HYPERFINE INTERACTION PARAMETERS FOR $^{121}$Sb AND $^{127}$I IN (CH$_3$)$_n$SbX$_{3-n}$ ($X = \text{Cl, Br, I}$) ($n = 0, 1, 2, 3$)

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HYPERFINE INTERACTION PARAMETERS FOR $^{121}$Sb AND $^{127}$I IN (CH$_3$)$_n$SbX$_{3-n}$ (X = Cl, Br, I) ($n = 0, 1, 2, 3$)

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Résumé. — Les variations de déplacement isomérique et d’interaction quadrupolaire au site de $^{121}$Sb dans la série de composés (CH$_3$)$_n$SbX$_{3-n}$ ($n = 0, 1, 2, 3$ et $X = \text{Cl, Br, I}$) sont discutées en fonction de la géométrie moléculaire, du changement d’ionicité des liaisons Sb-ligand et des interactions intermoleculaires ; ces interactions intermoléculaires ont été mises en évidence dans les composés Sb$_3$ et CH$_3$SbI$_2$ par spectroscopie Mössbauer sur $^{127}$I. L’évolution des paramètres d’interaction hyperfine au site de $^{121}$Sb est interprétée dans l’approximation de Townes et Dailey ainsi qu’à l’aide d’un modèle de charges ponctuelles.

Abstract. — The variations of the isomer shift and quadrupole interaction at the $^{121}$Sb nucleus in the series (CH$_3$)$_n$SbX$_{3-n}$ ($n = 0, 1, 2, 3$ and $X = \text{Cl, Br, I}$) are discussed in terms of the geometrical molecular parameters, the changes in ionicity of the Sb to ligand bonds and the varying degree of intermolecular interactions. The occurrence of the latter interactions is clearly inferred from the $^{127}$I measurements in Sb$_3$ and (CH$_3$)$_3$SbI$_2$. The evolution of the hyperfine interaction parameters at the $^{121}$Sb nucleus is discussed in the Townes and Dailey approximation and using a point charge model.

1. Introduction. — The series of mixed antimony (III) organo-halides provides an interesting example to study the systematic dependence of the hyperfine interaction parameters on the chemical environment and the molecular geometry. We report here the Mössbauer investigations using the 37.15 keV resonance in $^{121}$Sb (spin states $5/2-7/2$) in the set of compounds (CH$_3$)$_n$SbX$_{3-n}$ where $n = 0, 1, 2, 3$ and $X = \text{Cl, Br, I}$. In addition, we have measured the $^{127}$I resonance spectra in Sb$_3$ and (CH$_3$)$_3$SbI$_2$. The halides, (CH$_3$)$_n$SbX and (CH$_3$)$_3$SbX$_2$ with $X = \text{Cl and Br}$, have been obtained either by reaction of CH$_3$X on metallic Sb or by thermal decomposition of the corresponding Sb(V) organo-halide. In each of these preparations both the halides were present which could be identified from their characteristic quadrupole patterns (see Fig. 1). In fact, it is not clear from the

![Image of Mossbauer spectra at 4.2 K of (a) : (CH$_3$)$_2$SbCl and (b) : CH$_3$SbCl$_2$ (containing some impurities of (CH$_3$)$_2$SbCl).](http://dx.doi.org/10.1051/jphyscol:1974634)
Hyperfine interaction parameters at 4.2 K of $^{121}$Sb in (CH$_3$)$_2$SbX$_3$ - . The isomer shift (IS) values refer to Ca$^{121m}$SnO$_3$ at 4.2 K. The parameters remeasured for Sb(CH$_3$)$_3$ at 4.2 K are IS = $-8.53 \pm 0.05$ mm/s, $e^2 q_z Q = 15.25 \pm 0.20$ mm/s and $\eta = 0$

<table>
<thead>
<tr>
<th>$^{121}$Sb</th>
<th>IS (± 1 mm/s)</th>
<th>$e^2 q_z Q$ (± 2 mm/s)</th>
<th>$\eta$ (± 0.2)</th>
<th>IS (± 1 mm/s)</th>
<th>$e^2 q_z Q$ (± 2 mm/s)</th>
<th>$\eta$ (± 0.2)</th>
<th>IS (± 0.05 mm/s)</th>
<th>$e^2 q_z Q$ (± 0.2 mm/s)</th>
<th>$\eta$ (± 0.07)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>$-11.6$</td>
<td>$-26.0$</td>
<td>$0.9$</td>
<td>$-12.9$</td>
<td>$30.0$</td>
<td>$0$</td>
<td>$-14.3$</td>
<td>$12.2$</td>
<td>$0.19$</td>
</tr>
<tr>
<td>Br</td>
<td>$-12.0$</td>
<td>$-20.0$</td>
<td>$0.9$</td>
<td>$-12.5$</td>
<td>$19.0$</td>
<td>$0$</td>
<td>$-14.4$</td>
<td>$11.6$</td>
<td>$0.10$</td>
</tr>
<tr>
<td>I</td>
<td>$-13.6$</td>
<td>$27.0$</td>
<td>$0$</td>
<td>$-16.2$</td>
<td>$5.6$</td>
<td>$0$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The measured spectra were least-squares fitted using a transmission integral [4] including two quadrupole patterns of $^{121}$Sb. The analysis of the spectra measured on samples containing different amount of these halides yielded identical values for the hyperfine parameters.

