

The High Resolution Rotational Spectrum of Silylbromide, $\text{SiH}_3^{81}\text{Br}$

K.-F. Dössel and D. H. Sutter

Institut für Physikalische Chemie Abt. Chemische Physik der Universität Kiel

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The microwave spectrum of $\text{SiH}_3^{81}\text{Br}$ has been reanalysed in the frequency range 8–40 GHz under high resolution. From 64 observed hyperfine transitions improved values for the rotational constant $B = 4292646.2(4)$ kHz and the quadrupole coupling constant $eqQ = 279825(5)$ kHz were obtained. Furthermore the centrifugal distortion constants $D_J = 1.81(1)$ kHz and $D_{JK} = 29.19(4)$ kHz and the spin-rotation constants $C_N = -2.32(40)$ kHz and $C_K = -34.2(11)$ kHz were determined. From the values of C_N and C_K the ^{81}Br nuclear shielding tensor is calculated. An improved value of $|\mu| = 1.319(8)$ D is given for the molecular electric dipole-moment.

Introduction

When we started an investigation of the molecular Zeeman effect of $\text{SiH}_3^{81}\text{Br}$, we realized that, although its rotational spectrum had been investigated several times¹, the transition frequencies have not been reported yet. To achieve higher accuracy in our Zeeman study, we therefore decided to re-investigate the rotational spectrum of $\text{SiH}_3^{81}\text{Br}$ in the frequency range 8–40 GHz under high resolution. We observed all possible $J \rightarrow J+1$ transitions (64) with $J = 0, 1, 2, 3$; $K = 0, 1, 2, 3$; $F \rightarrow F+1$ and $F \rightarrow F$. With the high resolution obtained here, we were able to determine the centrifugal distortion constants D_J and D_{JK} , as well as the two spin-rotation coupling constants C_N and C_K , which were not known so far.

Experimental

Silylbromide was prepared by reaction of Hydrogenbromide with Phenylsilane at -78°C ². Because SiH_3Br readily reacts with water to form Disiloxane $((\text{SiH}_3)_2\text{O})$ and Hydrogenbromide, great care had to be taken to remove traces of water adsorbed at the walls of the waveguide cell. Despite these precautions, once admitted to the cell the sample decayed in the course of an hour.

So the cell was refilled about every 30 minutes. The spectra were recorded with a microwave spec-

trometer of the Hughes-Wilson type³ described previously⁴⁾⁵. Phase stabilized BWO's as radiation sources and 33 kHz square wave Stark-effect modulation were used throughout. An 8 metre double width X-band absorption cell⁶ was used to reduce the effect of wall-broadening and to provide a sufficiently uniform Stark-field over the absorption volume. The sample pressure was about 0.5 mTorr and the cell temperature about -70°C . The observed halfintensity halflinewidths were on the order of 30 kHz as can be seen from a recording of the $J \rightarrow J' = 0 \rightarrow 1$, $K = 0$, $F \rightarrow F' = 3/2 \rightarrow 3/2$ transition shown in Figure 1. This can be compared with a Gaussian- and Lorentzian lineshape function. Linebroadening is produced by the effects of:

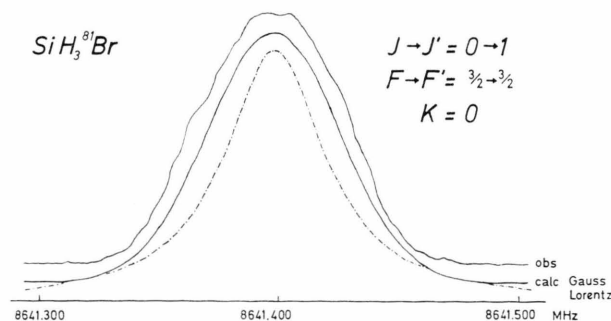


Fig. 1. High resolution recording of the $J \rightarrow J' = 0 \rightarrow 1$, $F \rightarrow F' = 3/2 \rightarrow 3/2$, $K = 0$ rotational transition of $\text{SiH}_3^{81}\text{Br}$. From a comparison between the experimental recording (upper trace), the Gaussian lineshape function calculated with a halfintensity halflinewidth (hwh) of 30 kHz (lower unbroken line) and the Lorentzian lineshape function calculated with a hwh of 25 kHz (lower broken line) it is seen, that the first type reproduces the observed lineform much better, than the second.

