Quadrupole Coupling Constants and Mössbauer Isomeric Shifts in Antimony Compounds within Gaussian 98

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Z. Naturforsch. **55 a,** 276–280 (2000); received August 23, 1999

Presented at the XVth International Symposium on Nuclear Quadrupole Interactions, Leipzig, Germany, July 25 - 30, 1999.

The electron density and quadrupole coupling constants of molecules containing Sb are analysed. The NQCC for antimony, calculated using the extended basis 6-311G** are much lower than the experimental data, while the use of the small 3-21G* basis led to NQCC closer to the experimental ones.

Key words: DFT; QCC; Isomeric Mössbauer Shifts; Antimony Compounds.

Introduction

Compounds of non-transition elements containing tin and antimony were studied by nuclear quadrupole resonance spectroscopy and Mössbauer effect [1 - 5]. The parametres like quadrupole splitting or quadrupole coupling constant (QCC) as well as Mössbauer isomeric shifts on nuclei ^{121}Sb and ^{119}Sn (δ) were determined. The studies of the electronic density distribution in a molecule and environment of the central atom, i. e. non-transition element, were performed mainly on the basis of semiempirical calculations. It is well known that such methods cannot be applied for a detailed analysis of bonding parameters or interpretation of the electronic structure of molecules. The correlations between the experimental and calculated Mössbauer isomeric shifts or QCC could also be significantly improved by the application of non-empirical methods. It should be pointed out that these methods have been widely used for large molecular systems. The semiempirical methods of quantum chemistry do not give comprehensive information concerning electronic structure of compounds of non-transition elements, for example those from group Kothekar [6] studied similar molecules by CNDO and obtained negative charges on central atoms (antimony and tin).

The Townes-Dailey approximation, in which various integrals are neglected and configuration interactions are taken into account to a different degree [7], is widely used for the estimation of QCC and Mössbauer isomeric shifts. Koster [8] suggests that, if we consider only one configuration for a ground state, it is equivalent to the assumption that each electron in an atom is in a field of the averaged central potential. The Coulomb repulsion between electrons is responsible for the mixing of various configurations of electrons in an atom. The magnitude of configuration interaction is especially important for heavy atoms, where the Coulomb repulsion between electrons is relatively larger than attraction to nuclear charge.

The main idea of the Townes-Dailey approximation [9] is that the main contribution to the electric field gradient comes from valence electrons of the atom considered. Therefore, we expected that the best QCC values (i. e. the closest to the experimental results) could be calculated using a nuclear core pseudopotential.

Non-empirical calculation performed by us for tin, antimony and iodine molecules, with the use of the extended 6-311G** basis set [10, 11] provided much lower QCC values than the experimental ones, whereas the NQR frequencies from chlorine atoms were well correlated with experimental values.

Computational Details

The calculations were performed within the Gaussian 98 [12] package at the B3LYP level of the theory

0932–0784 / 00 / 0100–0276 $ 06.00

Table 1. Geometrical and NQR parameters for some complexes containing antimony.

