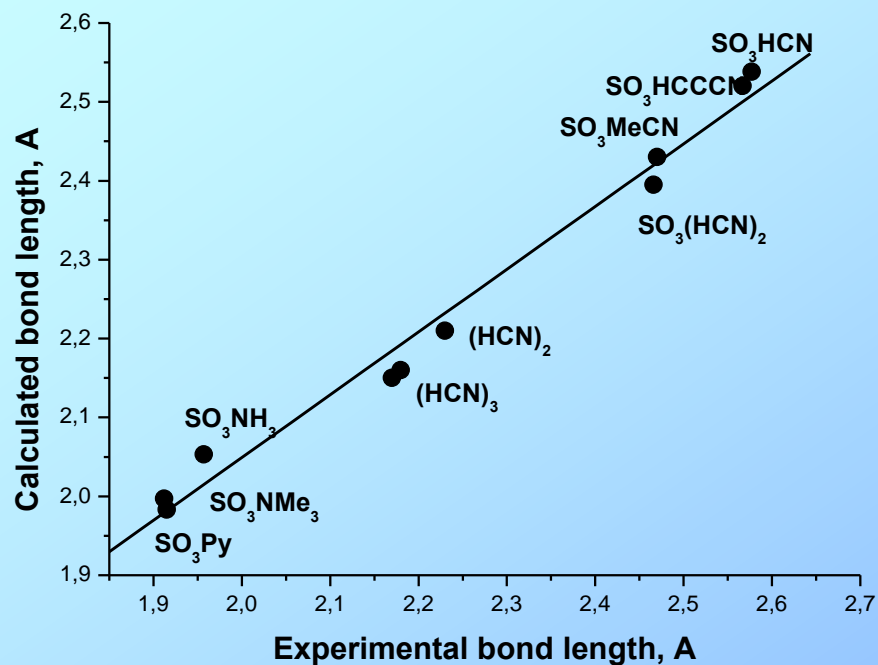
| | |
|---------------------------------------|--|
| SO₃-B complexes | B3PW91/6-311+G(df,pd) BP86/TZ2P+ in ADF |
| XY-B complexes | BHandHLYP/aug-cc-pVTZ 3-21G*,DGDZVP (iodine) BP86E/TZ2P+(ZORA) in ADF |
| MHal-B complexes | B3LYP/SDD, B3LYP/DGDZVP BP86/TZ2P+(ZORA) in ADF |

Bond Lengths

| Complex | $R_{D-A}, \text{\AA}$ | | Complex | $R_{D-A}, \text{\AA}$ | |
|--|-----------------------|-------|------------------------------|-----------------------|-------|
| | Exp. | Cal. | | Exp. | Cal. |
| $\text{HCN}\cdot\text{SO}_3$ | 2.577 | 2.538 | $\text{ICl}\cdot\text{CO}$ | 3.011 | 2.960 |
| $\text{H}_3\text{N}\cdot\text{SO}_3$ | 1.957 | 2.053 | $\text{ICl}\cdot\text{NH}_3$ | 2.711 | 2.600 |
| $\text{Py}\cdot\text{SO}_3$ | 1.915 | 1.983 | $\text{ICl}\cdot\text{Py}$ | 2.290 | 2.519 |
| $(\text{CH}_3)_3\text{N}\cdot\text{SO}_3$ | 1.912 | 1.997 | $\text{I}_2\cdot\text{Py}$ | 2.310 | 2.644 |
| $\text{Cl}_2\cdot\text{NH}_3$ | 2.730 | 2.685 | $\text{AuCl}\cdot\text{CO}$ | 2.217 | 2.259 |
| $\text{SbCl}_5\cdot\text{OPMe}_3$ | 1.94 | 2.11 | $\text{AuCl}\cdot\text{Ar}$ | 2.198 | 2.261 |
| $\text{SnCl}_4\cdot(\text{OSMe}_2)_2$ | 2.11 | 2.24 | $\text{AgBr}\cdot\text{CO}$ | 2.373 | 2.400 |
| $\text{TiCl}_4\cdot(\text{CH}_3\text{CN})_2$ | 2.21 | 2.28 | $\text{AgBr}\cdot\text{Ar}$ | 2.393 | 2.427 |
| $\text{TiCl}_4\cdot(\text{OPCl}_3)_2$ | 2.22 | 2.20 | $\text{CuF}\cdot\text{CO}$ | 1.736 | 1.758 |
| $\text{ICl}\cdot\text{Ar}$ | 3.576 | 3.761 | $\text{CuBr}\cdot\text{CO}$ | 2.182 | 2.225 |

- A comparison of the geometrical parameters calculated by us with the experimental data of free molecules and complexes displays that the bond lengths have been overestimated.
- Analysis leads to the following correlations between the calculated and experimental bond lengths and valence angles for the compounds studied.

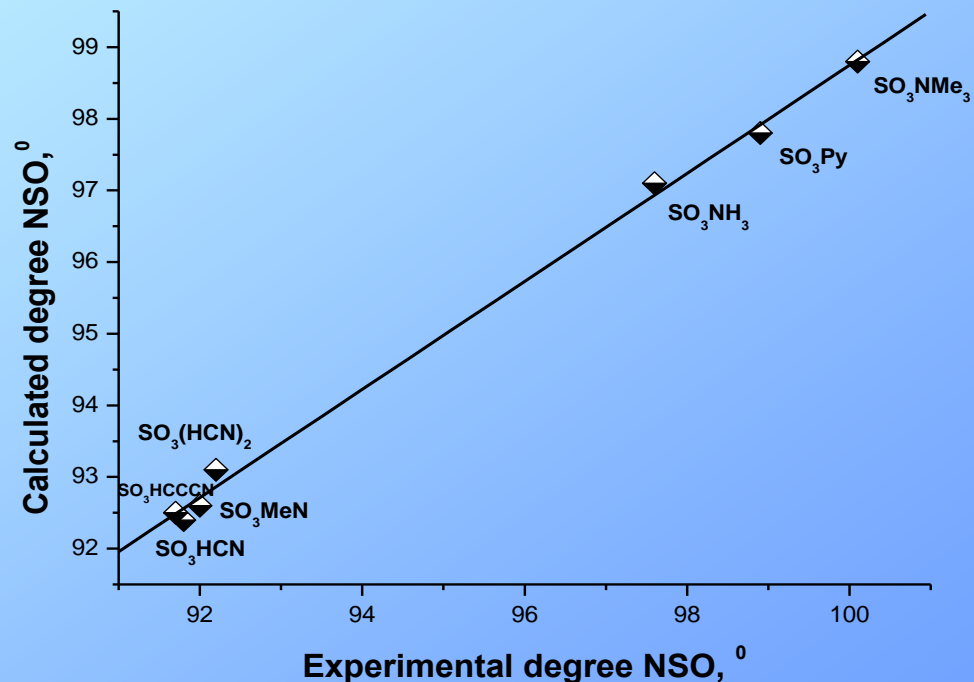
SO₃-B complexes



$$R(\text{cal.}) = 0.46 + 0.79 R(\text{exp.})$$

($r=0.991$; $s=0.03$; $n=9$)

Correlation between experimental and calculated at B3PW91/6-311+G(df,pd) level bond lengths.

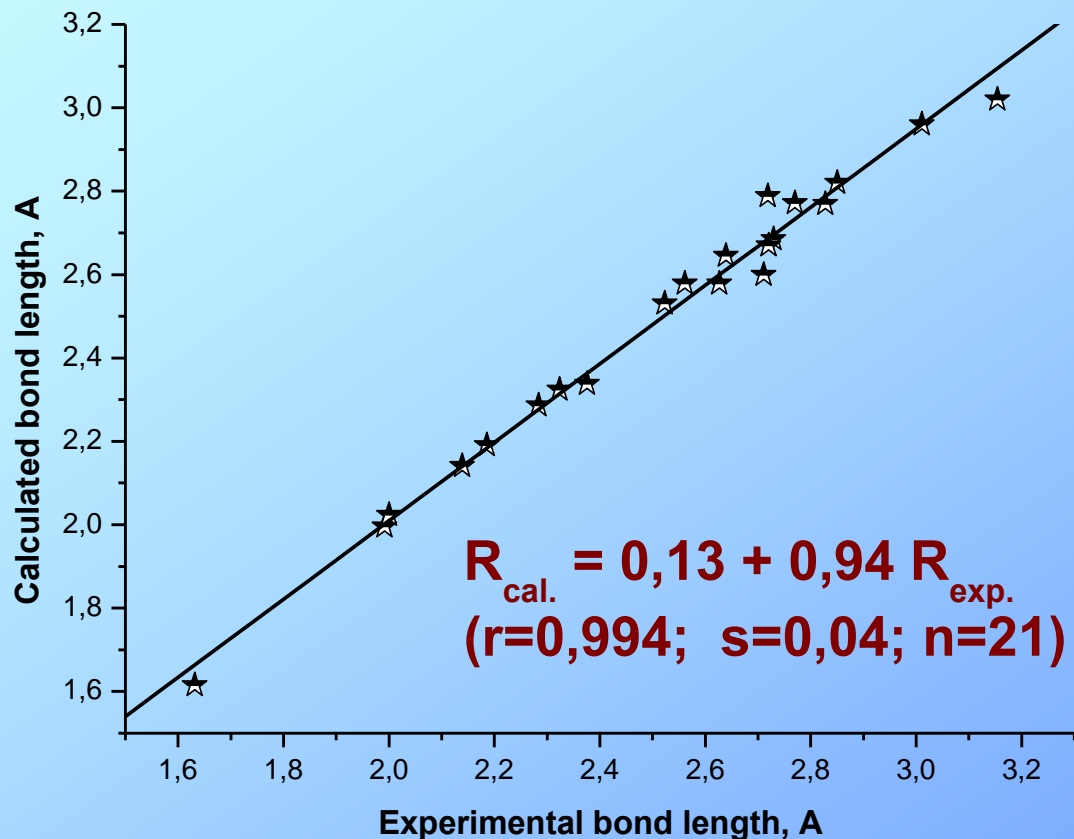


$$NSO(\text{cal.}) = 23.3 + 0.75 NSO(\text{exp.})$$

($r=0.999$; $s=0.16$; $n=7$)

Correlation between experimental and calculated at B3PW91/6-311+G(df,pd) level valence degree