In the case of iodide, we were able to obtain pure (CH$_3$)$_2$SbI$_2$; however, (CH$_3$)$_2$SbCl could not be prepared.

The experimental results of $^{121}$Sb and $^{127}$I are summarized in Tables I and II.

### Table I

<table>
<thead>
<tr>
<th>Parameters of $^{127}$I at 4.2 K in SbI$_3$ and (CH$_3$)SbI$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{127}$I</td>
</tr>
<tr>
<td>IS (± 0.05 mm/s)</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>SbI$_3$</td>
</tr>
<tr>
<td>(CH$_3$)SbI$_2$</td>
</tr>
</tbody>
</table>

### 3. Interpretation and discussion.

3.1 Quadrupole interactions in SbX$_3$ (X = Cl, Br) and Sb(CH$_3$)$_3$.

- The large value for the asymmetry parameter ($\eta$) deduced from the $^{127}$I Mössbauer spectra in SbI$_3$ reveals the existence of strong intermolecular interactions between the Sb ion and the I ion of a neighbouring molecule. From the $^{127}$I hyperfine interaction parameters one deduces that the ionicity of the intramolecular Sb-I bond is 53% whereas the intermolecular character is 14% (see appendix).

Similar intermolecular interactions are known to occur in the other two halides from previous NQR investigations [2]. They however cannot exist in Sb(CH$_3$)$_3$ as deduced from the bonding characters of the CH$_3$ ligand. The analysis of the $^{121}$Sb spectra in all the SbX$_3$ compounds reveal a small $\eta$ (Table I). One may hence assume an axial molecular symmetry with a C$_3$ axis along the hybrid orbital carrying an electron doublet (i. e. the z axis). Using Townes and Dailey approximation the principal component of the electric-field-gradient (efg) tensor is proportional to [5]:

$$(- N_0 + N_\lambda \left(3 \cos \alpha \left(\cos \alpha - 1\right)\right).$$

Here, $N_0$ and $N_\lambda$ represent the electron populations of the hybrid orbital carrying the lone electron pair and along the Sb-X direction, respectively and $\alpha$ is the X-Sb-X angle.

The negative sign of the principal component of the efg tensor reveals that $N_0 > N_\lambda$, i. e. that there is an excess of electron population in the hybrid orbital along the z axis compared to that in the three orbitals along the Sb-X directions.

Assuming that the angle $\alpha$ is approximately a constant within the series, the decrease of the absolute value of $e^2 q_z Q$ on changing the CI$^-$ anion by Br$^-$ and I$^-$ can be attributed to an increasing strength of intermolecular interactions in that order (which decreases $N_\lambda$) associated with a decrease of the Sb-X ionicity (which increases $N_0$). Thus $(- N_0 + N_\lambda)$ keeps its negative sign in all the compounds whereas its absolute value decreases from the chloride to the iodide.

The intermolecular interactions vanish in Sb(CH$_3$)$_3$; as a result, $N_0$ is considerably increased and this accounts for the higher value of $|e^2 q_z Q|$ ($= 15.25$ mm/s) observed in this compound.

3.2 Quadrupole interactions in (CH$_3$)SbX$_2$ and (CH$_3$)$_2$SbX. — Strong intermolecular interactions also occur in these organo-halides of Sb(III) as revealed by the large value of $\eta$ deduced from the spectra of $^{127}$I in (CH$_3$)SbI$_2$ (Table II). Interpreting the results of the $^{127}$I spectra, one deduces that the intramolecular Sb-I bond ionicity is 52% whereas the intermolecular bonding character amounts to 16% (see appendix).

The $^{121}$Sb data reveal that the sign of the quadrupole interaction in the two types of organo-halides is opposite whereas the magnitudes are nearly equal. The asymmetry parameter $\eta$ practically vanishes in
HYPERFINE INTERACTION PARAMETERS FOR $^{121}\text{Sb}$ AND $^{127}\text{I}$ (CH$_3$)$_2$SbX, and is close to unity in (CH$_3$)$_2$SbX (Table I).