Geometr. and NQR param.	Experimental	Hondo [10] MP2/6-311G**	Gaussian B3LYP/3-21G*
Dimer Sb_2Cl_{10}:			
$R_{Sb-Cl\,eq}$ [Å]	2.346[a]	2.311	2.355
$R_{Sb-Cl\,ax}$ [Å]	2.388[a]	2.322	2.365
$R_{Sb-Cl\,br}$ [Å]	2.620[a]	2.642	2.630
$\angle Cl_{br}SbCl_{br}$ [°]	98.8[a]	102.6	101.4
ν_{Cl}^{eq} [MHz]	27.76	28.78 (η = 0.092)	26.36 (η = 0.10)
ν_{Cl}^{ax} [MHz]	30.18	31.78 (η = 0.002)	28.10 (η = 0.018)
ν_{Cl}^{br} [MHz]	18.76	20.36 (η = 0.67)	20.18 (η = 0.63)
$e^2Qq_{zz}^{Sb}$ [MHz]	180 (η = 0.79)	2.4 (η = 0.60)	135.0 (η = 0.76)
$SbCl_5$:			
$R_{Sb-Cl\,eq}$ [Å]	2.277	2.292	2.357
$R_{Sb-Cl\,ax}$ [Å]	2.338	2.350	2.382
ν_{Cl}^{eq} [MHz]	30.18	30.50 (η = 0.23)	27.05 (η = 0.24)
ν_{Cl}^{ax} [MHz]	27.85	27.60 (η = 0)	25.74 (η = 0)
$e^2Qq_{zz}^{Sb}$ [MHz]	84.54 (η = 0.01)	1.9 (η = 0)	74.90 (η = 0)
Complex $SbCl_5 \cdot OPCl_3$:			
$R_{Sb-Cl\,eq}$ [Å]	2.32, 2.33, 2.35	–	2.36, 2.39
$R_{Sb-Cl\,ax}$ [Å]	2.33	–	2.38, 2.40
R_{O-P} [Å]	1.47	–	1.50
R_{P-Cl} [Å]	1.95	–	1.99
$\angle SbOP$[°]	145	–	152
R_{Sb-O} [Å]	2.17	–	2.21
ν_{Cl}^{eq} [MHz]	24.399 (η = 0.113) 25.821 (η = 0.025) 26.119 (η = 0.047)	–	25.23 (η = 0.076)
ν_{Cl}^{ax} [MHz]	27.314 (η = 0.049)	–	25.76 (η = 0.066)
$\nu_{Cl}(PCl_3)$ [MHz]	30.565 (η = 0.026) 30.632 (η = 0.029)	–	28.82 (η = 0.011) 28.86 (η = 0.010)
$e^2Qq_{zz}^{Sb}$ [MHz]	204.4 (η = 0.30)	–	199.3 (η = 0.05)
Complex $SbCl_5 \cdot NCCl$:			
$R_{Sb-Cl\,eq}$ [Å]	2.36[b]	–	2.39
$R_{Sb-Cl\,ax}$ [Å]	2.35[b]	–	2.36
$\angle SbON$ [°]	84.9[b]	–	83.4
R_{Sb-N} [Å]	2.23[b]	–	2.34
ν_{Cl}^{eq} [MHz]	26.392, 26.895	–	25.42 (η = 0.091)
ν_{Cl}^{ax} [MHz]	25.425	–	25.37 (η = 0.0008)
$\nu_{Cl}(NCl)$ [MHz]	42.005	–	39.84 (η = 0)
$e^2Qq_{zz}^{N}$ [MHz]	–	–	1.25 (η = 0)
$e^2Qq_{zz}^{Sb}$ [MHz]	236.4 (η = 0)	–	183.8 (η = 0.001)
Complex $SbCl_3 \cdot C_6H_5NH_2$:			
R_{Sb-Cl} [Å]	2.323, 2.335, 2.516	–	2.429, 2.435, 2.444
$\angle ClSbCl$ [°]	96.1	–	92.9
$\angle ClSbN$ [°]	83.2	–	78.1
R_{Sb-N} [Å]	2.525	–	2.562
ν_{Cl}^{eq} [MHz]	19.36 20.39	–	19.40 (η = 0.087) 19.54 (η = 0.1)
ν_{Cl}^{ax} [MHz]	13.95	–	16.74 (η = 0.07)
ν_N [MHz]	–	–	3.30 (η = 0.21)
$e^2Qq_{zz}^{Sb}$ [MHz]	226.2 (η = 0.03)	–	261.6 (η = 0.1)
Complex $SbCl_3 \cdot C_6H_6$[c]:			
R_{Sb-Cl} [Å]	2.347, 2.348 2.367	–	2.413

using the 3-21G* basis set with full geometry-optimisation. Relativistic effects were not taken into account.

Table 1 (continued).

Geometr. and NQR param.	Experimental	Hondo [10] MP2/6-311G**	Gaussian B3LYP/3-21G*
$\angle ClSbCl$ [°]	91.6, 94.4, 94.7	–	96.4, 96.8, 97.0
$R_{Sb-ring}$ [Å]	3.30	–	2.45
ν_{Cl} [MHz]	18.87 20.33	–	18.70 (η = 0.05) 19.38 (η = 0.05)
$e^2Qq_{zz}^{Sb}$ [MHz]	390.2 (η = 0.1)	–	313.0 (η = 0.1)

[a] Experimental geometrical parameters were taken for $Sb_2Cl_6Ph_4$. [b] Experimental geometrical parameters were taken for $SbCl_5 \cdot NCCH_3$ complex. [c] Experimental geometrical parameters were taken for $2SbCl_3 \cdot C_6H_6$ complex.