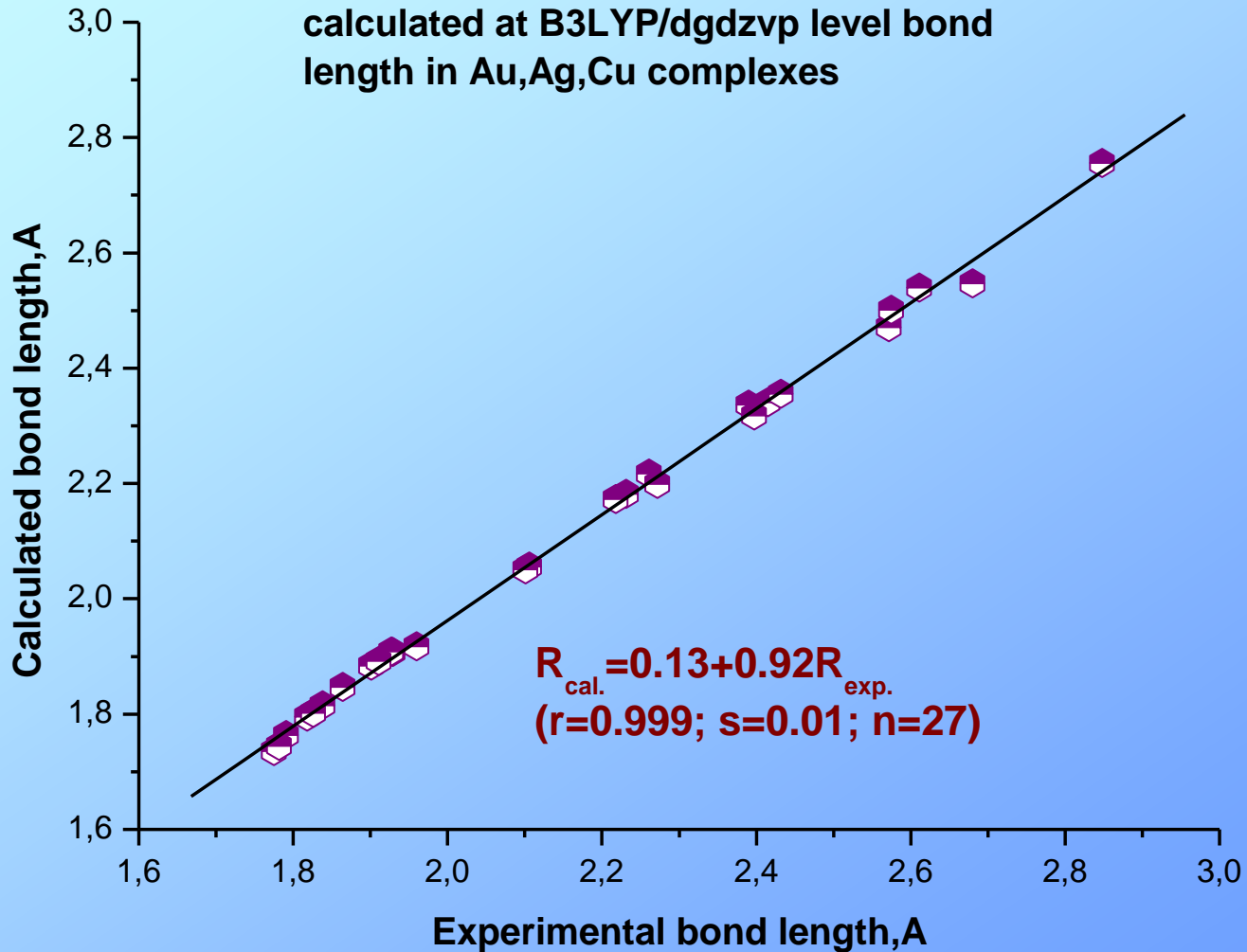
XY-B complexes



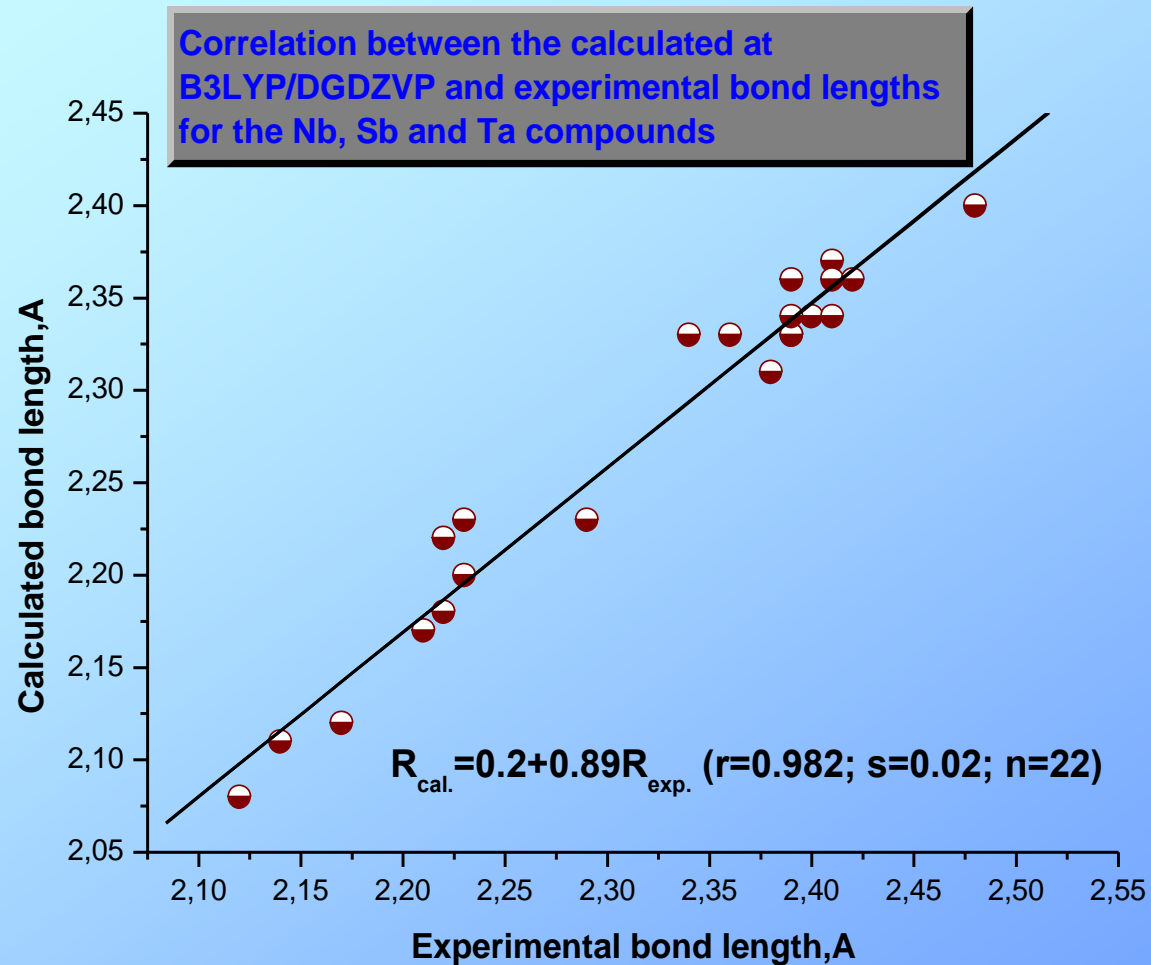
Dependence between experimental and calculated at BHandHLYP/aug-cc-pVTZ level bond lengths.

HaM-L complexes

Dependence between experimental and calculated at B3LYP/dgdzvp level bond length in Au,Ag,Cu complexes



HaIM-L complexes



Rotational constants

| Complex | B ₀ , MHz | | Complex | B ₀ , MHz | |
|---|----------------------|------|-----------------------|----------------------|------|
| | Exp. | Cal. | | Exp. | Cal. |
| H ₃ N·SO ₃ | 4378 | 4189 | ClFCH ₃ CN | 919 | 919 |
| (CH ₃) ₃ N·SO ₃ | 1633 | 1585 | ICI·CO | 903 | 888 |
| HCN·SO ₃ | 409 | 445 | ICI·NH ₃ | 1608 | 1604 |
| CH ₃ CN·SO ₃ | 1016 | 1038 | AuCl | 3519 | 3306 |
| HCCCN·SO ₃ | 655 | 665 | AuClCO | 1404 | 1367 |
| (HCN) ₂ ·SO ₃ | 409 | 419 | CuClCO | 1563 | 1527 |
| Cl ₂ ·NH ₃ | 1895 | 1890 | CuBrCO | 1034 | 1011 |
| ClFNH ₃ | 3316 | 3328 | AgClCO | 1316 | 1299 |
| BrCl·NH ₃ | 1801 | 1815 | AgBrCO | 852 | 840 |

$$B_0(\text{cal.}) = -38 + 1.05 B_0(\text{exp.}) \quad (r=0.9999; s=14; n=7)$$

for SO₃ complexes

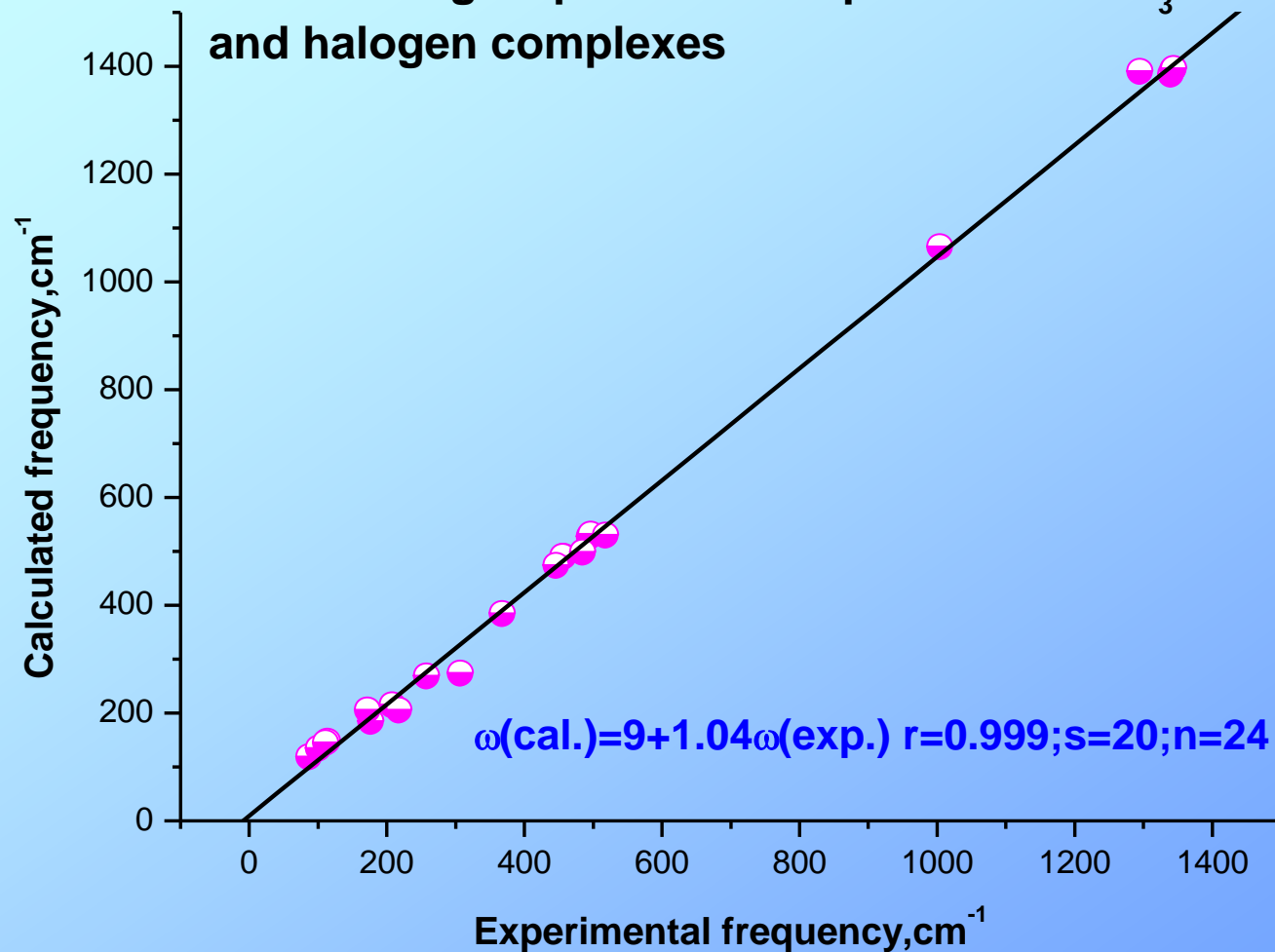
$$B_0(\text{cal.}) = 10.7 + 0.99 B_0(\text{exp.}) \quad (r=0.9999; s=34; n=22)$$

for halogen complexes

$$B_0(\text{cal.}) = 15.1 + 0.95 B_0(\text{exp.}) \quad (r = 0.998; s = 49; n = 13)$$

