ABSOLUTE SHIELDING SCALE FOR ^{29}Si

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Simultaneous T_1 measurements for ^{29}Si and ^{1}H or ^{19}F in SiH_4 and SiF_4 gas lead to spin–rotation constants for ^{29}Si which provide shielding values $\sigma_0(^{29}Si, SiH_4) = 475.3 \pm 10$ ppm and $\sigma_0(^{29}Si, SiF_4) = 482 \pm 10$ ppm. The absolute shielding in Me_4Si liquid reference is 368.5 ± 10 ppm, with which ^{29}Si chemical shifts can be converted to absolute shielding. We find that the ^{1}H absolute shielding scale, the ^{19}F absolute shielding scale and the two completely independent determinations of the ^{29}Si shielding scale are all in agreement.

1. Introduction

The NMR chemical shift is a very sensitive probe of the adequacy of ab initio molecular calculations. Reasonably accurate calculations are now available for nuclei in the first row of the periodic table in molecules with 1–6 first-row atoms [1], and for hydrides of nuclei in the second row [2]. ^{29}Si is a nucleus of particular interest. Near Hartree–Fock basis sets have been used for ab initio calculations of the ^{29}Si shielding in SiF_4, SiF_5^-, SiF_6^{2-}, SiO_4^{4-}, and SiH_4 [3,4]. Smaller bases have been used for calculations on Si analogs of ethane, ethylene, and acetylene [5]. There are also a large number of semi-empirical calculations of ^{29}Si shifts or semi-empirical analyses of shifts using populations and charge densities from ab initio ground-state wavefunctions for a variety of molecules [6]. The motivation for the calculations on larger molecules is the large body of ^{29}Si chemical shift tensor data in $R_2Si{=}SiR_2$ [7] and in silicates, aluminosilicates and zeolites. Several correlations with Si–O–M bond angles, Si–O bond lengths, and number and types of –OM ($M \neq Si$) bonds have been useful for diagnostic applications [8] but a theoretical basis for these correlations is still elusive. The success of calculations on the simpler molecules SiH_4, SiF_4, and SiO_4^{4-} can only be gauged if an absolute shielding scale is known experimentally. Experimental chemical shifts are the observed *differences* in nuclear shielding. Thus, the SiH_4–SiF_4 chemical shift can be compared only with the *difference* between the theoretical shielding values of these molecules. On the other hand, if the shielding of ^{29}Si in one molecule (say SiH_4) were known absolutely, then the observed chemical shift between SiH_4 and any other molecule (such as SiF_6^{2-}) can be converted to an absolute shielding, which can then be compared directly with theoretical calculations on SiF_6^{2-}. Furthermore, the liquid reference (Me_4Si) can be placed on the same scale so that any experimental chemical shift tensor components can be converted to shielding components and compared with the results of ab initio calculations.

One standard technique of establishing an absolute shielding scale for nucleus M is by combining the results of two experiments. The first is an atomic beam magnetic resonance experiment or an optical pumping experiment which measures the ratio of γ for the M nucleus to γ for the electron in the free M atom. Since the electron γ can be calculated from the

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known electron magnetic moment and electronic g value of the atomic state, the value of γ(M, free atom) may be obtained precisely. The second is an NMR experiment which measures the ratio of the Larmor frequencies of M and ^{1}H in an infinitely dilute $M^{n+}_{(aq)}$ ion in aqueous solution. This provides the ratio $\gamma(^1H, H_2O, \ell)/\gamma(M, M^{n+}_{(aq)})$. The key here is that $\gamma(^1H, H_2O, \ell)$ is known precisely for pure liquid water from experiments [9] and is assumed to be the same in the infinitely dilute aqueous solution of $M^{n+}_{(aq)}$ ion, so $\gamma(M, M^{n+}_{(aq)})$ can be obtained. Then, from the definition of the nuclear magnetic shielding σ relative to the bare nucleus, $\gamma=(1-\sigma)\gamma_0$, where γ_0 is the magnetogyric ratio of the bare nucleus,

$$\frac{\sigma(\text{M, free atom})-\sigma(\text{M}, \text{M}^{n+}_{(aq)})}{1-\sigma(\text{M}, \text{M}^{n+}_{(aq)})} = 1-\frac{\gamma(\text{M, free atom})}{\gamma(\text{M}, \text{M}^{n+}_{(aq)})}\,. \tag{1}$$

Since σ(M, free atom) is theoretically known [10], the absolute shielding of M in the aqueous solution of $M^{n+}_{(aq)}$ is thereby established. This method has been applied to ^{111}Cd, alkali metal nuclei, ^{71}Ga, and ^{207}Pb, among others [11–13]. It is applicable when the aqueous solution of the metal ion is a convenient reference and extrapolation to infinite dilution is possible. The ratio γ(M, free atom)/γ(M, liq. ref.) has to be known to 1 part in 10^5 if the σ(M, liq. ref.) $-\sigma$(M, free atom) is to be determined to ± 10 ppm.