Results

In the paper [13] we applied the density functional theory (DFT) to obtain reliable values of QCC and Mössbauer isomeric shifts for halogen containing compounds.

In this paper we apply the same method, i. e. B3LYP/3-21G*, which allows us to take into account all the electrons of the atoms in a molecule. The QCC values were calculated from the components of the electric field gradient tensor in the principal axes.

The studied systems were simple compounds of Sb^{III} and Sb^{V} as well as their complexes, for which the QCC from NQR and Mössbauer isomer shifts have been reliably determined.

The experimental [14 - 17] and calculated geometrical parameters as well as NQR parameters for some $SbCl_5$ and $SbCl_3$ complexes are presented in Table 1.

The B3LYP/3-21G* overestimates bond lengths whereas the valency angles are reproduced correctly.

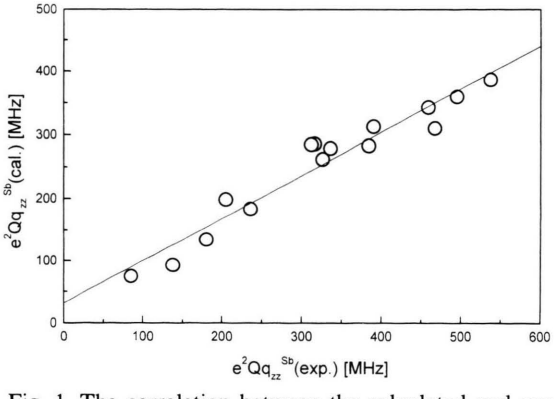

Fig. 1. The correlation between the calculated and experimental $e^2Qq_{zz}h^{-1}$ values for the compounds containing antimony atoms.

The same tendency has been observed in the results for halogen compounds [13].

The correlation between the experimental and calculated bond lengths obtained from Fig. 1. is

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

Here, similarly as in the case of halogen-halogen bonds [13], the factor preceding $R_{Sb-X}{}^{exp.}$, being close to unity, indicated the high reliability of the calculations, despite of the presence of coordinating antimony-ligand bonds.

These bonds are usually reproduced with large error, and the bond lengths calculated from full optimisation are much larger then the values measured (see for example the complexes of $SbCl_5$, $SnCl_4$ and $TiCl_4$ with hydrogen sulfide [10]).

The geometries of the monomer and dimer forms of $SbCl_5$ are compared in Table 1. The results of the calculations obtained with the use of the extended basis set 6-311G** taken from [10] are compared with those obtained with the 3-21G* basis set. The geometrical parameters for dimer agree well with the X-Ray data for a molecule $Sb_2Cl_6Ph_4$ [18], in which the lengths of axial bonds were found greater than the equatorial ones.

Although the relation between bond lengths and NQR frequencies of chlorine atoms for the complexes with Sb-Cl [19] and Sn-Cl [20] bonds are well known, we cannot say that there is a correlation, it is only a trend.

The NQR frequency depends on the electric field gradient at the site of the resonating nuclei and therefore to a larger degree reflects the influence of the magnitude of the charge in the atom containing this nucleus than that of the chemical bond length including the same atom. This confirms that in our previous paper [21] the NQR frequencies were adequately ascribed for the axial and equatorial chlorine atoms. Moreover, it should be pointed out that the assignment based on NQR frequency ratios for a monomer and dimer (Table 1) given in this work is correct, in contrast to the results concerning dimer Sb_2Cl_{10} from [22] as well as in [23].

The following correlation between the calculated and experimental [1, 19, 23 - 26] QCC on antimony atoms (Table 2) was found (Figure 1):

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

Table 2. The experimental and calculated NQR and Mössbauer parameters for Sb compounds.