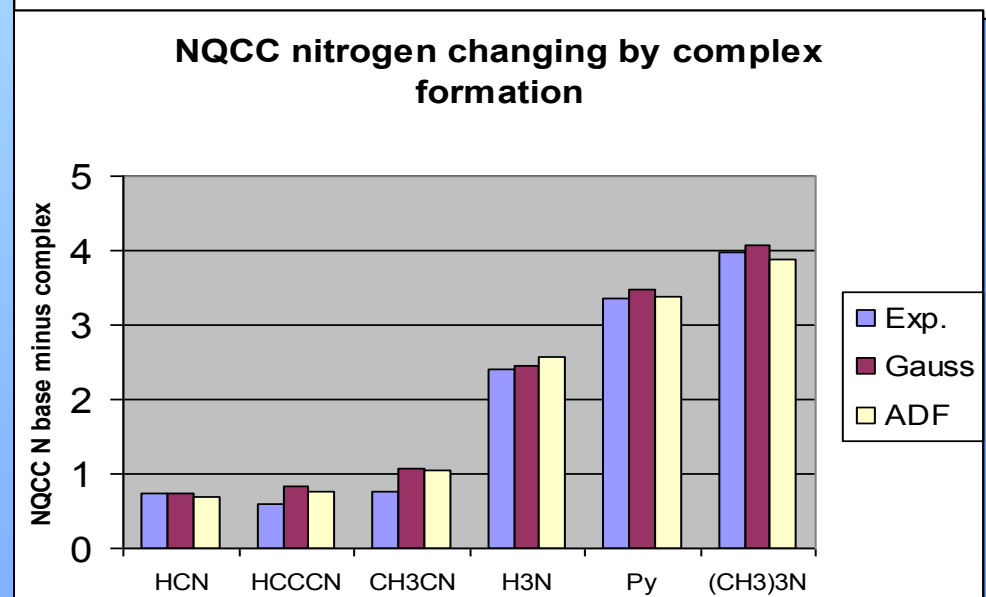
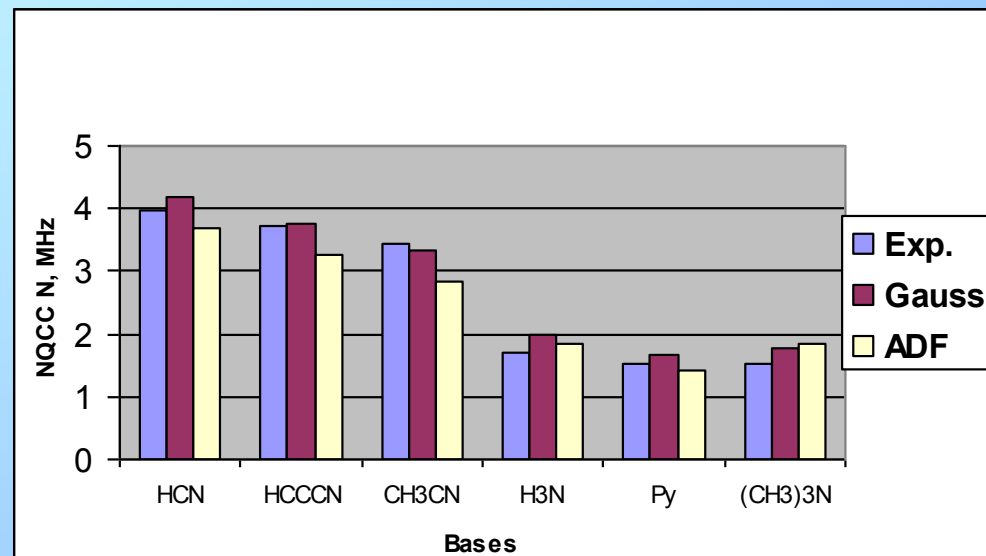
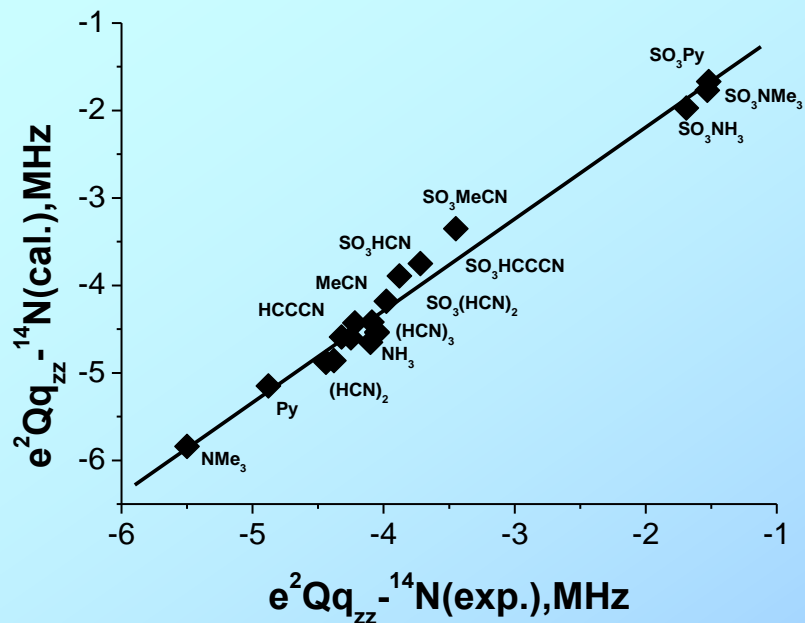
for metal complexes

**Correlation between experimental and calculated
at B3LYP/dgdzvp level IR-frequencies in SO₃
and halogen complexes**



- The halogen, metal and nitrogen nuclear quadrupole coupling constants obtained by these calculations substantially corresponded to the data of microwave spectroscopy in the gas phase. An analysis of the quality of the calculations that employ the pseudo-potential and the expanded basis set for the halogen compounds was carried out. The ZORA model is
- shown to be a viable alternative to the computationally demanding pseudo-potential model for the calculation of the iodine and metal (Nb, Au, Sb) quadrupole coupling constants in molecules.

NQCC ^{14}N in SO_3 complexes



Correlation between experimental and calculated at B3PW91/6-311+G(df,pd) level ^{14}N -NQCC in SO_3 complexes.

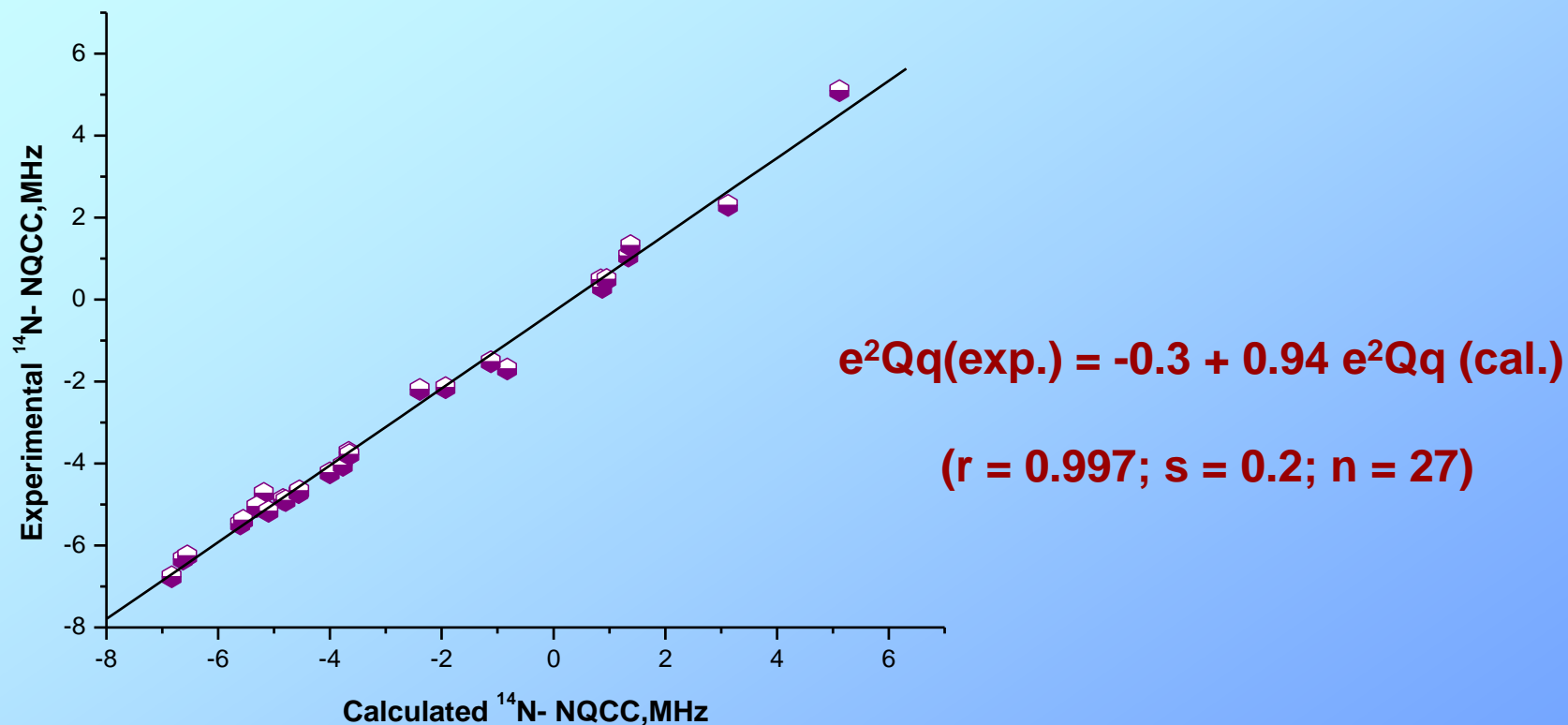
$$e^2Qq_{zz}^{14}\text{N}(\text{cal.}) = -0.09 + 1.05e^2Qq_{zz}^{14}\text{N}(\text{exp.})$$

($r=0.989$; $s=0.2$; $n=18$)

$$e^2Qq_{zz}^{14}\text{N}(\text{cal.}) = -0.05 + 0.96 e^2Qq_{zz}^{14}\text{N}(\text{exp.})$$