Reprint requests to Prof. Dr. D. Sutter, Institut für Physikalische Chemie der Universität Kiel, Abteilung Chemische Physik, Olshausenstraße 40–60, D-2300 Kiel.



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Dopplerbroadening, which can be calculated to be $2(\Delta\nu)_D = 8$ kHz, wall broadening, which is approximately $2(\Delta\nu)_W = 30$ kHz, pressure broadening $2(\Delta\nu)_P = 10$ kHz and modulation broadening. Of these four effects, the first one is reproduced by a Gaussian- and the following two by a Lorentzian lineshape function. The effect of modulation broadening can not be described by any simple function. From Fig. 1 is seen, that the observed lineshape is reproduced by a Gaussian type of lineshape function very well. We therefore used this type of lineshape function to analyse the lineform of two unresolved transitions shown in Figure 2. Figure 2 shows the

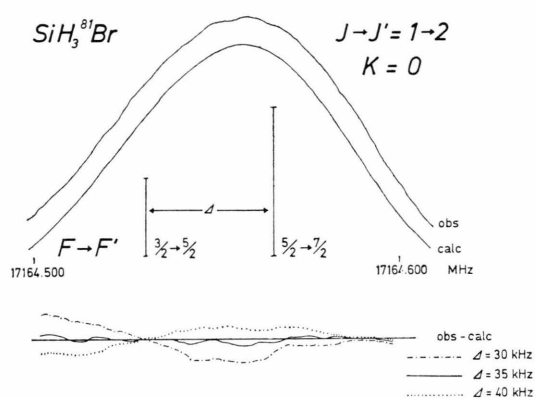


Fig. 2. High resolution recording of the $J \rightarrow J' = 1 \rightarrow 2$, $F \rightarrow F' = 3/2 \rightarrow 5/2$ and $5/2 \rightarrow 7/2$, $K = 0$ rotational transition of SiH₃⁸¹Br (upper trace) and Gaussian lineshape function calculated with a halfintensity halflinewidth of 30 kHz (lower trace). The comparison between both is shown in an enlarged scale in the lower part of this picture. It is seen, that the splitting of the two transitions although not resolved, can be determined to better than 5 kHz.

observed and calculated lineform of the $J \rightarrow J' = 1 \rightarrow 2$, $K = 0$, $F \rightarrow F' = 3/2 \rightarrow 5/2$ and $5/2 \rightarrow 7/2$ transitions, which are 36 kHz apart. With the experimental halfintensity halflinewidth of 30 kHz these lines would begin to appear separated, if they were of equal intensity. Nevertheless it can be seen from the plot of obs-calc in the lower part of Fig. 2, that the splitting is determined to better than 5 kHz.

Theory

For the vibrational groundstate the energy levels of the effective rotational Hamiltonian may be approximated as:

$$W_{(J,K,F)}/h = BJ(J+1) + (A-B)K^2, \quad (1a)$$

$$-D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4 \quad (1b)$$

$$+ \left(\frac{3K^2}{J(J+1)} - 1 \right) Y_{(I,J,F)} e q Q \\ + E_Q^{(2)}(I,J,F) \frac{(e q Q)^2}{B} \\ + E_Q^{(3)}(I,J,F) \frac{(e q Q)^3}{B^2} \quad (1c)$$

$$- \frac{1}{2} \left[C_N + (C_K - C_N) \frac{K^2}{J(J+1)} \right] \\ \cdot [F(F+1) - I(I+1) - J(J+1)], \quad (1d)$$