Compound	$e^2Qq_{zz}{}^{Sb}$ (exp.) [MHz]	$e^2Qq_{zz}{}^{Sb}$ (cal.) [MHz]	δ, mm/s, relative to $CaSnO_3$	$N_s{}^{Sb}$	$N_p{}^{Sb}$
SbH_3	459	343	–	–	–
SbF_3	537	387	–14.9	1.676	1.871
$SbCl_3$	384	283	–14.4	1.460	2.081
$SbBr_3$	316	286	–14.42	1.465	2.283
SbI_3	85	211	–15.84	1.489	2.503
Sb_2Cl_{10}	180	135	–3.1	0.771	1.976
$SbCl_5 \cdot OPCl_3$	204	199	–2.67	0.744	1.907
$SbCl_5 \cdot NCCl$	236	184	–2.87	0.761	1.919
$SbCl_3 \cdot C_6H_5NH_2$	326	262	–14.8	1.467	2.002
$SbCl_3 \cdot C_6H_6$	390	213	–14.2	1.482	2.022
SbSBr	336	279	–	–	–
SbSI	312	285	–	–	–
$SbF_4{}^-$	467	310	–	–	–
$SbCl_4{}^-$	267	123	–16.0	1.501	1.943
$SbBr_4{}^-$	138	93	–16.6	1.534	2.164
$SbI_4{}^-$	99	26	–15.9	1.551	2.312
$SbCl_6{}^-$	0	0	–2.74	0.708	1.874
$SbCl_5Br^-$	–	10	–2.94	0.715	1.893
$SbMe_3$	495	360	–	–	–
$SbMe_3Cl_2$	663	202	–6.0	1.010	2.126

The correlation coefficient is not very high, but the standard curve fit error does not exceed 10%. Some of the compounds, i.e. SbI_3, $SbI_4{}^-$, $SbCl_4{}^-$ and $SbMe_3Cl_2$, fall out of this relation due to the rather strong coordination interactions in solid state. For example the QCC on the antimony atom in antimony iodide [1] is much modified because the intramolecular interactions are of the same order as the intermolecular ones.

Table 2 presents the experimental values of the Mössbauer isomer shifts [5, 6, 27 - 30] and the calculated populations of the 5s- and 5p-orbitals of antimony atom.

Literature gives the Mössbauer isomeric shifts relative to InSb, $CaSnO_3$ or $BaSnO_3$. For the sake of comparison, the Mössbauer isomeric shifts presented in Table 2 were recalculated and values for all antimony compounds are listed relative to $CaSnO_3$. The Mössbauer isomeric shift for InSb relative to $CaSnO_3$ (or $BaSnO_3$) is –8,5 $mm \cdot s^{-1}$ [4]. The QCC values obtained from NQR frequencies are reliable enough, whereas those obtained from the Mössbauer isomeric shifts for the antimony compounds have a considerable scatter. Let us consider for example $SbCl_3$. For this compound the Mössbauer isomeric shifts change from –5,24 up to –6,94 $mm \cdot s^{-1}$ relative to InSb [27]. Disregarding this fact, we have selected the most

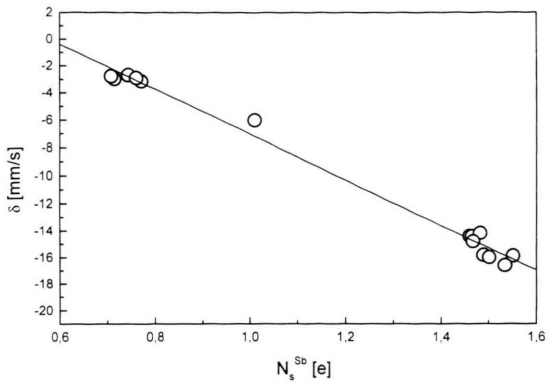

Fig. 2. The correlation between the experimental Mössbauer isomeric shift (δ) and the calculated population of the 5s-orbital (N_s^{Sb}) of antimony atom.

probable δ values and listed them in Table 2. For antimony pentachloride the data were calculated for the dimer form because the measurement of Mössbauer isomeric shifts was carried out at 77 K [30], i. e. at the temperature in which $SbCl_5$ is a dimer.