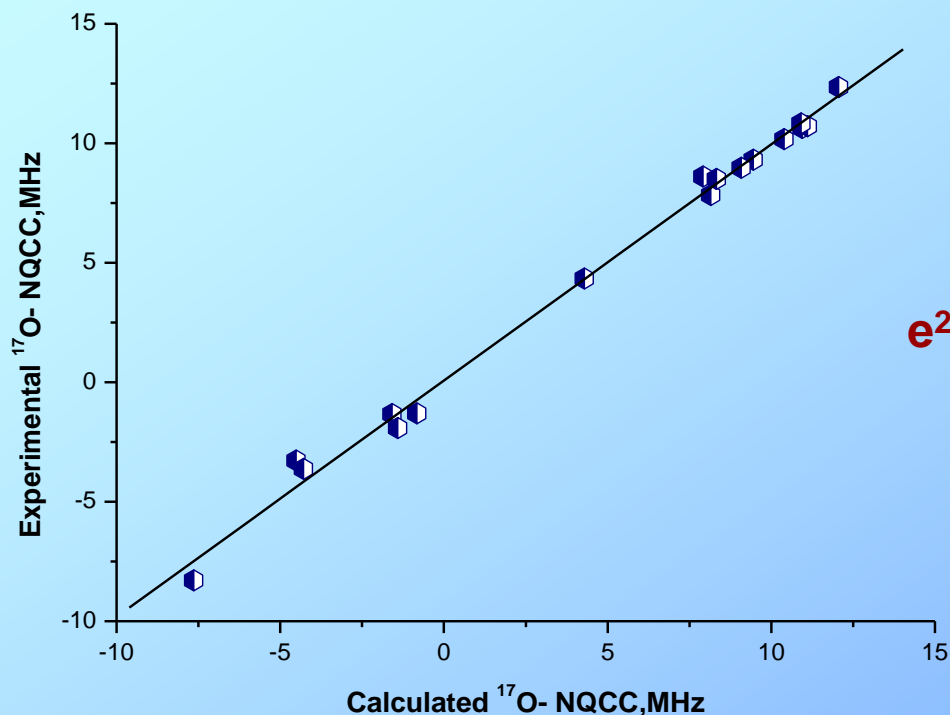
($r = 0.970$; $s = 0.3$; $n = 11$)
from ADF calculations

^{14}N -NQCC in nitrogen molecules



Dependence between experimental and calculated at BP86/TZ2P+ level NQCC values of N nuclei in nitrogen molecules

^{17}O -NQCC in oxygen molecules

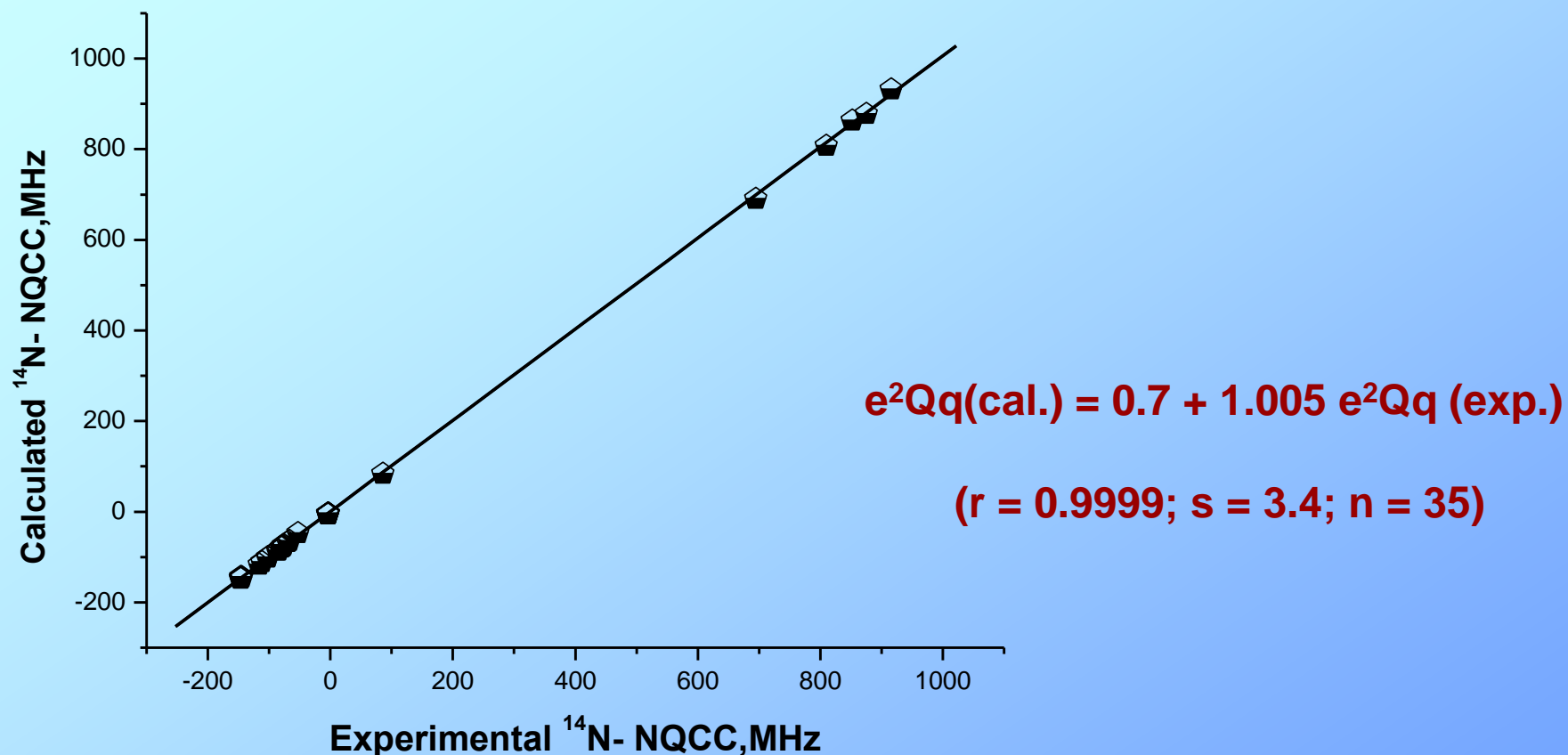


$$e^2Qq(\text{exp.}) = 0.1 + 0.99 e^2Qq(\text{cal.})$$

$$(r = 0.997; s = 0.5; n = 17)$$

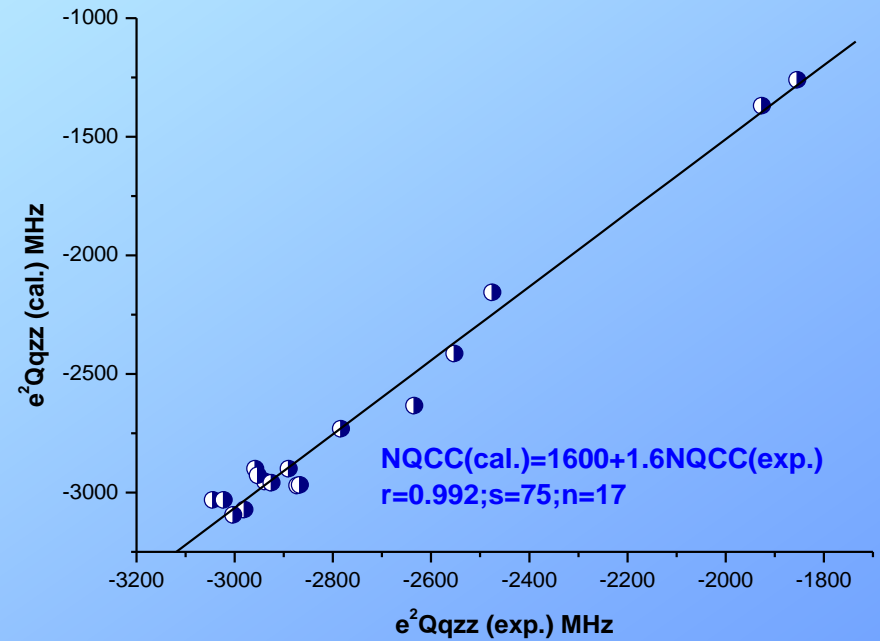
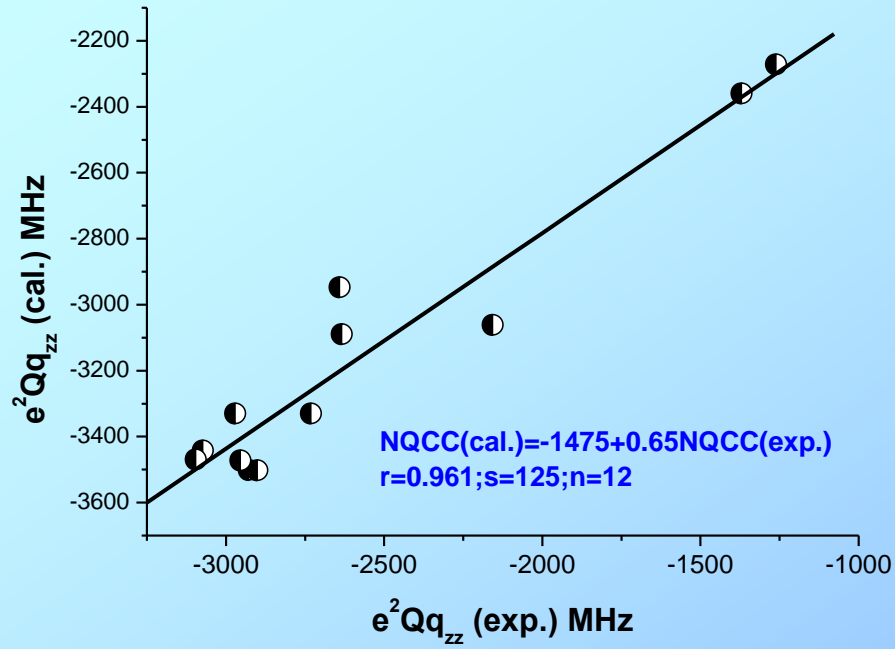
Dependence between experimental and calculated at BP86/TZ2P+ level NQCC values of O nuclei in oxygen molecules

NQCC in XY-B complexes



Dependence between experimental and calculated at BHandHLYP/aug-cc-pVTZ level NQCC values of Cl, Br, N nuclei in XY-B complexes

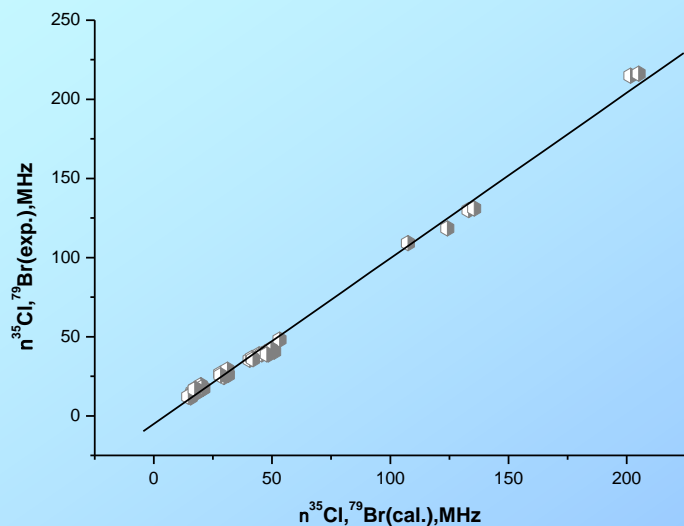
NQCC iodine nuclei



Dependence between calculated and experimental ^{127}I -NQCC values of the XY...B(XY=I) complexes at ZORA in ADF

