

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/243955839>

# Using density functional theory for analysis of quadrupole coupling constants and mössbauer isomer shifts of halogen compounds

ARTICLE *in* JOURNAL OF STRUCTURAL CHEMISTRY · JULY 2000

Impact Factor: 0.51 · DOI: 10.1007/BF02683935

CITATIONS

2

READS

8

3 AUTHORS, INCLUDING:



Oleg Kh Poleshchuk

Томский государственный педагогический университет

102 PUBLICATIONS 276 CITATIONS

SEE PROFILE



Jolanta Natalia Latosińska

Adam Mickiewicz University

90 PUBLICATIONS 441 CITATIONS

SEE PROFILE

# USING DENSITY FUNCTIONAL THEORY FOR ANALYSIS OF QUADRUPOLE COUPLING CONSTANTS AND MÖSSBAUER ISOMER SHIFTS OF ANTIMONY COMPOUNDS

O. Kh. Poleshchuk, J. N. Latosinska, and V. G. Yakimov

UDC 541.6

In our previous communication, density functional theory was used for QCC and isomer shift calculations for halogen compounds and gave reliable results. Here we also employ the B3LYP/3-21G\* method, which makes it possible to take into account all electrons of atoms constituting the molecules. QCC were estimated from the diagonal components of the electric field gradient tensor with a specially devised program. The group of compounds chosen for investigation included  $\text{Sb}^{\text{III}}$  and  $\text{Sb}^{\text{V}}$  compounds and complexes for which exact QCC values and Mössbauer isomer shifts are available. The calculations were carried out with full geometry optimization with GAUSSIAN-98 [1] on a personal computer.

Table 1 lists the most important calculated and experimental [2-5] geometrical parameters of the  $\text{SbCl}_5$  and  $\text{SbCl}_3$  complexes. As for halogen compounds [6], the B3LYP/3-21G\* calculated bond lengths are exaggerated, but there is good

**TABLE 1.** Principal Geometrical Parameters (Å and deg), QCC Values, and Nuclear Quadrupole Resonance Frequencies for Some Antimony Complexes

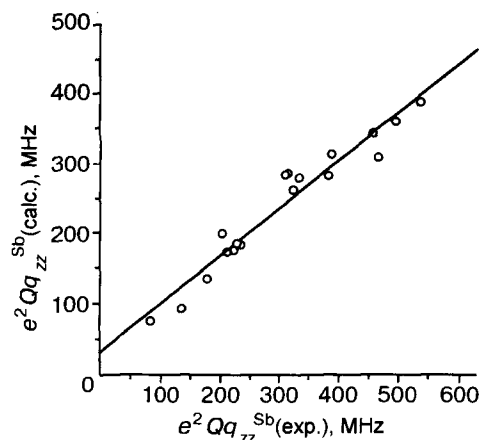
Geometrical and NQR parameters	Experimental values	HONDO MP2/6-311G** [7]	GAUSSIAN B3LYP/3-21G*
1	2	3	4
<b>Dimer <math>\text{Sb}_2\text{Cl}_{10}</math></b>			
$R_{\text{Sb-Cl}_{\text{eq}}}$	2.346*	2.31	2.355
$R_{\text{Sb-Cl}_{\text{ax}}}$	2.388*	2.322	2.365
$R_{\text{Sb-Cl}_{\text{br}}}$	2.620*	2.642	2.630
$\angle \text{Cl}_{\text{br}}\text{SbCl}_{\text{br}}$	98.8*	102.6	101.4
$\nu_{\text{Cl}}^{\text{eq}}$ , MHz	27.76	28.78( $\eta = 0.092$ )	26.36( $\eta = 0.10$ )
$\nu_{\text{Cl}}^{\text{ax}}$ , MHz	30.18	31.78( $\eta = 0.002$ )	28.10( $\eta = 0.018$ )
$\nu_{\text{Cl}}^{\text{br}}$ , MHz	18.76	20.36( $\eta = 0.67$ )	20.18( $\eta = 0.63$ )
$e^2Qq_{\text{zz}}^{\text{Sb}}$ , MHz	180( $\eta = 0.79$ )	2.4( $\eta = 0.60$ )	135.0( $\eta = 0.76$ )
<b>Monomer <math>\text{SbCl}_5</math></b>			
$R_{\text{Sb-Cl}_{\text{eq}}}$	2.277	2.292	2.357
$R_{\text{Sb-Cl}_{\text{ax}}}$	2.338	2.350	2.382
$\nu_{\text{Cl}}^{\text{eq}}$ , MHz	30.18	30.50( $\eta = 0.23$ )	27.05( $\eta = 0.24$ )
$\nu_{\text{Cl}}^{\text{ax}}$ , MHz	27.85	27.60( $\eta = 0$ )	25.74( $\eta = 0$ )
$e^2Qq_{\text{zz}}^{\text{Sb}}$ , MHz	84.54( $\eta = 0.01$ )	1.9( $\eta = 0$ )	74.90( $\eta = 0$ )
<b>Complex <math>\text{SbCl}_5 \cdot \text{OPCl}_3</math></b>			
$R_{\text{Sb-Cl}_{\text{eq}}}$	2.32; 2.33; 2.35		2.36; 2.39