$$+ W_{SS}/h. \quad (1e)$$

The Eqs. (1a) and (1b) represent the rotational energy including centrifugal distortion up to the fourth order⁷. Equation (1c) gives the quadrupole interaction energy up to the third order^{8,9,10}. $Y_{(I,J,F)}$ is Casimir's function. The contribution from the second order term is quite important, giving rise to line-shifts up to 500 kHz, whereas the third order term only gives rise to lineshifts below 2 kHz and has been neglected. Equation (1d) gives the spin-rotation interaction term, resulting from the magnetic coupling of the quadrupole nucleus to the rotating molecule^{8,9,11}. C_K is the principal value of the coupling along the symmetry axis and C_N is the principal value normal to this axis. The contribution from this spin-rotation interaction term to the observed line frequencies is up to 90 kHz for SiH₃⁸¹Br. W_{SS} is the ¹H-⁸¹Br spin-spin interaction term^{8,9}, which would lead to a further splitting of the observed lines, if it were important. Since this is not observed, this term can be neglected.

Houghen¹² showed, that if centrifugal distortion is important, the quadrupole coupling "constant" used in Eq. (1c) is no longer constant for all rotational states, but has to be expanded in the form

$$e q Q = \chi_0 + \chi_J J(J+1) + \chi_K K^2 \quad (2)$$

and the extra term $\chi_a \frac{K^2(4K^2-1)}{J(J+1)} Y_{(I,J,F)}$ has to be added. These new centrifugal distortion constants are very small and if included in the fit, their uncertainties become bigger than their values.

Table 1. Microwave spectrum of SiH₃⁸¹Br. The observed frequencies (MHz) are compared to the values calculated from the molecular constants listed in Table 2 according to Equation (1).

J	K	$F \rightarrow F'$	ν_{obs}	obs-calc
0	0	3/2 5/2	8 571.379	0.001
0	0	3/2 3/2	8 641.397	0.000
0	0	3/2 1/2	8 515.515	0.002
1	0	5/2 7/2	17 164.566	- 0.002
1	0	3/2 5/2	17 164.531	- 0.002
1	0	1/2 3/2	17 240.678	0.006
1	0	5/2 5/2	17 234.546	- 0.006
1	0	3/2 3/2	17 114.791	0.003
1	0	1/2 1/2	17 170.524	0.002
1	1	5/2 7/2	17 153.484	- 0.002
1	1	3/2 5/2	17 223.640	0.006
1	1	1/2 3/2	17 135.758	- 0.005
1	1	5/2 5/2	17 188.588	0.003
1	1	3/2 3/2	17 198.683	0.002
1	1	1/2 1/2	17 100.898	0.006
2	0	7/2 9/2	25 752.367 ^a	- 0.005
2	0	5/2 7/2	25 752.367 ^a	0.011
2	0	3/2 5/2	25 769.594	0.004
2	0	1/2 3/2	25 769.721	0.011
2	0	7/2 7/2	25 822.335	- 0.004
2	0	5/2 5/2	25 719.841	- 0.005
2	0	3/2 3/2	25 699.560	0.000
2	1	7/2 9/2	25 748.045	0.002
2	1	5/2 7/2	25 765.466	0.004
2	1	3/2 5/2	25 765.974	0.002
2	1	1/2 3/2	25 748.393	- 0.011
2	1	7/2 7/2	25 800.564	0.002
2	1	5/2 5/2	25 741.016	- 0.003
2	1	3/2 3/2	25 713.530	- 0.003
2	2	7/2 9/2	25 735.018	0.003
2	2	5/2 7/2	25 805.089	- 0.006
2	2	3/2 5/2	25 755.143	- 0.006
2	2	1/2 3/2	25 685.240	- 0.003
2	2	7/2 7/2	25 735.107	- 0.011
2	2	5/2 5/2	25 804.941	0.002
2	2	3/2 3/2	25 755.347	- 0.007
3	0	9/2 11/2	34 338.595 ^a	- 0.005
3	0	7/2 9/2	34 338.595 ^a	0.004
3	0	5/2 7/2	34 346.666	0.000
3	0	3/2 5/2	34 346.706	0.009
3	0	9/2 9/2	34 408.558	0.000
3	0	7/2 7/2	34 314.158	0.002
3	0	5/2 5/2	34 276.671	0.004
3	1	9/2 11/2	34 336.367	0.010
3	1	7/2 9/2	34 343.315	- 0.006
3	1	5/2 7/2	34 346.959	0.001
3	1	3/2 5/2	34 339.925	- 0.010
3	1	9/2 9/2	34 395.841	0.001
3	1	7/2 7/2	34 322.515	0.000
3	1	5/2 5/2	34 287.500	0.005
3	2	9/2 11/2	34 329.610	- 0.007
3	2	7/2 9/2	34 357.544	- 0.009
3	2	5/2 7/2	34 347.818	0.002
3	2	3/2 5/2	34 319.727	0.002
3	2	9/2 9/2	34 357.651	- 0.006
3	2	7/2 7/2	34 347.665	0.005
3	2	5/2 5/2	34 319.924	- 0.006
3	3	9/2 11/2	34 318.352	- 0.000