Dependence between calculated and experimental ^{127}I -NQCC values of the XY...B(XY=I) complexes at B3LYP/dgdzvp level

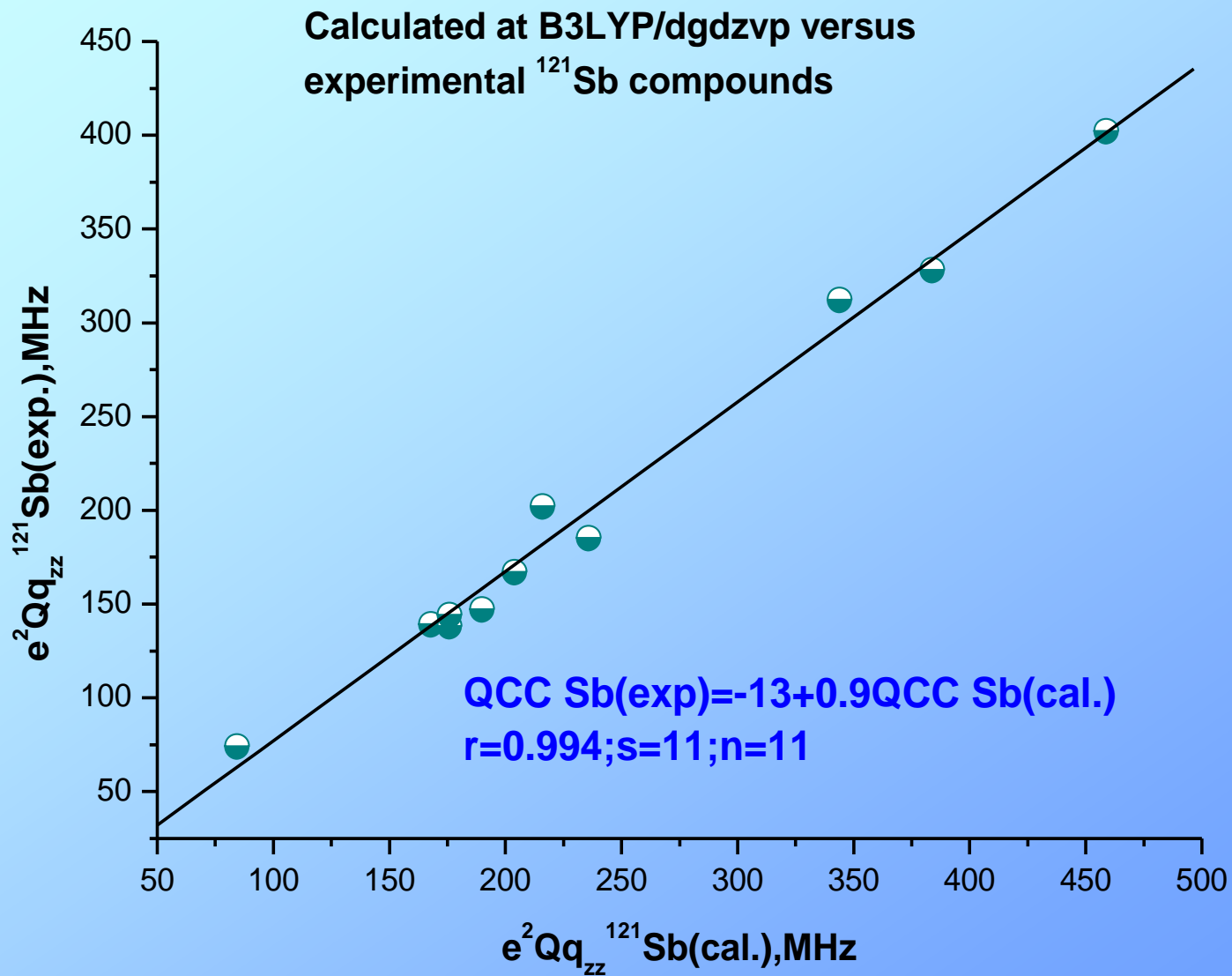
^{35}Cl - NQCC in XY-B complexes



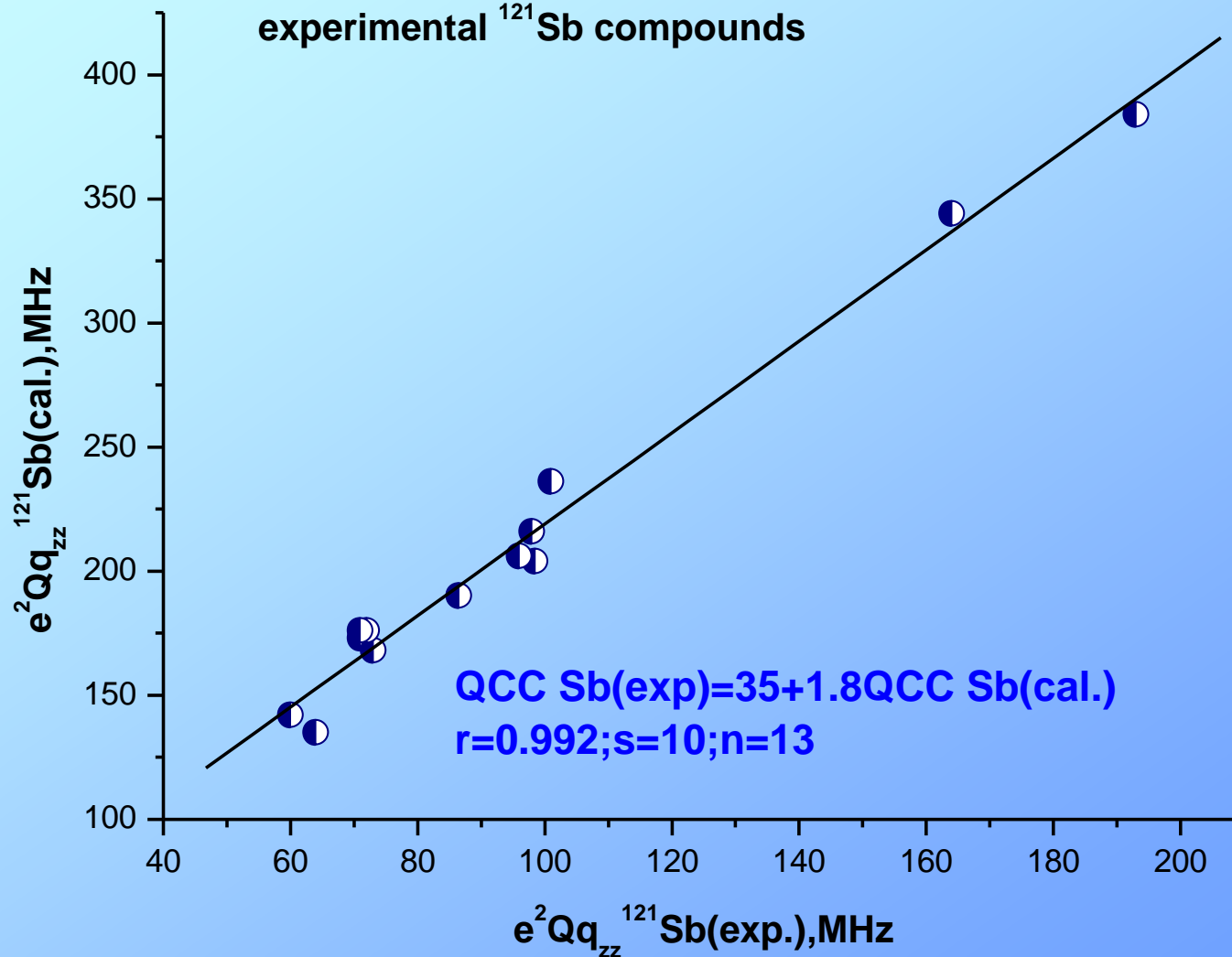
$$e^2Qq(\text{exp.}) = -5.1 + 1.05 e^2Qq(\text{cal.})$$

$$(r = 0.997; s = 3.5; n = 48)$$

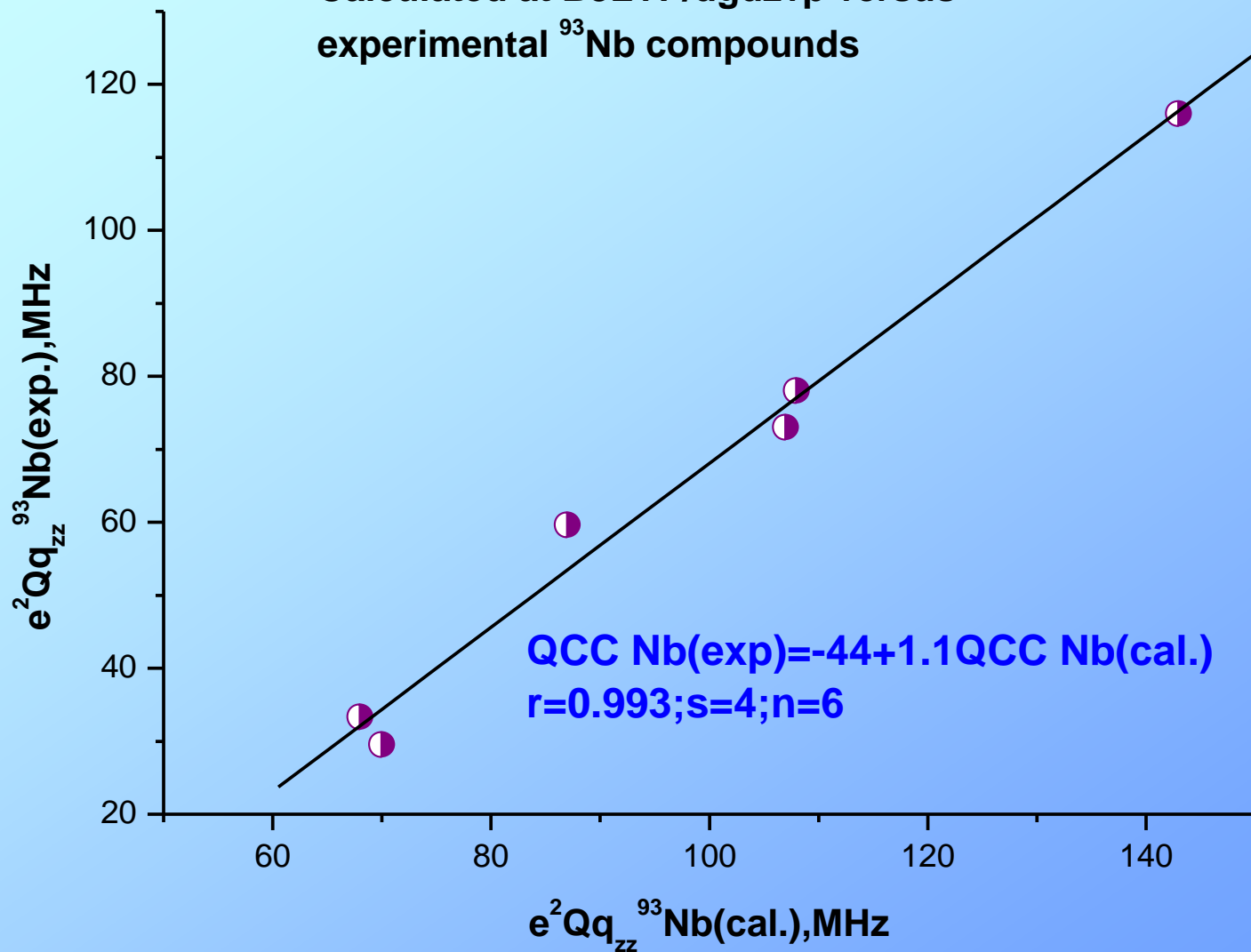
Dependence between experimental and calculated at BP86/TZ2P+ level NQCC values of Cl and Br nuclei in XY-B complexes