The multiparameter dependence between the Mössbauer isomeric shifts and the 5s- and 5p- populations of antimony atom is characteristic of this class of compounds and both one-parameter as well as multiparameter dependencies were investigated in previous papers [2 - 4]. On the basis of the results of our calculations we can point out the existence of various dependencies i. e.:

$$\delta = 9.6 - 16.6\, N_s^{Sb} \quad (r = 0.995;\ s = 0.62;\ n = 14), \quad (3)$$

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

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

The relation between the Mössbauer isomeric shifts (δ) and 5s-orbital populations of antimony atom (N_s^{Sb}) are shown in Figure 2. The slope in (3) is chracteristic of antimony compounds and could be explained in terms of the negativity of $\Delta R/R$. The two- or four-parameter dependencies can be used for the explanation of the Mössbauer isomeric shifts in a series of compounds. However, the last one is preferable because of its higher correlation coefficient. The factors at the population coefficients characterise direct influence of 5s-electrons and screening effects on the electronic density at the site of the antimony nucleus. A similar dependence was found earlier on the basis of simple semiempirical calculations for tin complexes [31]. It seems very important that the population of the 5s-orbital mainly determines the Mössbauer isomeric shifts and the screening effects play only a minor role. The same conclusion was drawn for tin complexes [31]. Taking into account that similar results were obtained for iodine containing compounds [13], it is possible to infer that a similar situation is typical of all compounds containing non-transition elements.

Table 3. Changes in the effective atomic charges* (in e) upon complex formation.

Compound	Δq_{Sb}	Δq_{Cl}	$\Delta q_{O,N,S}$	Δq_P	$\Delta P\alpha$, eV	Δq_L
$SbCl_5 \cdot OPCl_3$	–0,183	0,437	0,095	–0,079	–0.274	–0,254
$SbCl_5 \cdot SPCl_3$	–0,084	0,324	0,015	–0,018	–0.078	–0,240
$SbCl_5 \cdot NCCl$	–0,161	0,439	–0,042	–	–	–0,278
$SbCl_3 \cdot NH_2C_6H_5$	–0,048	0,258	–0,048	–	–	–0,210
$SbCl_3 \cdot C_6H_6$	–0,036	0,120	–	–	–	–0,084

An interesting feature seems to be the electron density distribution on atoms in the complexes of antimony halogenides. Changes in the electronic density distribution upon complexation (i. e. due to the coordination of acceptors by ligands) calculated on the basis of Mulliken populations of atomic orbitals are listed in Table 3.

Most important seems to be the increase of the positive charge on antimony atom upon complex formation. This conclusion was confirmed by X-Ray Electron and Fluorescence spectra [32, 19] and is in contradiction to our earlier results. The calculations performed by HONDO [10] suggested a decrease of the positive charge on antimony and tin atoms upon complex formation.

Thus, the electronic density increases on chlorine atoms and decreases on the acceptor central atom, which is characteristic of weaker complexes of antimony (III) chloride. The magnitude of the transferred electronic density is quite reasonable and in a good agreement with Gutmann's donor numbers [33]. A small Δq_L for the complex with benzene can be explained in terms of the interaction between π-electrons coming from the ring and antimony atom.

From the position of the ligand the following image of the complex behaviour can be drawn. While the coordinating oxygen and sulfur atoms become a pump of the electron density from the other atoms of the ligand, the nitrogen atom transfers the electron density

directly to the acceptor. This could be explained by the different electron properties, i. e. for O(–1.5), S(–2.1) and N(0.1) (all values in eV).

This qualitative analysis suggests that oxygen and sulphur atoms can easily accept additional electronic density, whereas the nitrogen atom will pass it to the acceptor. A consequence of the increase of the positive charge on the phosphorus atom upon complex formation is the increase of $\Delta PK\alpha$ shifts in $SbCl_5 \cdot OPCl_3$ and $SbCl_5 \cdot SPCl_3$ complexes determined in X-Ray emission spectra [19]. This conclusion agrees well with the results of calculations listed in Table 3.

Conclusions

The application of the Gaussian 98 program and the use of the hybrid functional B3LYP (i. e. taking into account all atom electrons) leads to very reliable QCC values.

On the basis of the obtained correlation between Mössbauer isomeric shifts and orbital populations of antimony atoms, the contributions of the 5s- and 5p-orbital populations in δ could be estimated. The redistribution of the electron density on atoms upon complex formation suggested by the results of the calculations are in a good agreement with the conclusions drawn from the X-Ray Electron and X-Ray Emission spectra.

Acknowledgements

We would like to thank Dr. Elin V. P. for providing us with $PK\alpha$ shifts in X-Ray emission spectra. This work was supported within a grant from the Russian Ministry of Education.