Another standard method of establishing an absolute shielding scale is based on the following relationships [14]:

$$\sigma=\sigma^{\text{p}}+\sigma^{\text{d}}\,, \tag{2}$$

$$\sigma^{\text{p}}=\sigma^{\text{SR}}-\frac{e^2}{3mc^2}\sum_{N'}\frac{Z_{N'}}{r_{N'}}\,, \tag{3}$$

$$\sigma^{\text{SR}}=\frac{m_{\text{p}}}{2m_{\text{e}}g}\frac{1}{3}\sum\frac{C_{\alpha\alpha}}{B_{\alpha\alpha}} = \frac{m_{\text{p}}}{2m_{\text{e}}g}\frac{C_{\text{av}}}{B} \quad \text{for a spherical top}\,, \tag{4}$$

for the isotropic average shielding. In eq. (3) the sum includes all other nuclei N' of charge $Z_{N'}e$ at distance $r_{N'}$. B is the rotational constant of the molecule, g is the nuclear g factor of the nucleus of interest, and m_{p} and m_{e} are the masses of the proton and electron.

The relationship (3) and (4) between the paramagnetic shielding σ^{p} and the spin–rotation constant C provides the absolute shielding since C can be measured independently, usually from MBER (molecular beam electric resonance) spectroscopy. Where C is known, eq. (3) gives the "experimental" σ^{p} for that nucleus in the molecule, which is then combined with an ab initio theoretical value of σ^{d}, if available. For example, the ^{13}C shielding scale has been established from spin–rotation constants measured by MBMR (molecular beam magnetic resonance) spectroscopy of ^{13}CO [15]. Otherwise, the Flygare approximation for the diamagnetic shielding may be used [16]

$$\sigma^{\text{d}}\approx\sigma(\text{free atom})+\frac{e^2}{3mc^2}\sum_{N'}\frac{Z_{N'}}{r_{N'}}\,, \tag{5}$$

so that

$$\sigma\approx\sigma^{\text{SR}}+\sigma(\text{free atom}) \tag{6}$$

and also, for a spherical top

$$\sigma_{\parallel}-\sigma_{\perp}\approx\frac{C_{\parallel}-C_{\perp}}{B}\frac{m_{\text{p}}}{2m_{\text{e}}g}\,. \tag{7}$$

In this paper we use a technique which we have introduced and tested in $^{13}CH_4$, $^{77}SeF_6$, and $^{125}TeF_6$ systems [17]. This method is applicable when M has spin 1/2 and spin relaxation in MH_n (or MF_n) in the *gas phase* is dominated by spin–rotation interaction for both M and ^{1}H (or ^{19}F).

The spin–rotation relaxation time under extreme narrowing conditions in the gas phase is given by [18]

$$\frac{1}{T_1}=\tfrac{2}{3}\times4\pi^2C^2_{\text{eff}}\langle J(J+1)\rangle\tau_J\,. \tag{8}$$

The method involves simultaneous measurement of $T_1(^{19}\text{F})$ or $T_1(^1\text{H})$, and T_1(M) in a gas sample of MF_n or MH_n. For nuclei in the *same* molecule in the same gas sample, the thermal average $\langle J(J+1)\rangle$ and τ_J are the same. Thus, the ratio of T_1 values gives the ratio of C^2 for the M nucleus to C^2_{eff} for ^{1}H (or ^{19}F) in the molecule. The C^2_{eff} in eq. (8) for spherical top molecules is [19]

$$C^2_{\text{eff}}=C^2_{\text{av}}+\tfrac{4}{45}C^2_{\text{d}}\,, \tag{9}$$

where C_{av} and $C_{\text{d}}=C_{\parallel}-C_{\perp}$ are the average and the anisotropy of the spin–rotation constant. Where the latter are known or can be determined independently, for ^1H or ^{19}F in the MH_n or MF_n molecule, C for the M nucleus can be obtained from the T_1 ratios. The value of C for the M nucleus then permits the calculation of σ from eqs. (4) and (6).

It is important that the T_1 measurements be carried out in the gas phase rather than in condensed phases. Only in the gas phase is there a clear relationship between the spin–rotation-dominated longitudinal spin relaxation times and the spin–rotation constants, independent of the buffer gas, the composition and total density of the sample, and the temperature. The several models which have been used in liquids do not provide such a unique relationship. Different models predict different relationships between spin–rotation and quadrupolar relaxation times of nuclei in the same molecule in liquids [20]. For example, T_1 studies in $SnCl_4$, $SnBr_4$, SnI_4 liquids yield ^{119}Sn shielding values which do not comprise a shielding scale that is consistent with the observed chemical shifts of these compounds [20], and T_1 studies in liquid $PbCl_4$ yield a shielding value for ^{207}Pb which is inconsistent with the results obtained for $Pb^{2+}_{(aq)}$ in solution using eq. (1) [20].