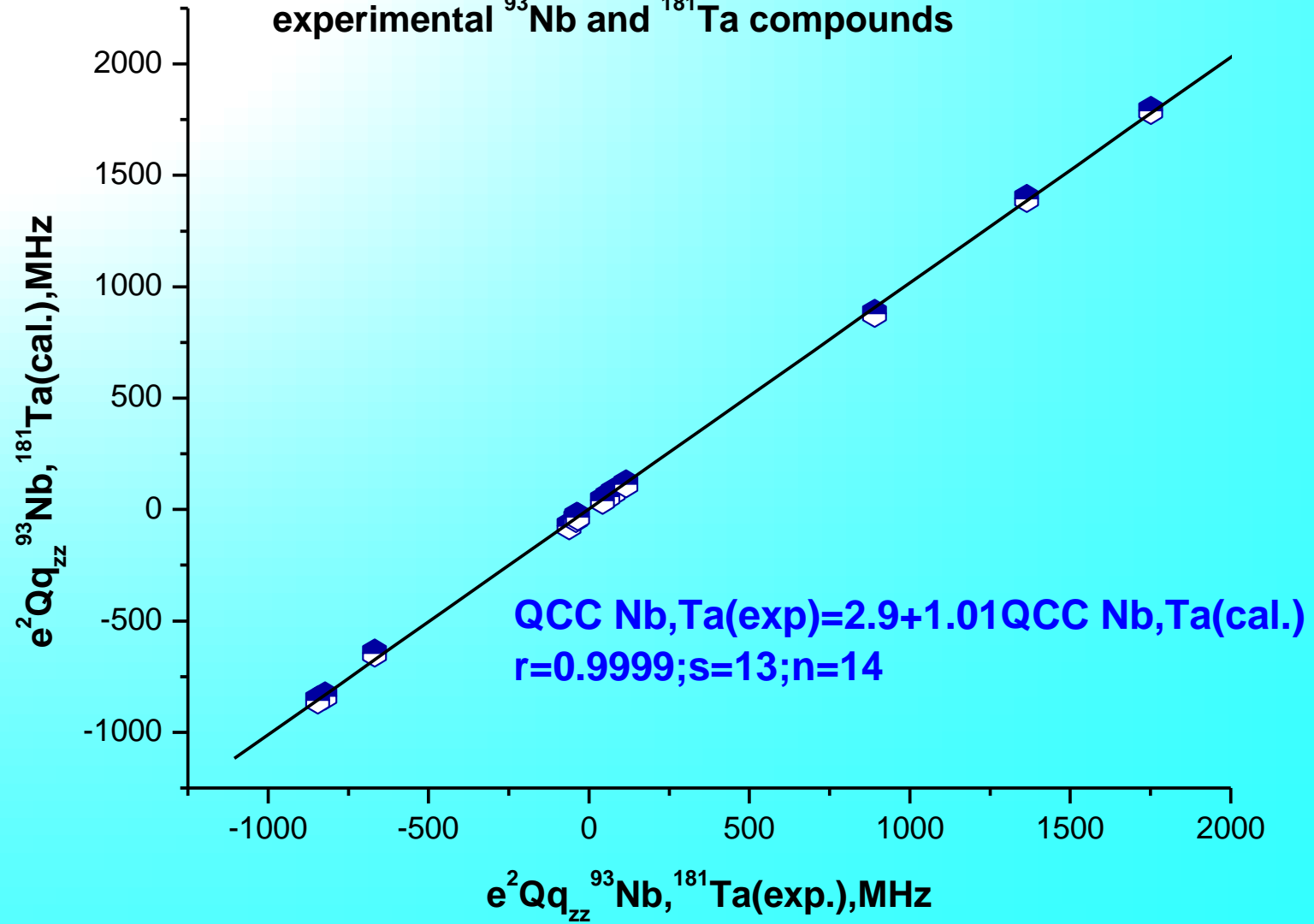
Calculated at BP86/TZ2P+(ZORA) versus
experimental ^{121}Sb compounds



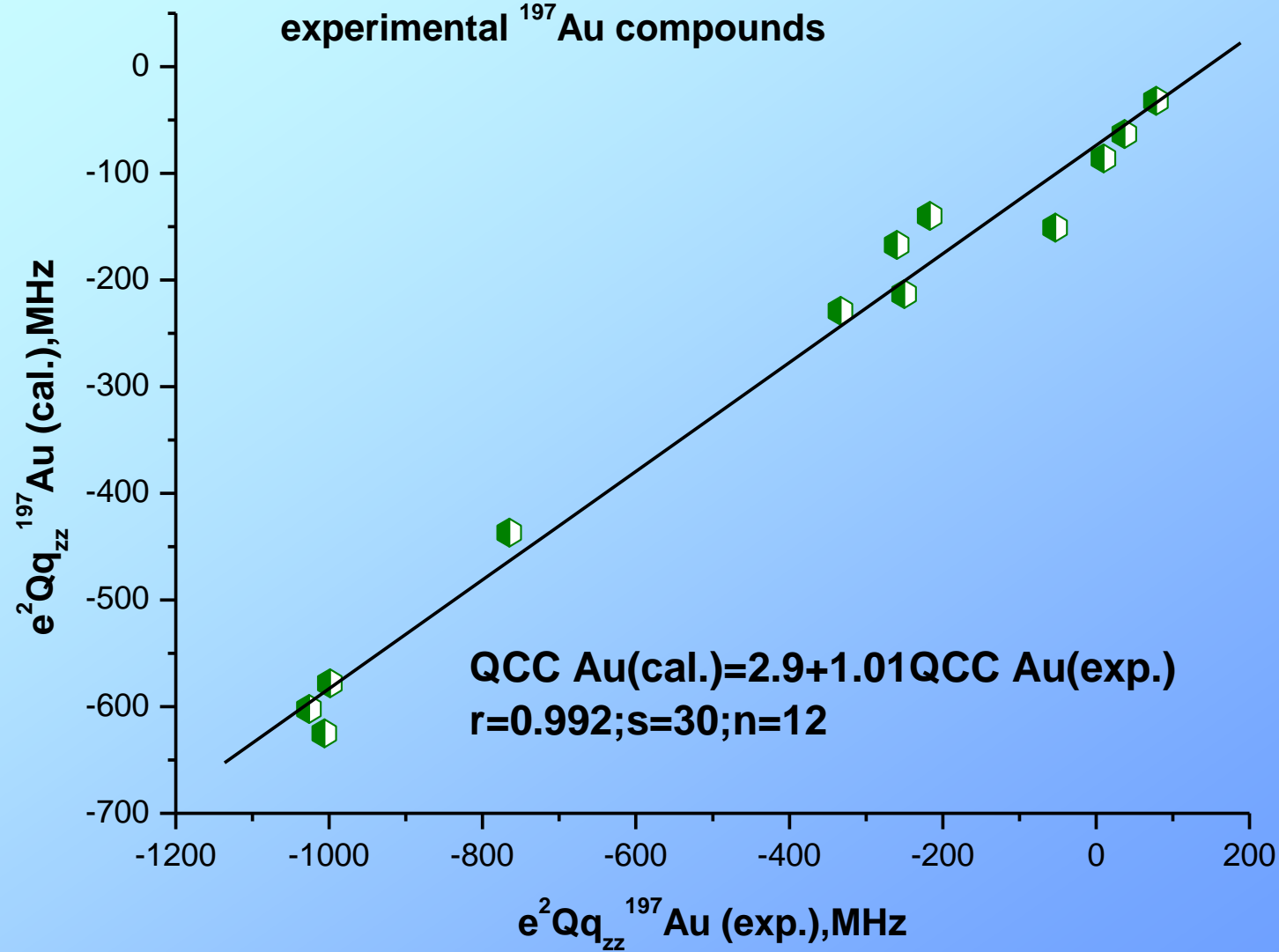
Calculated at B3LYP/dgdzvp versus
experimental ^{93}Nb compounds



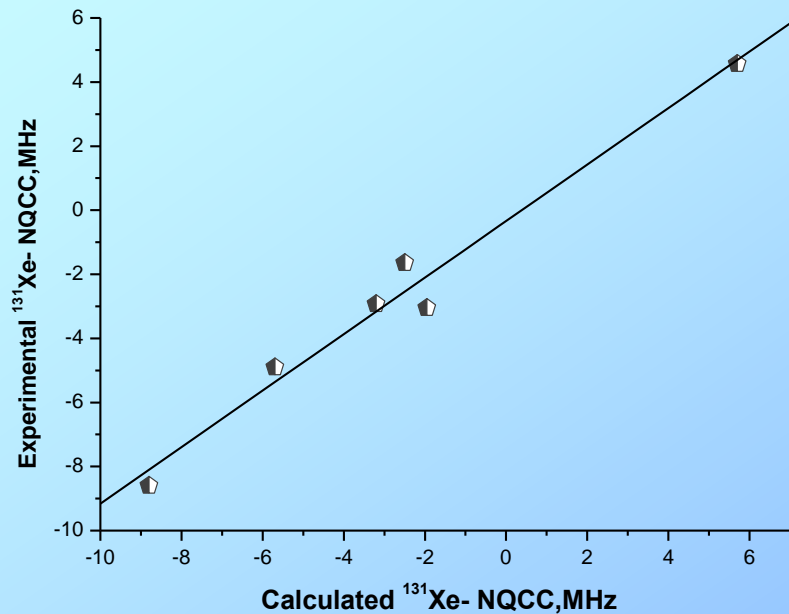
Calculated at BP86/TZ2P+(ZORA) versus
experimental ^{93}Nb and ^{181}Ta compounds



Calculated at BP86/TZ2P+(ZORA) versus
experimental ^{197}Au compounds



NQCC in Xe-B complexes



$$e^2Qq(\text{exp.}) = -0.3 + 0.9 e^2Qq(\text{cal.})$$

$$(r = 0.987; s = 0.8; n = 6)$$

Dependence between experimental and calculated at B3LYP/DGDZVP level NQCC values of Xe nuclei in Xe-B complexes