Tomsk State Pedagogical University. Institute of Physics, Poznan University, Poland. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 41, No. 4, pp. 853-858, July-August, 2000. Original article submitted May 12, 1999.

TABLE 1 (Continued)

1	2	3	4
$R_{\text{Sb-Cl}_{\text{ax}}}$	2.33		2.38; 2.40
$R_{\text{O-P}}$	1.47		1.50
$R_{\text{P-Cl}}$	1.95		1.99
$\angle \text{SbOP}$	145		152
$R_{\text{Sb-O}}$	2.17		2.21
$\nu_{\text{Cl}}^{\text{eq}}$ , MHz	24.399( $\eta = 0.113$ )		25.23( $\eta = 0.076$ )
	25.821( $\eta = 0.025$ )		
	26.119( $\eta = 0.047$ )		
$\nu_{\text{Cl}}^{\text{ax}}$ , MHz	27.314( $\eta = 0.049$ )		25.76( $\eta = 0.066$ )
$\nu_{\text{Cl}}(\text{PCl}_3)$ , MHz	30.565( $\eta = 0.026$ )		28.82( $\eta = 0.011$ )
	30.632( $\eta = 0.029$ )		28.86( $\eta = 0.010$ )
$e^2Qq_{\text{Sb}}^{\text{Sb}}$ , MHz	204.4( $\eta = 0.30$ )		199.3( $\eta = 0.05$ )
Complex $\text{SbCl}_5 \cdot \text{NCCl}$			
$R_{\text{Sb-Cl}_{\text{eq}}}$	2.36**		2.39
$R_{\text{Sb-Cl}_{\text{ax}}}$	2.35**		2.36
$\angle \text{SbON}$	84.9**		83.4
$R_{\text{Sb-N}}$	2.23**		2.34
$\nu_{\text{Cl}}^{\text{eq}}$ , MHz	26.392		25.42( $\eta = 0.091$ )
	26.895		
$\nu_{\text{Cl}}^{\text{ax}}$ , MHz	25.425		25.37( $\eta = 0.0008$ )
$\nu_{\text{Cl}}(\text{NCl})$ , MHz	42.005		39.84( $\eta = 0$ )
$e^2Qq_{\text{N}}^{\text{N}}$ , MHz	—		1.25( $\eta = 0$ )
$e^2Qq_{\text{Sb}}^{\text{Sb}}$ , MHz	236.4( $\eta = 0$ )		183.8( $\eta = 0.001$ )
Complex $\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{NH}_2$			
$R_{\text{Sb-Cl}}$	2.323		2.429
	2.335		2.435
	2.516		2.444
$\angle \text{ClSbCl}$	96.1		92.9
$\angle \text{ClSbN}$	83.2		78.1
$R_{\text{Sb-N}}$	2.525		2.562
$\nu_{\text{Cl}}^{\text{eq}}$ , MHz	19.36		19.40( $\eta = 0.087$ )
	20.39		19.54( $\eta = 0.1$ )
$\nu_{\text{Cl}}^{\text{ax}}$ , MHz	13.95		16.74( $\eta = 0.07$ )
$e^2Qq_{\text{N}}^{\text{N}}$ , MHz	—		3.30( $\eta = 0.21$ )
$e^2Qq_{\text{Sb}}^{\text{Sb}}$ , MHz	226.2( $\eta = 0.03$ )		261.6( $\eta = 0.1$ )
Complex $\text{SbCl}_3 \cdot \text{C}_6\text{H}_6^{***}$			
$R_{\text{Sb-Cl}}$	2.347		2.413
	2.348		
	2.367		
$\angle \text{ClSbCl}$	91.6; 94.4; 94.7		96.4; 96.8; 97.0
$R_{\text{Sb-ring}}$	3.30		2.45
$\nu_{\text{Cl}}$ , MHz	18.87		18.70( $\eta = 0.05$ )
	20.33		19.38( $\eta = 0.05$ )
$e^2Qq_{\text{Sb}}^{\text{Sb}}$ , MHz	390.2( $\eta = 0.1$ )		313.0( $\eta = 0.1$ )