^a not resolved.

J	K	$F \rightarrow F'$	ν_{obs}	obs-calc
3	3	7/2 9/2	34 381.414	0.007
3	3	5/2 7/2	34 349.184	0.003
3	3	3/2 5/2	34 286.308	0.006
3	3	9/2 9/2	34 293.926	0.006
3	3	7/2 7/2	34 389.792	0.007
3	3	5/2 5/2	34 373.805	- 0.010

(χ_J , χ_K and χ_d are calculated to be $\chi_J = -0.9 \pm 0.8$ kHz, $\chi_K = 2.8 \pm 3.8$ kHz, $\chi_d = -1.8 \pm 1.6$ kHz). In the final fit they were set to zero.

The molecular constants, which were obtained from a least squares fit to the observed spectrum, are listed in Table 2.

Table 2. Molecular constants (all values in kHz) derived from a least squares fit to the spectrum of SiH₃⁸¹Br listed in Table 1. Uncertainties (in parenthesis) give one standard deviation and refer to the last figure quoted.

B	4292646.2	(4)
D_{JK}	29.19	(4)
D_J	1.81	(1)
eqQ	279825.	(5)
C_N	- 2.32	(40)
C_K	- 34.2	(11)

Table 3. ⁸¹Br nuclear magnetic shielding tensor elements in SiH₃⁸¹Br (in ppm) as calculated according to Eqs. (6), (7), and (8). The given uncertainties for σ paramagnetic arise from the single standard deviations for C_K and C_N . Uncertainties in the structure determination were neglected.

	σ total	σ paramagnetic	σ diamagnetic
σ_{\perp}	2789	- 430 (55)	3219
σ_{\parallel}	2874	- 277 (8)	3151
$\sigma_{\text{ov}} = 1/3 (\sigma_{\parallel} + 2 \sigma_{\perp})$	2817	- 379 (39)	3196
$\Delta\sigma = \sigma_{\perp} - \sigma_{\parallel}$	- 85	- 153 (63)	68

The Molecular Electric Dipolemoment

The molecular Stark effect has been measured for the transitions $J \rightarrow J' = 0 \rightarrow 1$, $F \rightarrow F' = 3/2 \rightarrow 3/2$ and $3/2 \rightarrow 5/2$ with $K = 0$, $\Delta K = 0$ and $\Delta M_F = 0$. Because the zero-field hyperfine splittings (see Table 1) are much bigger than the Stark splittings (see Table 4) the formula given by Fano¹³ for the weak field case was used to determine the dipole-moment from the observed Stark shifts. From the last column of Table 4 it is seen, that this works quite well except for the transition $J \rightarrow J' = 0 \rightarrow 1$, $F \rightarrow F' = 3/2 \rightarrow 5/2$, $K = 0$, $M_F = \pm 3/2$ where the

Table 4. Stark satellites of the $J \rightarrow J' = 0 \rightarrow 1$, $K = 0$, $F \rightarrow F'$, $\Delta M_F = 0$ transitions of SiH₃⁸¹Br.

