SOVIET PHYSICS JETP VOLUME 28, NUMBER 1 JANUARY, 1969

ISOMER SHIFTS OF THE MÖSSBAUER γ LINE IN TRIVALENT ANTIMONY HALIDES

V. KOTHEKAR, B. Z. IOFA, S. I. SEMENOV, and V. S. SHPINEL'

Nuclear Physics Institute, Moscow State University

Submitted February 26, 1968

Zh. Eksp. Teor. Fiz. 55, 160—163 (July, 1968)

The isomer chemical shifts (ICS) of the Sb^{121} 37.2-keV Mössbauer γ line in trivalent antimony halides are measured. The value of $\Delta r/r$ (change of nuclear charge radius due to excitation) is obtained for Sb^{121} by comparing the ICS values for the tri- and pentavalent antimony compounds $SbCl_3$ and HSb $HSbCl_6 \cdot xH_2O$ and found to be $(-9.5 \pm 3) \times 10^{-4}$. The ICS for $SbHal_3$ compounds increases linearly with increasing of ionicity of the bonds β. From a comparison of the observed slope of the straight-line plot of the ICS against β with the calculated value it follows that the change of the density $\psi_{5S}(O)^2$ due to screening by valence electrons in these compounds is insignificant.

In the investigation of the spectra of resonant absorption of 37.2-keV γ rays by Sb^{121} nuclei in various compounds of pentavalent antimony[1], we obtained for the ratio $\rho = \Delta r/r$ of the changes in the radius of the distribution of the nuclear charge in Sb^{121} and Sn^{119} a value $\rho(Sb^{121})/\rho Sn^{119} = -5.5$, which agrees well with the results of Ruby et al.[2]

We have continued the investigation of the isomer chemical shift (ICS) in halides of trivalent antimony ($SbCl_3$, $SbPr_3$, SbI_3).

The spectra of resonant absorption of 37.2-keV γ rays by Sb^{121} nuclei were measured with an electrodynamic setup operating in constant velocity mode. The measurements were carried out at liquid-nitrogen temperature. The γ rays were recorded with a standard scintillation spectrometer with NaI(Tl) crystal (thickness 0.3 mm). The γ-radiation source was the isotope Sn^{121} in SnO_2.

In all the investigated compounds, the resonant spectrum was an unresolved asymmetrical line with noticeable broadening (see Fig. 1). Eight components of the quadrupole structure for the nuclear transition 7/2 → 5/2 could not be resolved, owing to the large width of the nuclear level (Γ = 1.052 mm/sec). The ICS obtained by us (δ) are listed in the table. The values of the ICS were obtained by adding eight peaks, the positions of which were determined by the equation

$$V_{m^* m} = \frac{c}{4E_\gamma} e^2qQ[RC(I^*, m^*) - C(I, m)] + \delta, \tag{1}$$

where

$$C(I, m) = [3m^2 - I(I+1)]/I(2I-1),$$

R = Q*/q—ratio of the quadrupole moments of the excited and ground states, I*, I—spins and m*, m—their projections for the excited and ground states. The intensities of these peaks were determined by the squares of the Clebsch-Gordan coefficients[3]. For an analysis of the experimental spectra, we used data on the nuclear quadrupole resonance (NQR)[4,8] (see the table). According to the NQR data, the gradient of the electric field increases from iodine to chlorine, which is in good agreement with Γ_{exp} (experimental line width) for these compounds.

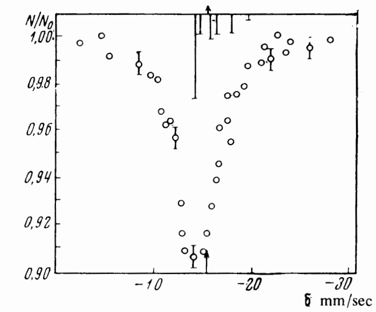

FIG. 1. Absorption spectrum of $SBCl_3$. The form of the spectrum corresponds to an unresolved hyperfine structure due to quadrupole interaction. The positions of the individual components of the hyperfine structure are shown by lines in the lower part of the figure. The velocity corresponding to the isomer shift is indicated by the arrow.