Energy decomposition analysis (kcal/mol)

| Complex | $\Delta E_{\text{prep.}}$ | ΔE_{Pauli} | $\Delta E_{\text{electr.}}$ | $\Delta E_{\text{orb.}}$ | $D_e^{\text{ADF}}/D_0^{\text{gauss}}$ |
|---|---------------------------|---------------------------|-----------------------------|--------------------------|---------------------------------------|
| $\text{HCN}\cdot\text{SO}_3$ | 0.86 | 22.44 | -13.25 | -10.57 | 0.5/4.2 |
| $\text{HCCCN}\cdot\text{SO}_3$ | 0.94 | 23.4 | -13.57 | -11.13 | 0.4/3.5 |
| $(\text{HCN})_2\cdot\text{SO}_3$ | 0.67 | 31.42 | -18.79 | -16.08 | 2.8/7.0 |
| $\text{CH}_3\text{CN}\cdot\text{SO}_3$ | 1.72 | 35.15 | -21.05 | -18.22 | 2.4/7.8 |
| $\text{H}_3\text{N}\cdot\text{SO}_3$ | 6.51 | 125.26 | -76.37 | -71.53 | 16.1/18.4 |
| $\text{Py}\cdot\text{SO}_3$ | 9.98 | 153.33 | -90.53 | -89.73 | 17.0/23.1 |
| $(\text{CH}_3)_3\text{N}\cdot\text{SO}_3$ | 11.55 | 162.94 | -97.37 | -97.49 | 20.4/28.7 |

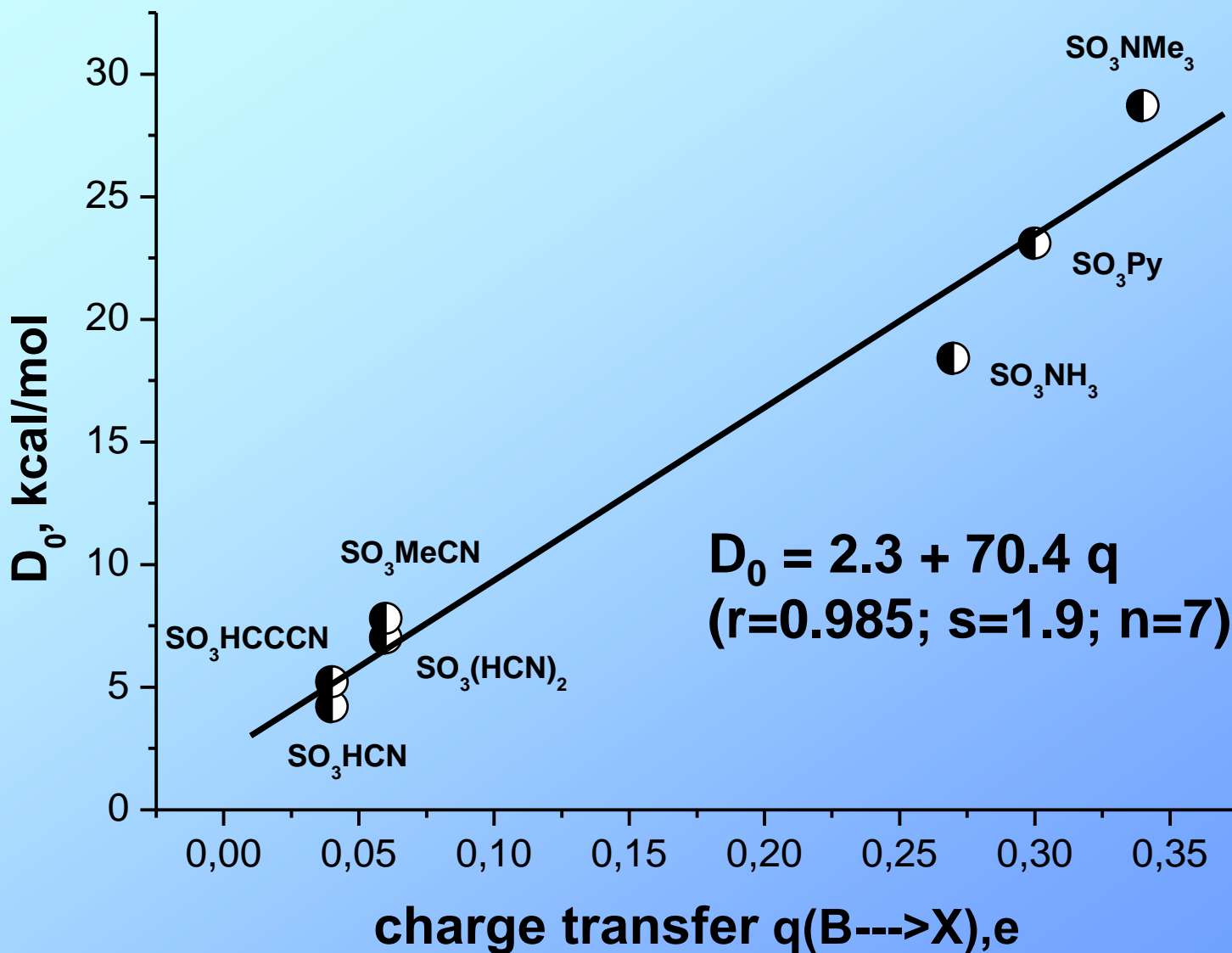
- The $\Delta E_{\text{elstat.}}$ term in all complexes is close to the ΔE_{orb} term, although for weakly bound complexes the electrostatic interactions tend to be slightly larger than the covalent ones.
- The calculated values of the bonding energy in these complexes using the ADF package differ from those obtained at the B3PW91/6-311+G(df,pd) level. However, the variation from one system to another is similar:
- $D_e^{\text{ADF}} = -4.5 + 0.83 D_0^{6-311+G(df,pd)}$
($r=0.990$; $s=1.4$; $n=7$)

NBO analysis for SO₃ complexes

| Complex | Orbital | Occupied | Hybridization of S atom (%) | | | E _{ij} ⁽²⁾ (kcal/mol) | Interaction between bonding and anti-bonding orbitals |
|---|---------|----------|-----------------------------|------|------|--|---|
| | | | s | p | d | | |
| HCN·SO ₃ | LP(N) | 1.942 | 33.1 | 65.3 | 1.6 | 8.1 | LP(N)→BD*(S-O) |
| HCCCN·SO ₃ | LP(N) | 1.937 | 32.1 | 66.3 | 1.6 | 8.6 | LP(N)→BD*(S-O) |
| (HCN) ₂ ·SO ₃ | LP(N) | 1.920 | 31.2 | 67.0 | 1.8 | 13.1 | LP(N)→BD*(S-O) |
| CH ₃ CN·SO ₃ | LP(N) | 1.906 | 33.0 | 65.3 | 1.7 | 15.4 | LP(N)→BD*(S-O) |
| H ₃ N·SO ₃ | BD(N-S) | 1.888 | 17.7 | 43.5 | 38.8 | 93.1 | BD(N-S)→BD*(S-O) |
| PySO ₃ | BD(N-S) | 1.851 | 16.4 | 46.8 | 36.8 | 105.4 | BD(N-S)→BD*(S-O) |
| (CH ₃) ₃ N·SO ₃ | LP(O) | 1.751 | 12.5 | 85.1 | 2.4 | 142.8 | LP(O)→BD*(N-S) |

SO₃...B complexes

- NBO second-order interaction energies of nπ-complexes shown that the **LP(N) → π*_{SO3}** (LP=lone electron pair) donor-acceptor interaction is the source of such intermolecular charge transfer.
- $D_e^{\text{ADF}}/\text{kcal/mol} = 5.4 + 0.2 \Delta E_{ij}^{(2)}/\text{kcal/mol}$
(r=0.998; s=0.7; n=7)



Bonding energy versus charge transfer (NAO) for SO_3 complexes

Energy decomposition and NBO analysis (kcal/mol)

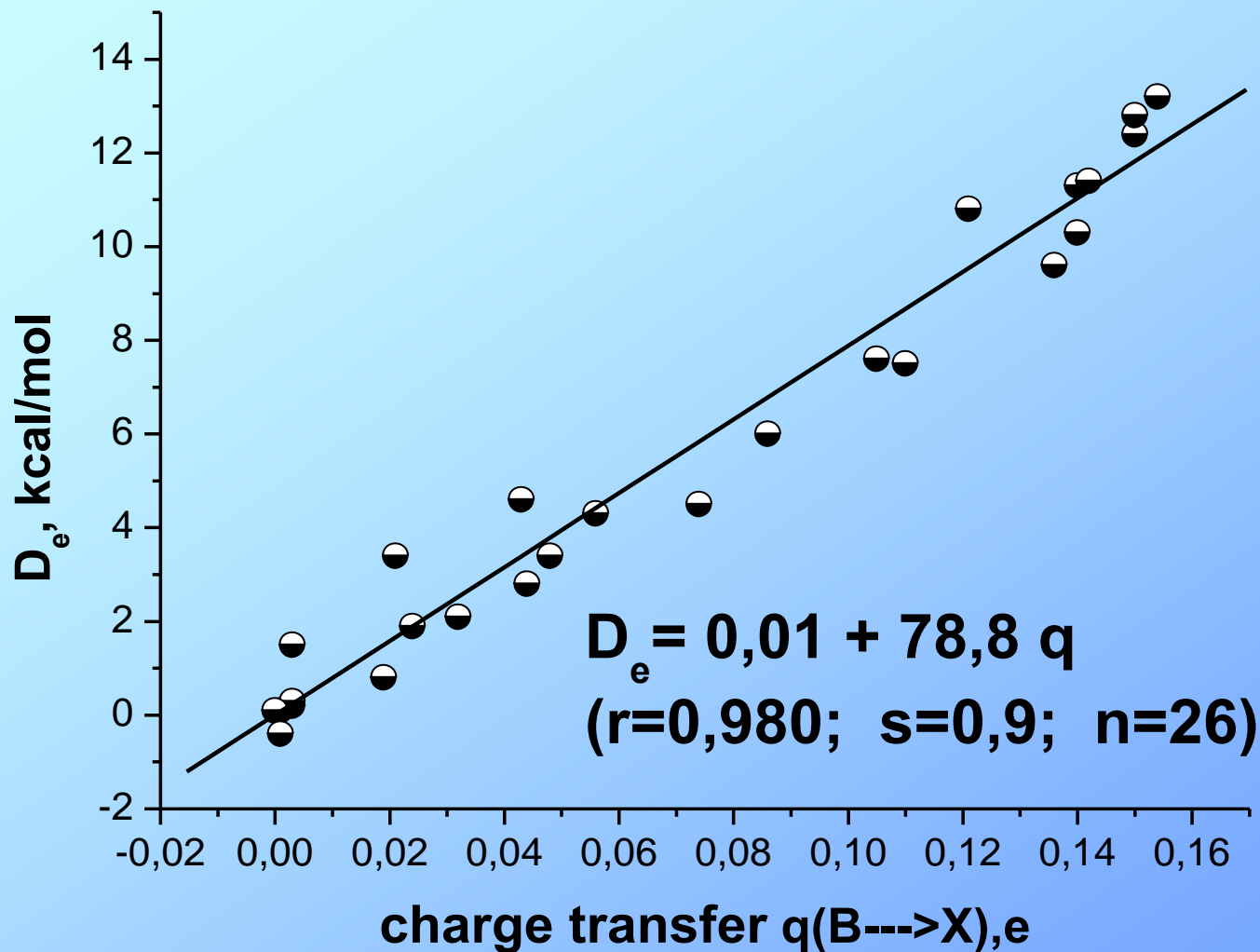
| Complex | $\Delta E_{\text{prep.}}$ | ΔE_{Pauli} | $\Delta E_{\text{electr.}}$ | $\Delta E_{\text{orb.}}$ | D_e | $R_{\text{B-Y}}^{\text{cal.}}$ | $E_{ij}^{(2)}$ |
|---|---------------------------|---------------------------|-----------------------------|--------------------------|-------|--------------------------------|----------------|
| IClAr | 0.0 | 0.1 | 0.0 | -0.2 | 0.1 | 4.433 | 1.0 |
| IClCO | 0.7 | 67.8 | -34.3 | -36.5 | 2.3 | 2.413 | 13.5 |
| I ₂ Py | 0.4 | 48.6 | -32.1 | -25.6 | 8.7 | 2.564 | 36.4 |
| IBrPy | 1.7 | 44.9 | -31.3 | -24.9 | 9.6 | 2.576 | 45.2 |
| I ₂ N(CH ₃) ₃ | 1.8 | 50.0 | -33.2 | -28.4 | 9.7 | 2.601 | 40.2 |
| IClNH ₃ | 1.3 | 45.2 | -32.6 | -24.1 | 10.1 | 2.576 | 53.5 |
| IClPy | 1.9 | 59.4 | -40.9 | -31.5 | 11.1 | 2.475 | 56.8 |