$F \rightarrow F'$	V/cm^a	$\pm M_F$	$\Delta\nu/\text{MHz}$	obs-calc/MHz
$3/2 \rightarrow 3/2$	423.4	1/2	2.34	0.01
	635.1	1/2	5.33	0.08
	846.8	1/2	9.36	0.03
	1058.5	1/2	14.50	− 0.08
	423.4	3/2	3.80	− 0.01
	635.1	3/2	8.51	− 0.05
	846.8	3/2	15.06	− 0.16
	1058.5	3/2	23.67	− 0.11
$3/2 \rightarrow 5/2$	529.3	1/2	5.99	0.04
	635.1	1/2	8.55	− 0.01
	741.0	1/2	11.70	0.05
	846.8	1/2	15.19	− 0.03
	1058.5	1/2	23.81	− 0.03
	529.3	3/2	5.01	− 0.07
	635.1	3/2	7.09	− 0.23
	741.0	3/2	9.54	− 0.42
	846.8	3/2	12.18	− 0.83
	1058.5	3/2	18.96	− 1.37

^a The uncertainty in the electric field calibration is $\pm 0.2\%$.

observed shifts are systematically too small. They therefore have not been included in the fit. The dipolemoment was calculated by a least squares fit. Because deviations from the weak field case might become important at higher electric fields, the observed shifts have been weighted by the inverse of the applied field. The value of $|\mu| = 1.319 \pm 0.008$ D obtained in this fit is in good agreement with earlier

measurements (1.31 ± 0.03 D¹⁴ and 1.32 ± 0.03 D¹⁵). The spectrometer was calibrated using OCS with $\mu = 0.71521$ D as standard¹⁶.

Spin Rotation Coupling and Nuclear Magnetic Shielding for ⁸¹Br

The observed spin rotation coupling constants C_K and C_N (see Table 2) may be used to predict values for the hitherto unknown elements of the nuclear magnetic shielding tensor for the ⁸¹Br nucleus in H₃Si⁸¹Br, i.e. for $\sigma_{\parallel\text{Br}}$ and $\sigma_{\perp\text{Br}}$.

For the convenience of the reader we briefly recall the underlying theory. Within the phenomenological rotational Hamiltonian the presence of a nuclear magnetic moment at the k -th nucleus leads to the following contribution*:

$$\mathcal{H}_{kk} = -\boldsymbol{\mu}_k \cdot (\mathbf{1} - \boldsymbol{\sigma}_k) \cdot \mathbf{H} - \mathbf{I}_k \cdot \mathbb{M}_k \cdot \mathbf{J} \quad (3)$$

$$\begin{aligned} \boldsymbol{\mu}_k &= g_k \mu_N \mathbf{I}_k \text{ with } \mu_N = \frac{e\hbar}{2m_p c} \\ &= \text{nuclear magneton,} \\ g_k &= \text{nuclear } g\text{-factor } (g_k = 2.270^9) \text{ for } ^{81}\text{Br}, \\ \mathbf{I}_k &= \text{spin vector measured in units of } \hbar, \\ \boldsymbol{\sigma}_k &= \text{nuclear shielding tensor for the } k\text{-th nucleus,} \\ \mathbf{H} &= \text{vector of the exterior magnetic field } (\mathbf{H} = 0 \\ &\quad \text{for the present investigation),} \\ \mathbb{M}_k &= \text{spin-rotation coupling tensor for the } k\text{-th} \\ &\quad \text{nucleus.} \end{aligned}$$

For ⁸¹Br, situated on the symmetry axis of the H₃Si⁸¹Br molecule, \mathbb{M}_k is diagonal:

$$\mathbb{M}_k = \mathbb{M}_{\text{Br}} = \begin{pmatrix} M_{aa} & 0 & 0 \\ 0 & M_{bb} & 0 \\ 0 & 0 & M_{cc} \end{pmatrix} = \begin{pmatrix} M_{\parallel} & 0 & 0 \\ 0 & M_{\perp} & 0 \\ 0 & 0 & M_{\perp} \end{pmatrix}.$$