ANALYSIS OF THE EXPERIMENTAL DATA

The expression for the ICS, with allowance for the screening of the internal s-electrons and for the change of the density of the valence s-electrons on the Sb nucleus, owing to the change in the ionicity of the bond, can be written in the form

$$\delta = A\{(1-\beta_0)(N_s' - N_s) + 2b(N - N')N_s'\}, \tag{2}$$

where

$$A = \frac{c}{E_\gamma} K(Z) \frac{\Delta r}{r} |\psi_{5s}(0)|_{Sb}^2,$$

N_S', N_S—number of valence s-electrons of the absorber and of the source, N′, N—number of valence electrons, β_0—Crawford-Schawlow correction[9], for which we assumed the value $\beta_0 = 0.17$, the same as for Sn^{119} [10], and b—parameter that depends on the screening of the 5s electron by other electrons of the same shell.

X-ray diffraction studies of the compounds $SbCl_3$[11], $SbBr_3$[12], and SbI_3[13] show that the molecules of these compounds have a configuration of a trigonal pyramid with $\theta \approx 95.5°$ (where θ—angle between the Hal-Sb-Hal

Compound	δ, mm/sec	Γ_{exp} mm/sec	e^2qQ, on Sb^{121}, MHz	e^2qQ on Hal., MHz	β
$SbCl_3$	−15,5±0,2	4,3±0,2	383,7 [3]	40,4 [5]	0,48
$SbBr_3$	−15,85±0,2	3,35±0,2	343,97 [4]	337 [5]	0.42
SbI_3	−16,5±0,3	2,85±0.2	169,74 [4]	1163 [6]	0.35

Note: β – ionicity of bonds calculated from the formula $\beta = 1 - Up - s^2$ (where s – hybridization of the bond ≈ 0.15 [7]).

bonds). On this basis it can be assumed that the bond in the $SbHal_3$ molecules has an sp^3-hybrid character[14], where one of the vertices of the tetrahedron is occupied by an unshared pair of electrons.

Making up the hybrid wave functions for the antimony atom[15], we can obtain

$$N_s = 2-3\alpha - 3\alpha\beta, \quad N = 5 - 3\beta, \tag{3a}$$

where $\alpha = \cos\theta/(\cos\theta - 1) = 0.09$ gives the contribution of the s-electrons to the bonding orbital, and β is the ionicity of the bonds.

At the present time there is large scatter $(1.2-3.3) \times 10^{-4}$ in the values of $(\Delta r/r)\,Sn^{119}$ obtained by different authors[10,16-19]. This uncertainty does not make it possible to obtain a reliable value of $\Delta r/r$ for Sn^{121} from the ratio $\rho(Sb^{121})/\rho(Sn^{119})$. Therefore, for an independent determination of $(\Delta r/r)Sb^{121}$, we compared the shifts for the compounds $SbCl_3$ and $HSbCl_6 \cdot xH_2O$. For the second compound, on the basis of the sp^3d^2 hybrid functions, we can obtain

$$N_s = (1-\beta), \quad N = 6(1-\beta). \tag{3b}$$

Using (2) and (3), we get for the ICS of these compounds

$$\delta_{(SbCl_3)} - \delta_{(HSbCl_6\cdot x\,H_2O)} = A\{(1-\beta_0)(1-3\alpha-3\alpha\beta'+\beta) + 2b(1-6\beta+3\beta')(2-3\alpha-3\alpha\beta')\}, \tag{4}$$

where β, β'—ionicities of the bonds in $HSbCl_6 \cdot xH_2O$ and $SbCl_3$. From the NQR data for $SbCl_3$ we obtain a value $\beta' = 0.48$[19]. Starting from the electronegativities of the trivalent and pentavalent antimony (1.8 and 2.18)[5], we can assume that β is 20% smaller. Substituting in (4) the measured values $\delta_{(SbCl_3)} = -15.5$ mm/sec and $\delta_{(HSbCl_6\cdot xH_2O)} = -3$ mm/sec[1] and neglecting the second term in the curly brackets (this results in an error $< 2\%$) we obtain $A = -15.1$ mm/sec. Further, using $K(Z) = -1.085 \times 10^{-4}\, a_0^3\, eV$ and the value $\psi_{5S}(O)^2 = 18.28\, a_0^{-3}$ (obtained in[2] for the sp^3 state of the antimony atom by the Hartree-Fock self-consistent field method), we obtain from Eq. (2)

$$\Delta r/r = (-9.5 \pm 3)\cdot 10^{-4}.$$

This value of $\Delta r/r$ is 50% smaller than that obtained in[1] under the assumption that the differences of the electronegativities $\Delta\chi = 2$ correspond to a 50% ionic bond, and for $\psi_{5S}(O)^2$ we used the nonrelativistic value 1.34×10^{26} cm^{-3}. This value of $\Delta r/r$ is 10% larger than the results obtained by Ruby et al.[2] This difference is apparently connected with the fact that in the present paper we used the experimental values of β, whereas in[2] they assumed the atomic configurations s^0p^3 and sp^3 for the compounds SbF_6^{-1} and SbF_2, respectively.