Bonding energy by ADF is close to outcomes at the BHandHLYP/aug-cc-pVTZ

$$D_e^{\text{ADF}} = -0.1 + 0.9 D_e^{\text{aug-cc-pVTZ}} \quad (r=0.995; s=0.5; n=7)$$

ICI...B complexes

- The $\Delta E_{\text{elstat.}}$ term in all complexes is larger than the ΔE_{orb} term. This suggests that the Y-B bonding in these complexes is more electrostatic than covalent.
- NBO second-order interaction energies of $n\sigma$ -complexes shown that the **LP(B)→ σ^* XY** (LP=lone electron pair, B=N, C, Ar coordinated atom) donor-acceptor interaction is the source of such intermolecular charge transfer.
- $D_e^{\text{ADF}}/\text{kcal/mol} = 0.2 + 0.2 \Delta E_{ij}^{(2)}/\text{kcal/mol}$
($r=0.978$; $s=1.0$; $n=7$)



Dependence between D_e and electron transfer (NAO) in
 XY...B complexes

- The calculated bonding energies for both complexes are strongly correlated with the extent of electron transfer from base to the acceptor from the natural atomic charges.
- These correlations contrasts with the different situation found for the main group and transition metal complexes.
- Apparently, related to this is the observation that, according to our calculations, the electronic charge changes are significant only on the two atoms immediately involved in the intermolecular bond, while in metal chloride complexes such changes are appreciable on all atoms.

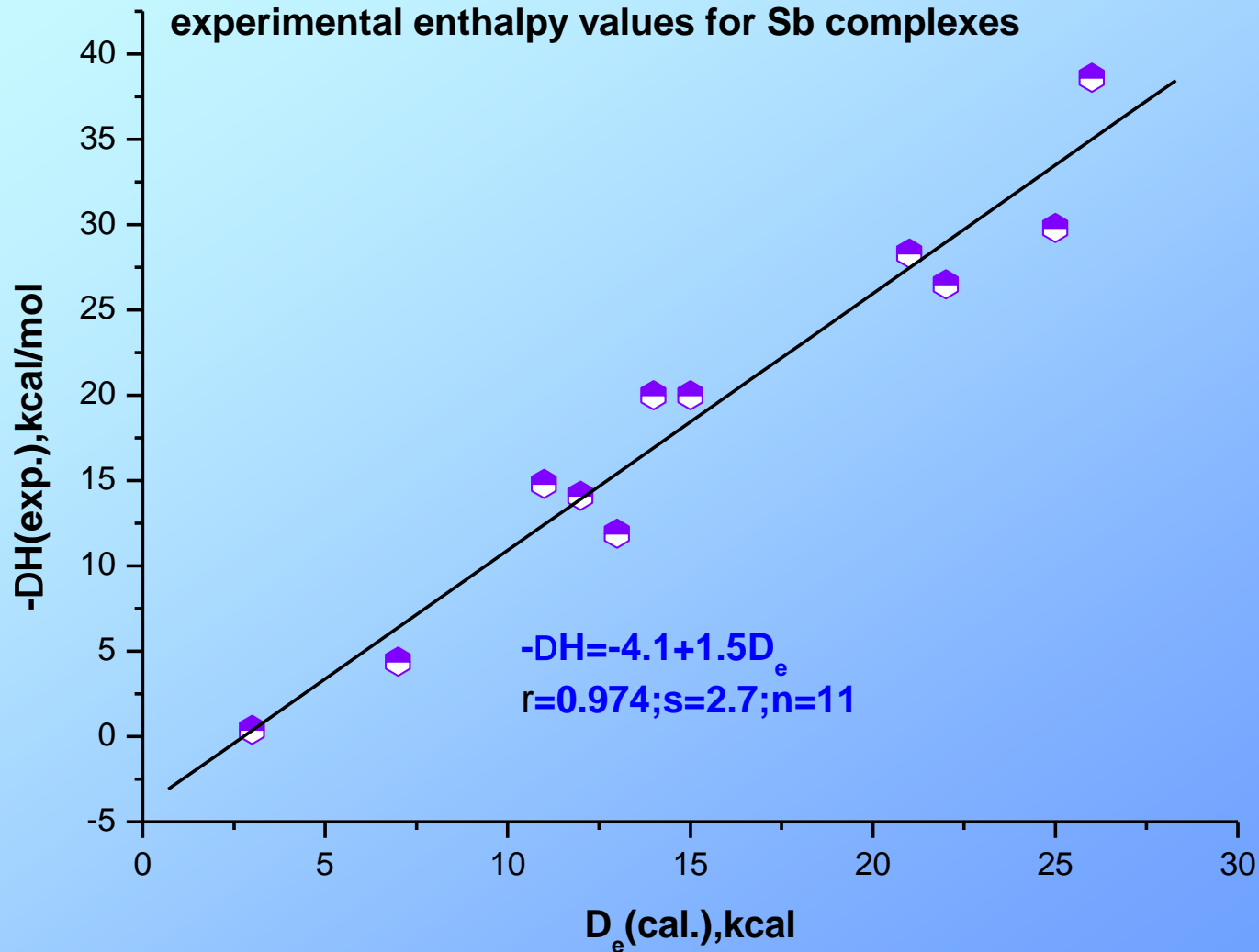
Energy decomposition analysis, kcal/mol

| Complex | $\Delta E_{\text{prep.}}$ | ΔE_{Pauli} | $\Delta E_{\text{electr.}}$ | $\Delta E_{\text{orb.}}$ | D_e^{ADF} | D_e^{Gauss} | $\Delta E_{ij}^{(2)}$ |
|---|---------------------------|---------------------------|-----------------------------|--------------------------|--------------------|----------------------|-----------------------|
| OC-CuCl | 0.0 | 96.0 | -80.5 | -56.7 | 41.2 | 36.0 | 110 |
| OC-AgCl | -0.1 | 99.7 | -77.6 | -44.5 | 22.5 | 24.6 | 103 |
| OC-AuCl | -0.2 | 176.9 | -139.4 | -86.0 | 48.7 | 46.4 | 256 |
| Py-CuCl | 0.7 | 77.4 | -80.5 | -33.9 | 36.3 | 38.3 | 66 |
| Py-AgCl | 0.4 | 68.7 | -66.2 | -24.7 | 21.8 | 27.5 | 56 |
| Py-AuCl | 0.7 | 111.1 | -102.6 | -46.5 | 37.3 | 40.7 | 119 |
| (CH ₃) ₃ PO-CuCl | 1.7 | 60.3 | -63.6 | -28.6 | 30.2 | 36.2 | 79 |
| (CH ₃) ₃ PO-AgCl | 1.0 | 49.6 | -49.5 | -20.2 | 19.1 | 26.0 | 23 |
| (CH ₃) ₃ PO-AuCl | 1.9 | 72.8 | -67.4 | -34.6 | 27.3 | 33.6 | 58 |

Decomposition of the formation energy of the complexes by ADF, kcal/mol

| Complex | ΔE_{prep} | ΔE_{Pauli} | ΔE_{elstat} | ΔE_{orbtot} | ΔE_{int} | D_e/D_0^{Gauss} |
|------------------------------|--------------------------|---------------------------|----------------------------|----------------------------|-------------------------|--------------------------|
| $\text{SbCl}_5\text{SMe}_2$ | 7.9 | 83.2 | -54.3 | -48.9 | -20.0 | 12.1/ 13.5 |
| $\text{SbCl}_5\text{OPMe}_3$ | 11.1 | 128.0 | -94.0 | -65.7 | -31.7 | 20.6/ 25.4 |
| $\text{SbCl}_5\text{NCCH}_3$ | 4.8 | 72.4 | -49.1 | -34.1 | -10.8 | 6.0/ 9.9 |
| $\text{SbCl}_5\text{OPCl}_3$ | 4.1 | 46.2 | -30.7 | -20.9 | -5.4 | 1.3/ 5.3 |
| $\text{SbCl}_5\text{OSCl}_2$ | 2.2 | 15.7 | -10.0 | -6.2 | -0.5 | 1.7/ 0.7 |
| SbCl_5Py | 9.4 | 109.3 | -79.6 | -56.6 | -26.9 | 17.5/ 20.0 |

Calculated bonding energy at PB86/TZ2P+(ZORA) versus experimental enthalpy values for Sb complexes



MCl_n...B complexes

- The $\Delta E_{\text{elstat.}}$ term in all complexes is larger than the ΔE_{orb} term. This suggests that the M-B bonding in these complexes is more electrostatic than covalent.
- NBO second-order interaction energies of nv-complexes shown that the **LP(B)→σ*MCl** (LP=lone electron pair, B=N, O, S, P coordinated atom) donor-acceptor interaction is the source of such intermolecular charge transfer.
- $D_e^{\text{ADF}}/\text{kcal/mol} = 19.6 + 0.12 \Delta E_{ij}^{(2)}/\text{kcal/mol}$
($r=0.80$; $s=6.0$; $n=12$)

Conclusions

- The calculations clearly show that the calculated by Gaussian and ADF bond lengths, IR-spectra correlate with the experimental values.
- The halogen, nitrogen and metal NQCC's obtained by both calculations substantially corresponded to the data of microwave and NQR-spectroscopy.
- The calculated by both methods stabilization energies are close to the experimental values.
- We have found the correlations between charge donation and the calculated bonding energies of the halogen and SO_3 complexes contrasts with the different situation found for the main group and transition metal complexes.
- From EPA scheme follows that for all complexes the electrostatic bonding is a little bit more than covalent bonding.