\*Geometrical parameters for  $\text{Sb}_2\text{Cl}_6\text{Ph}_4$ .\*\*Geometrical parameters for  $\text{SbCl}_5 \cdot \text{NCCH}_3$ .\*\*\*Geometrical parameters for  $2\text{SbCl}_3 \cdot \text{C}_6\text{H}_6$ .



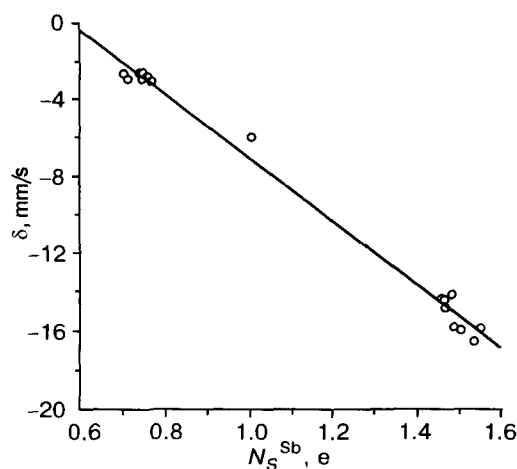
**Fig. 1.** Relation between the calculated and experimental QCC values of antimony atoms.

qualitative agreement between the experimental and calculated values of bond angles. A correlation dependence of bond length can be constructed:

$$R_{\text{Sb-X}}^{\text{calc}} = 0.093 + 0.981 R_{\text{Sb-X}}^{\text{exp}} \quad (r = 0.996, s = 0.02, n = 15). \quad (1)$$

As in the case of halogen-halogen bonds [6], the coefficient at  $R_{\text{Sb-X}}^{\text{exp}}$  is close to unity, and the confidence limit is narrow. This indicates that the calculation results are quite reliable, although the compounds contain antimony-ligand coordination bonds. The presence of the latter generally gives rise to problems since coordination bond lengths are usually considerably overestimated in the full optimization procedure, as indeed observed in our *ab initio* calculations of hydrogen sulfide complexes of  $\text{SbCl}_5$ ,  $\text{SnCl}_4$ , and  $\text{TiCl}_4$  [7].

For the monomer and dimer forms of  $\text{SbCl}_5$ , Table 1 gives the results of calculations in the extended basis 6-311G\*\* [7] and in the 3-21G\* basis. The geometrical parameters of the dimer agree well with the experimental values for  $\text{Sb}_2\text{Cl}_6\text{Ph}_4$  [8], where, according to X-ray data, three sorts of chlorine atom are present and the axial bonds are longer than equatorial. This supports our frequency assignment [9] for the axial and equatorial chlorine atoms whose ratio changes from monomer to dimer (Table 1).



**Fig. 2.** Relation between the experimental isomer shift and the occupation of the 5s orbital of the antimony atom.

**TABLE 2.** Variation of Effective Charges on Atoms (*e*) during Complexation

Complex	$\Delta q_{\text{Sb}}$	$\Delta q_{\text{Cl}}$	$\Delta q_{\text{O,N,S}}$	$\Delta q_{\text{P}}$	$\Delta q_{\text{L}}$
SbCl <sub>5</sub> ·OPCl <sub>3</sub>	-0.183*	0.437	0.095	-0.079	-0.254
SbCl <sub>5</sub> ·SPCl <sub>3</sub>	-0.084	0.324	0.015	-0.018	-0.240
SbCl <sub>5</sub> ·NCCl	-0.161	0.439	-0.042	—	-0.278
SbCl <sub>3</sub> ·NH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	-0.048	0.258	-0.048	—	-0.210
SbCl <sub>3</sub> ·C <sub>6</sub> H <sub>6</sub>	-0.036	0.120	—	—	-0.084

\*Minus denotes a decrease in electron density during complexation.

Using the calculated and experimental [10, 11] QCC of antimony atoms led to the following correlation dependence (Fig. 1):

$$e^2 Qq_{zz}^{\text{Sb}}(\text{calc}) = 31.9 + 0.68e^2 Qq_{zz}^{\text{Sb}}(\text{exp}) \quad (r = 0.967, s = 25, n = 15). \quad (2)$$

The correlation coefficient is certainly not very high, but the confidence limit is, on the average, not more than 10% of the experimental QCC values. SbI<sub>3</sub>, SbI<sub>4</sub><sup>-</sup>, SbCl<sub>4</sub><sup>-</sup>, and SbMe<sub>3</sub>Cl<sub>2</sub> disobey relation (2) since they probably involve rather strong solid state coordination interactions. Thus in antimony iodide [10], intermolecular interactions equal intramolecular ones in magnitude; this naturally affects QCC of antimony.

For Mössbauer shifts, one can consider several types of dependence on the occupancies of the 5*s*- and 5*p*-orbitals of antimony. The one- and many-parameter dependences are given in [12-14]. The existence of these dependences is supported by our calculations:

$$\delta = 9.6 - 16.6N_s \quad (r = 0.995, s = 0.62, n = 14), \quad (3)$$

$$\delta = -16.6N_s + 0.16N_p + 9.3 \quad (r = 0.991, s = 0.64, n = 14), \quad (4)$$

$$\delta = 6.12N_s - 0.08N_p - 10.0N_s^2 - 0.11N_s N_p - 1.63 \quad (r = 0.995, s = 0.51, n = 14). \quad (5)$$

The relationship between the isomer shift and the occupancy of the Sb5*s* atomic orbital is shown in Fig. 2. The slope is characteristic for antimony compounds and is explained by the negative sign of  $\Delta R/R$ . The two- as well as four-parameter relation adequately approximates the variation of the isomer shift in the series of compounds, but the latter relation is preferable because of the higher correlation coefficient and narrower confidence limit. The coefficients at the corresponding occupancies of the atomic orbitals of antimony define both the direct influence of the 5*s* electrons and the screening effects on electron density at the site of the antimony nucleus. A correlation of this kind was found previously by simple semiempirical calculations for tin complexes [15]. Noteworthy, as in the case of tin complexes, the isomer shift is mainly due to the occupation of the 5*s*-orbital, whereas the screening effects are of secondary importance. Since analogous results were obtained for iodine compounds [6], one can admit that this situation is typical of all Mössbauer nontransition atoms.

It is of interest to consider electron density distribution on atoms in antimony halide complexes. Table 2 gives variations of electron density due to acceptor coordination by ligands as calculated from Mulliken populations of atomic orbitals. The most important conclusion is that the positive charge on the antimony atom increases due to complexation, as confirmed by X-ray photoelectron and fluorescence spectra [11, 16]. This is especially important since our previous calculation with HONDO [7] led to a decreased positive charge on antimony and tin atoms. Thus electron density increases on chlorine atoms but decreases on the central acceptor atom. Analogous changes are typically observed for the weaker antimony trichloride complexes. The value of the transferred electron density is quite reasonable and agrees with Gutmann's donor numbers [17]. The small value of  $\Delta q_{\text{L}}$  for the benzene complex, where the ring  $\pi$ -electrons interact with the antimony atom, is quite reasonable.

From the viewpoint of ligands, the following picture is observed: while the coordinating oxygen and sulfur atoms accept electron density from other atoms of the ligand, the nitrogen atom donates it to the acceptor. This is not surprising

if we take into account electron affinities (in kJ/mole) of O (–141), S (–200), and N (+7) [18]. Indeed, this reasoning is merely qualitative but one can admit that the above-mentioned situation really takes place. The positive charge on the phosphorus atom increases due to complexation in agreement with  $\Delta PK_{\alpha}$  in X-ray fluorescent spectra; a comparison of  $SbCl_5$  complexes with  $OPCl_3$  (–0.274) with those with  $SPCl_3$  (–0.078) gives nearly quantitative coincidence [11].

Thus using the density functional method leads to good agreement between the calculated QCC values and isomer shifts in antimony compounds. The observed correlation dependences between the isomer shifts and the atomic orbital populations of antimony make it possible to evaluate the contributions of the 5s- and 5p-orbitals to  $\delta$ . The electron density redistribution on atoms due to complexation agrees with the results of the analysis of X-ray photoelectron and fluorescent spectra.

We are grateful to V. P. Elin for recording  $PK_{\alpha}$  X-ray fluorescent spectra of  $SbCl_5$  complexes with  $OPCl_3$  and  $SPCl_3$ . This work was supported by the Ministry of Education, Russian Federation.

## REFERENCES

1. *GAUSSIAN-98W. User's Reference*, E. Fritsch and M. J. Fritsch (eds.), Gaussian Inc., Pittsburgh (1998).
2. C. I. Branden and I. Lundqvist, *Acta Chem. Scand.*, **17**, No. 3, 363-361 (1963).
3. A. A. Ischenko, V. P. Spiridonov, and T. G. Strand, *ibid.*, **A42**, Nos. 3, 5, 651-673 (1988).
4. V. I. Nefedov and M. M. Hoffmann, *Itogi Nauki Tekh.*, No. 6 (1978).
5. Yu. A. Buslaev and R. L. Davidovich, *Koordinats. Khim.*, **15**, No. 8, 1444-1465 (1989).
6. O. Kh. Poleshchuk, J. N. Latosinska, and V. G. Yakimov, *Zh. Strukt. Khim.*, **41**, No. 4, 855-859 (2000).
7. O. Kh. Poleshchuk, G. N. Dolenko, Ya. Koput, and J. Latosinska, *Koordinats. Khim.*, **23**, No. 9, 643-650 (1997).
8. J. Bordner, G. O. Doak, and J. R. Peters, *J. Am. Chem. Soc.*, **96**, No. 13, 6763-6770 (1974).
9. O. Kh. Poleshchuk, Ya. Koput, and J. Latosinska, *Zh. Strukt. Khim.*, **37**, No. 3, 585-588 (1996).
10. G. K. Semin, T. A. Babushkina, and G. G. Yakobson, *Chemical Applications of Nuclear Quadrupole Resonance* [in Russian], Khimiya, Leningrad (1972).
11. O. Kh. Poleshchuk, "Electronic structure investigation of nontransition element complexes with organic ligands," Physical and Mathematical Sciences Candidate's Dissertation, Irkutsk (1997).
12. R. V. Parish, *Prog. Inorg. Chem.*, **15**, No. 1, 101-132 (1972).
13. R. V. Parish, *Coord. Chem. Rev.*, **42**, No. 1, 1-29 (1982).
14. L. H. Bowen and G. G. Long, *Inorg. Chem.*, **15**, No. 5, 1039-1044 (1976).
15. V. A. Varnek, O. Kh. Poleshchuk, L. N. Mazalov, and D. M. Kizhner, *Zh. Strukt. Khim.*, **23**, No. 1, 98-101 (1982).
16. L. N. Mazalov and V. D. Yumatov, *Electronic Structure of Extractants* [in Russian], Nauka, Novosibirsk (1984).
17. V. Gutmann, *Coord. Chem. Rev.*, **15**, No. 1, 207-237 (1975).
18. J. E. Huheey, *Inorganic Chemistry. Principles of Structure and Reactivity*, Harper and Row, New York (1983).