Due to the low molecular symmetry, the principal efg axis becomes arbitrarily oriented relative to the bonding directions and hence for this case the Townes and Dailey approximation becomes impracticable. To account for the experimental trends in the quadrupole interaction, we have thus attempted to use a point charge model.

Assuming the molecular model shown in figure 2, the efg components were calculated as a function of the following parameters: a charge of $-2$ on the electron pair at a distance $r_0$ from the Sb(III) ion, a charge, $a$, on the ligand A at a distance $r$, a charge, $b$, on the ligand B at the same distance $r$, and the angle $\alpha$ between MA, MB directions and the $xy$ plane. The values of $\sigma_{eq}$ and $\eta$ obtained by diagonalizing the efg tensor are represented in figure 3 as functions of the angle $\alpha$ and for various values of the ratio $r_0/r$. Changes of the strength of intermolecular interactions would be accounted for by different values of $r_0/r$. The upper example for $\alpha = 12.5^\circ$ and $r_0/r = 1$ the sign of $\sigma_{eq}$ changes for the MA$_2$B and MAB$_2$, although the absolute value is approximately constant. The

![Diagram](image1)

**Fig. 2.** Geometrical parameters used for the point charge model in the compounds MA$_2$B.

![Diagram](image2)

**Fig. 3.** Variation of the efg principal component ($\sigma_{eq}$) and of the asymmetry parameter ($\eta$) as functions of the angle $\alpha$ and for various values of $r_0/r$ in MA$_2$B. $a$ and $b$ are the charges on ligands A and B.
change in the sign of $eq_x$ furthermore implies a sharp variation in the asymmetry parameter $\eta$. The point charge model thus qualitatively accounts for the quadrupole interaction parameters and the changes in $\eta$ observed in $(\text{CH}_3)_2\text{SbX}_2$ and $(\text{CH}_3)_3\text{SbX}$. A similar variation has been reported in some nitrogen compounds from $^{14}\text{N}$ NQR experiments [5, 6].

The knowledge of the detailed crystal structure would be required in order to perform more quantitative evaluation of the experimentally observed trends using either the precise hybrid orbitals or molecular orbital theory.

3.3 ISOMER SHIFTS. — For a given halogen within a series $(\text{CH}_3)_n\text{SbX}_{3-n}$, the $^{127}\text{Sb}$ isomer shift increases with the number $n$ of methyl groups bound to the antimony ion. Thus, the s electron density at the Sb nucleus is higher in the $(\text{CH}_3)_2\text{SbX}$ compounds as compared to $(\text{CH}_3)_3\text{SbX}_2$. This trend, along with the fact that the Sb-CH$_3$ bond is more covalent than the Sb-X bond, reveals that the shielding effect of the p electrons on the s density at the nucleus represents the dominant parameter in these compounds.

The decrease in the isomer shift when replacing Cl$^-$ by Br$^-$ or by I$^-$ for a constant value of $\eta$ reveals an increase in the s electron density at the $^{127}\text{Sb}$ nucleus in that order, possibly due to a decrease in the p shell population. Chlorine being more electronegative than iodine one expects a larger withdrawal of electrons from the Sb ion in the former halide. The experimentally observed trend in the isomer shift would then indicate a larger s character of the Sb-X bonds so that the direct effect of the s shell depopulation would be predominant compared to the decreasing shielding effect of the p electrons. This explanation would however contradict to one suggested earlier to account for the changes in the isomer shift when increasing the number of halide ions, i.e. when changing the number $n$ in $(\text{CH}_3)_n\text{SbX}_{3-n}$ for constant X. It furthermore appears that the dependences of the isomer shift on the ligand electronegativity are in reverse order in the present compounds as compared to the series SbX$_4$ and Sb$_2$X$_6^-$ [7]. One may thus conclude that the different trends are related to the difference in geometries of these compounds and that in $(\text{CH}_3)_3\text{SbX}_{3-n}$ the intermolecular interactions are important. Due to the increased intermolecular bonding in the iodide as compared to the chloride, the p electron depopulation of the Sb ion might be increased in the former compound which would indeed result in a decreased isomer shift. One cannot however decide on the basis of the present results about the relative importance of the two mechanisms.

Appendix. — Using Townes and Dailey approximation to interpret the quadrupole interaction parameters at the $^{127}\text{Sb}$ site as a function of the electron populations in the p orbitals and knowing the relation between the isomer shift and the number of electron holes in the s and p shells [8]

$$IS = 3.07 h_s - 0.5 h_p + 0.16$$

one defines the ionicity of the iodine bond as

$$i = N_{p_s} - 1$$

and the proportion of intermolecular interaction as:

$$IM = 4 - (N_{p_s} + N_{p_p}) .$$

References