This leads to:

$$-\mathbf{I} \cdot \mathbb{M} \cdot \mathbf{J} = -\{I_a J_a (M_{\parallel} - M_{\perp}) + \mathbf{I} \cdot \mathbf{J} M_{\perp}\} \quad (4)$$

with the following matrix elements in the coupled basis:

$$\begin{aligned} -\langle F, I, J, K, M_F | \mathbf{I} \cdot \mathbb{M} \cdot \mathbf{J} | F, I, J, K, M_F \rangle &= -\frac{F(F+1) - I(I+1) - J(J+1)}{2J(J+1)} K^2 (M_{\parallel} - M_{\perp}) \\ &\quad - \frac{F(F+1) - I(I+1) - J(J+1)}{2} M_{\perp}. \end{aligned} \quad (5)$$

Comparison with Eq. (1.d) shows that C_K is equivalent to M_{\parallel}/\hbar and that C_N is equivalent to M_{\perp}/\hbar .

For the prediction of the shielding tensor from the measured M_{\parallel} and M_{\perp} values one needs the theoretical expressions for the \mathbb{M} and $\boldsymbol{\sigma}$ tensor elements. Within the rigid rotor model these are given by^{17, 18}:

* We note that our choice of sign for the spin rotation tensor is consistent with that in Ref.¹¹ whereas the opposite sign is used in Refs. 8, 9 and 17.

$$\sigma_{aak} = \frac{e^2}{2m c^2} \left[\langle 0 | \sum_{\epsilon}^{\text{electrons}} \frac{b_{\epsilon k}^2 + c_{\epsilon k}^2}{r_{\epsilon k}^3} | 0 \rangle \right. \\ \left. + \frac{1}{m} \sum_{n \neq 0}^{\text{excited states}} \frac{\langle 0 | \sum_{\epsilon} L_{a\epsilon k} | n \rangle \langle n | \sum_{\epsilon} \frac{L_{a\epsilon k}}{r_{\epsilon k}^3} | 0 \rangle + \langle 0 | \sum_{\epsilon} \frac{L_{a\epsilon k}}{r_{\epsilon k}^3} | n \rangle \langle n | \sum_{\epsilon} L_{a\epsilon k} | 0 \rangle}{E_0 - E_n} \right] = \sigma_{aak}^{(d)} + \sigma_{aak}^{(p)}, \quad (6)$$

$$M_{aak} = \frac{e \hbar g_k \mu_N}{c I_{aa}} \left[\sum_{\nu \neq k}^{\text{nuclei}} \frac{Z_{\nu} (b_{\nu k}^2 + c_{\nu k}^2)}{r_{\nu k}^3} \right. \\ \left. + \frac{1}{m} \sum_{n \neq 0}^{\text{excited states}} \frac{\langle 0 | \sum_{\epsilon} L_{a\epsilon k} | n \rangle \langle n | \sum_{\epsilon} \frac{L_{a\epsilon k}}{r_{\epsilon k}^3} | 0 \rangle + \langle 0 | \sum_{\epsilon} \frac{L_{a\epsilon k}}{r_{\epsilon k}^3} | n \rangle \langle n | \sum_{\epsilon} L_{a\epsilon k} | 0 \rangle}{E_0 - E_n} \right] = M_{aak}^{(\text{nuc.})} + M_{aak}^{(\text{el.})}. \quad (7)$$

The symbols have the following meaning (all quantities in cgs units) e = proton charge, m = electron rest mass, I_{aa} = molecular moment of inertia about the a -principal axis, Z_{ν} = atomic number of the ν -th nucleus, c = velocity of light, $\mathbf{r}_{\nu k} = (a_{\nu} - a_k) \cdot \mathbf{e}_a + (b_{\nu} - b_k) \mathbf{e}_b + (c_{\nu} - c_k) \mathbf{e}_c$ = vector pointing from the k -th nucleus to the ν -th nucleus ($\mathbf{e}_a, \mathbf{e}_b, \mathbf{e}_c$ = unit vectors in direction of the principal inertia axes), $b_{\nu k} = b_{\nu} - b_k$ etc.

$$L_{a\epsilon k} = (b_{\epsilon k} p_{c\epsilon} - c_{\epsilon k} p_{b\epsilon}) = \frac{\hbar}{i} \left(b_{\epsilon k} \frac{\partial}{\partial c_{\epsilon}} - c_{\epsilon k} \frac{\partial}{\partial b_{\epsilon}} \right)$$

operator corresponding to the a -component of the angular momentum of the ϵ -th electron relative to the spin carrying k -th nucleus.

From the known structure¹ and the measured M_{\parallel} - and M_{\perp} -values it is thus possible to calculate the perturbation sum in Eq. (7) which leads to the value of $\sigma^{(p)}$ in Equation (6). The diamagnetic contribution $\sigma^{(a)}$ which involves the average over the spatial electron distribution in the electronic ground state, may in principle be calculated from the knowledge of the ground state molecular wavefunctions. Instead we will use the empirical approach by Gierke and Flygare¹⁹. Within this approach we approximate $\sigma^{(d)}$ by:

$$\sigma_{aak}^{(d)} = \bar{\sigma}_{aak}^{(d)} + \frac{e^2}{2m c^2} \sum_{\nu \neq k}^{\text{nuclei}} \frac{Z_{\nu}}{r_{\nu k}^3} (b_{\nu k}^2 + c_{\nu k}^2) \\ + \frac{e^2}{2m c^2} \sum_{\nu \neq k}^{\text{nuclei}} \left(\frac{2}{3} \frac{\langle Q^2 \rangle_{\nu}}{r_{\nu k}^3} - \frac{(b_{\nu k}^2 + c_{\nu k}^2) \langle Q^2 \rangle_{\nu}}{r_{\nu k}^5} \right) \quad (8) \\ \text{(and cyclic permutations),}$$

where the necessary parameters $\bar{\sigma}_{aak}^{(d)}$ and $\langle Q^2 \rangle$ are taken from Ref.¹¹, Tables XIII and XIV. In Eq. (8)

the first and most important term is the free atom contribution ($\bar{\sigma}_{aak}^{(d)} = 3121$ ppm). The second term is the contribution of the electrons assigned to the different atoms in the molecule if they were replaced by point charges at the positions of the nuclei. The third term, called "quadrupole term", arises because the electronic charge distribution on the ν -th nucleus is not a point charge but is spatially extended. For $\sigma_{\parallel \text{Br}}^{(d)}$ its contribution is only 4 ppm. The "dipole term" (part III in Eq. (14) of Ref.¹⁹) was neglected because no $\langle \rho \rangle$ -values for Si are available at present. Since in general the dipole contributions are found to be quite small (less than a few ppm), its neglect appears to be tolerable. In Table 3 we have listed the thus predicted diamagnetic, paramagnetic and average nuclear shielding tensor elements.

In a subsequent paper on the molecular rotational Zeeman effect of H₃Si⁸¹Br we shall compare the values of the nuclear magnetic shielding tensor as determined there with those predicted here.

Discussion

From the value of $C_N = -13.2$ kHz given for CH₃⁸¹Br²⁰ it is possible to calculate the paramagnetic contribution to the nuclear shielding tensor of CH₃⁸¹Br. Using Eq. (8) we calculate $\sigma^{(p)} = -882$ ppm. It is now realized that $\sigma^{(p)}$ is more than twice as big for CH₃Br than for SiH₃Br. Since both molecules have a similar structure:

$$r(\text{C-Br}) = 1.939 \text{ \AA}^{21}, \quad r(\text{Si-Br}) = 2.210 \text{ \AA}^1,$$

this might be explained by an increase in the average electronic excitation energy in going from CH₃Br to SiH₃Br. In a recent study of the vacuum

UV-spectrum of SiH_3Br it has indeed been observed that the first electronic absorptions of SiH_3Br are higher in energy than the corresponding transitions in CH_3Br ²². The authors explain this by $d\pi - p\pi$ (Si-Br) interactions. Since these interactions are withdrawing electrons from the Br-nucleus towards the Si-atom, the matrix elements in the numerator of Eq. (6), which are weighted by the cubic inverse of the electron's distance from the Br-nucleus, are likely to become smaller again reducing the value of $\sigma^{(p)}$. Our results thus are in line with the idea of $d\pi - p\pi$ (Si-Br) bonding as it is proposed to explain the Si-Hal bond distances²³, UV-spectrum of

SiH_3Br ²² and ^{81}Br quadrupole coupling constant²⁶. These results contradict the results of CNDO/2 calculations and photoelectron spectroscopic data²⁵, which show no evidence of $d\pi - p\pi$ (Si-Br)-bonding.

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- ¹ R. Kewley, P. M. McKinney, and A. G. Robiette, *J. Mol. Spectry* **34**, 300 [1970].
- ² *Inorganic Synthesis*, Vol. XI, p. 159. McGraw-Hill Book Co., New York 1968.
- ³ R. H. Hughes and E. B. Wilson, Jr., *Phys. Rev.* **72**, 1265 [1946].
- ⁴ H. D. Rudolph, *Z. Angew. Phys.* **13**, 401 [1961].
- ⁵ U. Andresen and H. Dreizler, *Z. Angew. Phys.* **30**, 207 [1970].
- ⁶ F. Mönig, Diplom-Thesis, Freiburg 1963, p. 50—55; H. J. Tobler and A. Bauder, *Hs. H. Günthard, J. Sci. Instrum.* **42**, 236 [1965]; H. J. Tobler, H. U. Wemgler, A. Bauder, and Hs. H. Günthard, *loc. cit.* **42**, 240 [1965].
- ⁷ Z. F. Slawsky and D. M. Dennison, *J. Chem. Phys.* **7**, 509 [1939].
- ⁸ C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy*, Chapt. 6, 8. McGraw-Hill Book Co., 1955.
- ⁹ W. Gordy and R. L. Cook, *Microwave Molecular Spectra*, Chapter 9. Wiley-Interscience, New York 1970.
- ¹⁰ C. E. Miller, *J. Mol. Spectr.* **35**, 170 [1970].
- ¹¹ W. H. Flygare, *Chem. Rev.* **74**, 653 [1974].
- ¹² J. T. Houghen, *J. Chem. Phys.* **57**, 4207 [1972].
- ¹³ U. J. Fano, *J. Res. Natl. Bur. Std.* **40**, 215 [1948].
- ¹⁴ A. H. Sharbaugh, B. S. Pritchard, and V. G. Thomas, *Phys. Rev.* **79**, 189 [1950].
- ¹⁵ J. M. Mays and B. P. Dailey, *J. Chem. Phys.* **20**, 1695 [1952].
- ¹⁶ J. S. Muenther, *J. Chem. Phys.* **48**, 4544 [1968].
- ¹⁷ W. H. Flygare, *J. Chem. Phys.* **41**, 793 [1964].
- ¹⁸ N. F. Ramsey, *Phys. Rev.* **78**, 699 [1950].
- ¹⁹ T. D. Gierke and W. H. Flygare, *J. Amer. Chem. Soc.* **94**, 7277 [1972].
- ²⁰ J. Demaison, D. Boucher, J. Burie, and A. Dubrulle, *J. Mol. Spectry* **61**, 141 [1976].
- ²¹ W. Gordy, J. W. Simmons, and A. G. Smith, *Phys. Rev.* **74**, 243 [1948].
- ²² G. C. Causley, J. B. Clark, and B. R. Russel, *Chem. Phys. Lett.* **38**, 602 [1976].
- ²³ L. Pauling, *The Nature of the Chemical Bond*, Cornell, University Press, New York 1960, Chapter VII.
- ²⁴ Ref. ⁹, p. 588.
- ²⁵ W. B. Perry and W. L. Jolly, *Chem. Phys. Lett.* **17**, 611 [1972]; however see J. M. Howell and J. R. Van Wazer, *J. Amer. Chem. Soc.* **96**, 3064 [1974].
- ²⁶ Ref. ⁹, p. 588.