We also obtained the dependence of δ on β for the compounds $SbHal_3$ (Fig. 2). From (2) and (3) we get for the ICS of compounds of the type $SbHal_3$

$$\delta = A\{(1-\beta_0)[2-3\alpha-3\alpha\beta-N_s] + 2b[N-5+3\beta](2-3\alpha-3\alpha\beta)\}. \tag{5}$$

Neglecting the term $3\alpha\beta$, which is sufficiently small compared with 2, we obtain for the slope of the dependence of the ICS on β the relation

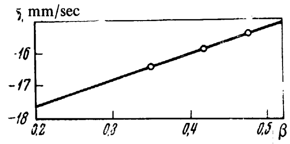

FIG. 2. Dependence of the ICS for 37.2-keV gamma transitions in the Sb^{121} nucleus on the ionicity β of the bonds for the compounds $SbCl_3$, $SbBr_3$, and SbI_3.

$$\delta E/\delta\beta = A\{(1-\beta_0)(-3\alpha) + 6b(2-3\alpha)\}. \tag{6}$$

Comparing (6) with the experimental slope $(\delta E/\delta\beta_{exp} = 8$ mm/sec), we can estimate the constant $b \sim -0.03$.

It follows from this value of b that the change of the density at the nucleus due to the change in the number of the valence p-electrons in these compounds is insignificant, i.e., the change of the electron density at the nucleus due to the screening by the valence p-electrons is compensated by the change of the density due to the $p_{1/2}$ electrons.

---

[1] V. A. Bryukhanov, B. Z. Iofa, V. Kothekar, S. I. Semenov, and V. S. Shpinel', Zh. Eksp. Teor. Fiz. **53**, 1582 (1967) [Sov. Phys.-JETP **26**, 912 (1968)].

[2] S. L. Ruby, G. M. Kalvius, G. B. Beard, and R. E. Snyder, Phys. Rev. **159**, 239 (1967).

[3] A. Simon, in: Deformatsiya atomnykh yader (Deformation of Atomic Nuclei) [Translation Collection], IIL, 1958, p. 365.

[4] R. G. Barne and P. J. Brays, J. Chem. Phys. **23**, 1177 (1955).

[5] M. Haissinsky, J. phys. radium **7**, 7 (1946).

[6] A. L. Schawlow, J. Chem. Phys. **22**, 1211 (1954).

[7] T. P. Das and E. L. Hann, Nuclear Quadrupole Resonance, Spectroscopy, Solid State Physics, 2d Supplement, 1958, p. 112.

[8] S. Ogawa, J. Phys. Soc. Japan **13**, 618 (1958).

[9] M. F. Crawford and A. L. Schawlow, Phys. Rev. **76**, 1310 (1949).

[10] T. P. Boquet, J. J. Chu, O. C. Kistner, M. L. Perlman, and G. T. Emery, Phys. Rev. Lett. **17**, 809 (1966).

[11] J. Lindquist and A. Niggli, J. Inorganic and Nuclear Chem. **2**, 345 (1956).

[12] J. Backer, Structural Reports **11**, 272 (1947).

[13] J. Trotter and T. Zabel, Z. Krist. **128**, 67 (1966).

[14] T. N. Polynova and M. A. Poraĭ-Koshits, Zh. strukt. khimii **7**, 146 (1966).

[15] W. Gordy, W. Smith and R. Trambarulo, Microwave Spectroscopy (Russ. Transl.), p. 280.

[16] V. I. Gol'danskiĭ, G. M. Gorodinskiĭ, S. V. Koryagin et al., Dokl. Akad. Nauk SSSR **147**, 127 (1962).

[17] A. J. F. Boyle, D. St. P. Bunbary, and C. Edwards, Proc. Phys. Soc. **79**, 416 (1962).

[18] T. Lee and P. A. Flinn, Phys. Lett. **19**, 186 (1965).

[19] H. G. Robinson, H. G. Dehmelt and W. Gordy, J. Chem. Phys. **22**, 511 (1954).

Translated by J. G. Adashko
21