[1] G. K. Semin, T. A. Babushkina, and G. G. Yakobson, Nuclear Quadrupole Resonance in Chemistry, Wiley & Sons, New York 1975.
[2] R. V. Parish, Prog. Inorg. Chem. **15**, 101 (1972).
[3] R. V. Parish, Coord. Chem. Rev. **42**, 1 (1982).
[4] L. H. Bowen and G. G. Long, Inorg. Chem. **15**, 1039 (1976).
[5] J. M.Friedt, G. K. Shenoy, and M. J. Burgard, Chem. Phys. **59**, 4468 (1973).
[6] V. Kothekar, Int. J. Quant. Chem. **10**, 993 (1976).
[7] O. Kh. Poleshchuk, J. Latosinska, and J. Koput, Russian Coord. Chem.**23**, 744 (1997).
[8] G. Koster, Phys. Rev. **86**, 148 (1952).
[9] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).
[10] O. Kh. Poleshchuk, G. N. Dolenko, J. Koput, and J. Latosinska, Russian Coord. Chem. **23**, 643 (1997).
[11] O. Kh. Poleshchuk, J. Koput, and J. Latosinska, Russian Coord. Chem. **24**, 72 (1998).
[12] GAUSSIAN 98W. User's Reference. Editors E. Fritsch and M. J. Fritsch, Pittsburgh: Gaussian Inc. 1998.
[13] O. Kh. Poleshchuk, J. N. Latosińska, and B. Nogaj, Z. Naturforsch. **55a**, 271 (2000).
[14] C. I. Branden and I. Lindqvist, Acta Chem. Scand. **17**, 363 (1963).
[15] A. A. Ischenko, V. P. Spiridonov, and T. G. Strand, Acta Chem. Scand. **42a**, 651 (1988).
[16] V. I. Nefedov and M. M. Gofman, Vzaimnoe vliyanie ligandov v neorganicheskih soedineniyah, Itogi nauki i tehniki. V. 6. VINITI, Moskow, 1978.
[17] Yu. A. Buslaev and R. L. Davidivich, Russian Coord. Chem. **15**, 1444(1989).
[18] J. Bordner, G. O. Doak, and J. R. Peters, J. Amer. Chem. Soc. **96**, 6763 (1974).
[19] O. Kh. Poleshchuk, Investigation of the Electron Structure of Non-transition element Complexes with the Organic Ligands. Diss., Irkutsk 1997.
[20] P. G. Huggett, R. J. Lynch, T. C. Waddington, and K. J. Wade, J. Chem. Soc. Dalton Trans. 1164 (1980).
[21] O. Kh. Poleshchuk, J. Koput, and J. N. Latosinska, Russian J. Struct. Chem. **37**, 585 (1996).
[22] G. K. Semin, T. L. Hoczanova, S. I. Kuznezov, and E. V. Bruhova, Russian J. Neorg. Chem. **41**, 250 (1996).
[23] O. Kh. Poleshchuk and Yu. K. Maksyutin, Izv. Akad. Nauk SSSR. Ser. Fiz. **39,** 2579 (1975).
[24] M. Mishima, J. Sci. Hirishima Univ. **46a**, 41 (1982).
[25] M. Burgard and E. A. C. Lucken, J. Mol. Struct. **14**, 397 (1972).
[26] T. Okuda, S. Gima, H. Ishihara, and H. Negita, J. Mol. Struct. **81**, 261 (1982).
[27] W. Ravenek, J. Jacobs, and A. Avoird, Chem. Phys. **78**, 391 (1983).
[28] J. G. Ballard, T. Birchall, J. Milne, and W. D. Moffett, Can. J. Chem. **52**, 2375 (1974).
[29] M. Yanaga, T. Miura, K. Endo, H. Nakahara, and M. Takeda, Bull. Chem. Soc. Japan. **59**, 3085 (1986).
[30] J. L. Resce and J. G. Stevens, J. De Physique. **37**, C6-531 (1976).
[31] V. A. Varnek, O. Kh. Poleshchuk, L. N. Mazalov, and D. M. Kizner, Russian J. Struct. Chem. **23**, 98 (1982).
[32] L. N. Mazalov and V. D. Yumatov, Electronnoe stroenie ekstragentov, Nauka, Novosibirsk, 1984.
[33] V. Gutmann, Coord. Chem. Rev. **15**, 207 (1975).