In this paper we establish the ^{29}Si shielding scale based on both SiH_4 and SiF_4 molecules. The absolute shielding of the neat liquid reference (Me_4Si) has also been determined.

2. Experimental

The technique is the same as that used to establish the ^{77}Se and ^{125}Te absolute shielding in SeF_6 and TeF_6 [17]. The nuclear spins (^1H, ^{19}F, and ^{29}Si) relax entirely by the spin–rotation mechanism in the gas phase so that the two nuclei k and k' in the same molecule are related by

$$\frac{T_1(k)}{T_1(k')} = \frac{C^2_{\text{eff}}(k')}{C^2_{\text{eff}}(k)} . \qquad (10)$$

Measurements were made in a Bruker AM-400 NMR FT spectrometer using a variable frequency probe tuned to ^{29}Si (79.4 MHz) in which the decoupling channel is tuned to either ^1H or ^{19}F. Inversion recovery experiments are programmed in both the observation and the decoupling channel for measurements in a sealed gas sample of about 40 amagat equimolar in SiH_4 and SiF_4 at 300 K. There was no evidence for chemical exchange. Using a gas mixture has two advantages. SiH_4 is an O_2 scavenger so that all traces of O_2 are scrupulously eliminated. Second, the observed ^{29}Si chemical shift between SiH_4 and SiF_4 in this sample is very close to the difference in σ_0 for these molecules. Since both molecules are observed in the same gas sample the bulk susceptibility contribution is identical for both molecules. The ^{29}Si nucleus is in the tetrahedral center of each, experiencing minimal change in its protected site, and in any case, SiH_4 and SiF_4 experience collisions with the same collection of molecules in the sample, therefore the intermolecular contributions to the shifts are nearly identical for ^{29}Si in both molecules. The results of these measurements are shown in table 1. We also measured the ^{29}Si chemical shift between SiH_4 and SiF_4, and corrected it to the zero pressure limit

$$\sigma_0(SiF_4) - \sigma_0(SiH_4) = 6.7 \pm 0.1 \text{ ppm} ,$$

and their chemical shifts relative to Me_4Si liquid.

The molecular parameters used in the calculations are shown in table 2. For ^1H in SiH_4, MBMR spectroscopy yields $C_{av} = 3.88 \pm 0.23$ kHz [22]. $C_{av}(^1H, SiH_4)$ can also be obtained from the ^1H nuclear shielding difference between SiH_4 and CH_4 in the limit of zero pressure. We measured these shifts in gas mixtures of CH_4 and SiH_4 and extrapolated to zero density in both

$$\sigma_0(^1H, SiH_4) - \sigma_0(^1H, CH_4) = -2.98 \pm 0.01 \text{ ppm} .$$

The absolute shielding for the proton nucleus in CH_4 is known: $\sigma_0(^1H, CH_4) = 30.611 \pm 0.024$ ppm [25], based on H atomic beam experiments. Thus

$$\sigma_0(^1H, SiH_4) = 27.63 \pm 0.03 \text{ ppm} .$$

Table 1
Spin relaxation times (s) and standard deviations

	SiH_4 gas	SiF_4 gas
$T_1(^1H)$	6.305 ±0.077	
$T_1(^{19}F)$	0.08778 ± 0.00074	0.5599 ± 0.0034
$T_1(^{29}Si)$		0.8867 ± 0.003
$T_1(^1H)/T_1(^{29}Si)$	71.83 ±0.27	
$T_1(^{19}F)/T_1(^{29}Si)$		0.6314 ± 0.0054

Table 2
Molecular and nuclear parameters used

	SiH_4	SiF_4
r_0 (Å)	1.4812	1.54 [d]
B (MHz)	8.5712×10^4 [a]	4.206×10^3
g	-1.1106 (^{29}Si)	
$C_a(^1H)$ (kHz)	3.88 ± 0.23 [b]	–
$C_d(^1H)$ (kHz)	9.0 ± 3.5 [b]	–
$C_a(^{19}F)$ (kHz)	–	2.42 ± 0.08 [b,e]
$C_d(^{19}F)$ (kHz)	–	2.22 [f]
σ(free atom) (ppm)	874.1 [c]	874.1

[a] Ref. [21]. [b] Ref. [22]. [c] Ref. [10]. [d] Ref. [23]. [e] