Electric Field Gradients for Small Antimony Based Zintl Clusters from Hartree-Fock Investigations *

F. Hagelberg[a], T. P. Das[a], and K. G. Weil[b]

[a] Department of Physics, State University of New York at Albany, Albany, NY 12222, USA
[b] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

Z. Naturforsch. **51a,** 557–559 (1996); received February 3, 1996

Electric Field Gradient (EFG) calculations have been carried out for Antimony based clusters with 20 and with 22 valence electrons. It is shown that EFGs are very sensitive to structural changes of the clusters under study. This feature can be used to demonstrate the validity of the Zintl-Klemm-Busmann principle for these systems through EFG determinations.

Key words: Ab Initio Theory, Atomic Clusters, Antimony Molecules, Electric Field Gradients, Zintl Clusters.

The investigations presented here focus on the electric field gradients (EFGs) at the nuclei of several antimony (Sb) based cluster species which were discovered by Knudsen Effusion Mass Spectrometry [1, 2]. Two main categories of these clusters can be distinguished: (a) Zintl systems analogous to the Sb_4 molecule, (b) Zintl systems analogous to the Sb_4^{2-} ion and alkali-antimony clusters of the compositions $A_{2N}Sb_4$ with A = Na, K, Cs and N = 1, 2, 3. In the following three paragraphs we comment on both cluster groups and give a motivation for the theoretical analysis reported in this text.

The elements of the first cluster group result from the extremely stable 20 valence electron system Sb_4 through isoelectronic substitution of one or several Sb atoms. The recently detected clusters Sb_2SnTe and Sn_2Te_2 give examples for neutral Sb_4 analogous Zintl molecules. Additionally, a number of Zintl anionic and Zintl cationic systems have been experimentally isolated. These clusters emerge from the Sb_4 unit by substitution of an element of the group III, IV or VI for one Sb atom. A count of 20 valence electron on these systems is achieved by addition of electron donors in the form of alkali atoms (as e.g. in the cluster $CsSb_3Sn$) or of electron acceptors in the form of halogen constituents (as e.g. in $ClSb_3Te$). With arguments based on the Zintl-Klemm-Busmann (ZKB) principle [3], one expects the cluster geometry to be preserved under a substitution of cluster elements which leaves the count of valence electrons unchanged. The tetratomic cluster nuclei Sb_3Sn of ASb_3Sn (A = alkali) or Sb_3Te as part of $HaloSb_3Te$ (Halo = Halogen) should therefore exhibit the tetrahedral geometry of the Sb_4 unit. It is, however, an open question if the ZKB principle, which has been successfully applied to liquids and solids, is applicable to the gaseous phase also. Performing Hartree-Fock geometry optimizations [4], we were able to demonstrate that the respective cluster nuclei indeed tend strongly towards tetrahedral geometry, corresponding to sizable charge transfer between the cluster nucleus and the electron donor or electron acceptor.

The doubly charged Sb_4^{2-} unit represents a 22 valence electron system. Addition of two electrons to the tetrahedral Sb_4 unit leads to the breaking of two Sb–Sb bonds. As can be shown by arguments based on the Jahn-Teller theorem, this results in a deformation of the tetrahedral into square planar geometry. With this observation, one can infer a likely geometry for the alkali-antimony cluster Na_2Sb_4 from the ZKB principle. It could consist in a square arrangement of four Sb atoms with one alkali atom above and another one below the Sb plane, as is confirmed by Hartree-Fock geometry optimization [5]. The two alkali atoms act here as electron donors, providing the charge which is necessary to flatten out the Sb_4 tetrahedron. In more complex A_NSb_4 clusters the Sb_4 unit tends to maintain square-planar structure [5].

While mass spectrometric measurements have yielded information about both abundances and ion-

---

* Presented at the XIIIth International Symposium on Nuclear Quadrupole Interactions, Providence, Rhode Island, USA, July 23–28, 1995.

Reprint requests to Prof. T. P. Das.

0932-0784 / 96 / 0500-0557 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen

ization potentials for many elements of the two cluster groups introduced above, no experimental data exist on their features related to aspects of structure and bonding. These pieces of information could be gained in principle by observation of hyperfine properties. The relevant cluster nuclei consist exclusively of elements with Mössbauer active isotopes. It is the aim of the present study to provide theoretical predictions for possible future determinations of EFGs in antimony based clusters by Mössbauer spectroscopy. In addition, we want to show that the EFGs are very sensitive with respect to structural changes of the clusters under study. Therefore, EFG determinations can allow one to distinguish between alternative cluster geometries and to identify different isomers of a particular cluster species.

We present our results first for the pure Sb_4 unit and for neutral Zintl systems derived from this molecule. We will then discuss Sb_4 analogous Zintl anionic systems and lastly go on to Sb_4^{2-} based clusters. Our findings are obtained by ab initio Hartree-Fock calculations; for all tetratomic systems studied, full geometry optimizations were carried out using all-electron basis sets [6]. For the more complex clusters, we performed full geometry optimizations based on a pseudopotential procedure [7], employing double zeta basis sets with polarization functions [8]. At optimized geometry, we calculated the EFG using an all-electron approach.

The preferred geometry of Sb_4, corresponding to minimal total energy is the tetrahedral one; in addition to this structure, two planar isomers are found. Sb_4 can exist in the form of a rhombus or a rectangle, both structures resulting from the distortion of the square planar structure which turns out to be Jahn-Teller unstable.

As expected for a perfectly tetrahedral structure, the ground state of Sb_4 is characterized by a small EFG and vanishing asymmetry parameter (see Table 1). The planar isomers of Sb_4, in contrast, exhibit sizably enhanced EFG parameters. For the rhombus structure, we find two different eV_{zz} values, corresponding to the two inequivalent Sb sites present in this molecule.

Table 1. EFG parameters for Sb_4 molecules and neutral Sb_4 analogous systems.

System	Structure	Site of nucleus	eV_{zz} [e/a_0^3]	η
Sb_4	Tetrahedron	Sb	−0.08	0.0
Sb_4	Rectangle	Sb	−2.41	0.64
Sb_4	Rhombus	SbI *	−6.64	0.48
		SbII *	7.18	0.58
Sb_2TeSn	Tetrahedron	Sb	3.99	0.98
		Te	−3.40	0.71
		Sn	2.14	0.51
Sn_2Te_2	Tetrahedron	Sn	−3.59	0.06
		Te	6.61	0.38

* SbI: First Sb site, referring to the two atoms separated by the large rhombus axis.
SbII: Second Sb site, referring to the two atoms separated by the small rhombus axis.

Table 2. EFG parameters for $NaSb_3Sn$ clusters. All values refer to the nuclear site of the Sn atom. The labels a, b, c are as in Figure 1.

System	eV_{zz} [e/a_0^3]	η
a	0.68	0.00
b	−1.02	0.88
c	−1.94	0.66

In keeping with our prediction based on the ZKB principle as applied to Sb_4 analogous systems, the units Sb_2TeSn and Sn_2Te_2 are found to stabilize as near-regular tetrahedra. Either cluster, however, is characterized by sizable internal charge transfer due to electronegativity differences between different cluster constituents. The EFG parameters evaluated at the nuclear sites of the various constituents therefore deviate strongly from those obtained for the homogeneous tetramer Sb_4 (see Table 1).

Replacement of one Sb atom in Sb_4 by Sn results in a sizable deformation of the tetrahedral structure [4]. The ZKB principle predicts a restoration of the original tetrahedral geometry when an alkali atom, acting as electron donor, is added to the Sb_3Sn complex. Our Hartree-Fock optimizations confirm this expectation. In its preferred state (see Fig. 1 a), the system ASb_3Sn (A = Na, K, Cs) contains the Sb_3Sn unit in the form of a near-regular tetrahedron. The geometries shown in Fig. 1 b and c, correspond to stable isomers of ASb_3Sn. The alkali species occupies in both cases sites of lesser symmetry than shown in Fig. 1 a, and therefore the Sb_3Sn units of the two isomers exhibit a slightly higher deviation from perfectly tetrahedral geometry than is found for the preferred configuration. In a spectroscopic experiment, all three geometric variants of the ASb_3Sn cluster might be populated. As demonstrated in Table 2 for the example of A = Na, EFG investigations at the Sn nucleus can provide

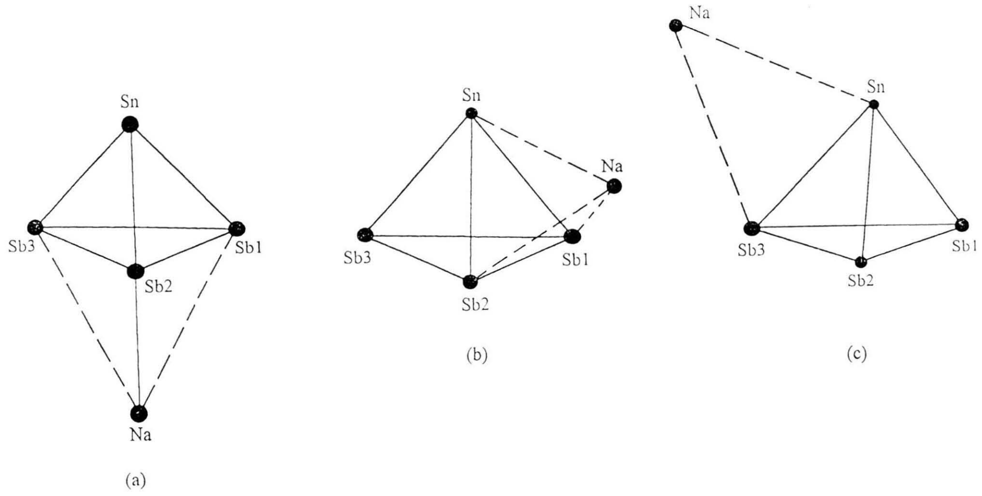

Fig. 1. The three stable structures identified for the cluster ASb_3Sn.

fingerprints for each of the three possible cluster geometries. We focus on the EFGs at the nuclear site of the substitutional atom Sn. The C_{3v} symmetry of the preferred structure leads to a small eV_{zz} value and a vanishing asymmetry parameter at the Sn site. For the two isomers, one finds an enhanced magnitude of the V_{zz} component as well as a sizable increase of the asymmetry parameter. These effects are due to both the asymmetric placement of the electron donor center and to the charge transfer from this center, which proceeds preferentially to the Sb atom(s) closest to the alkali species and thus introduces an inequivalence into the Sb_3 system.

Table 3 gives EFG parameters for Sb_4^{2-} and for Na_2Sb_4. The D_{4h} symmetry of both molecules is reflected by the fact that in each of them identical values of eV_{zz} and η result for all four Sb nuclei. The strong electron transfer from the alkali to the antimony subsystem yields high positive charges ($q(\mathrm{Na}) = 0.91$) which leads to a somewhat increased value of eV_{zz} and to a markedly enhanced asymmetry parameter in Na_2Sb_4 as compared to Sb_4^{2-}.

Table 3. EFG parameters at the Sb nuclei for Sb_4^{2-} and Na_2Sb_4 in D_{4h} symmetry.

System	eV_{zz} [e/a_0^3]	η
Sb_4^{2-}	2.21	0.03
Na_2Sb_4	2.52	0.19

As our calculations demonstrate, the EFG parameters involved are very sensitive with respect to structural features of the small antimony based Zintl clusters studied. Therefore, EFG determinations would allow one to distinguish between alternative cluster geometries, to identify different isomers of a particular cluster species and to test hypotheses related to bonding features and charge transfer in the investigated systems.

[1] T. Scheuring and K. G. Weil, Surf. Sci. **156,** 457 (1985).
[2] L. Poth and K. G. Weil, Ber. Bunsenges. Phys. Chem. **96,** 1621 (1992).
[3] H. Schafer, B. Eisenmann, and W. Muller, Angew. Chem. **12,** 694 (1974).
[4] F. Hagelberg, Sudha Srinivas, N. Sahoo, T. P. Das, and K. G. Weil, Phys. Rev. A **53,** 353 (1996).
[5] F. Hagelberg, S. Neeser, N. Sahoo, T. P. Das, and K. G. Weil, Phys. Rev. A **50,** 557 (1994).
[6] S. Huzinaga et al., Gaussian Basis Sets for Molecular Calculations, Elsevier, New York 1985.
[7] e.g. W. A. Harrison, Electronic Structure and the Properties of Solids 359, W. H. Freeman and Company, San Francisco 1980.
[8] P. J. Hay, and W. R. Wadt, J. Chem. Phys. **82,** 270 (1985).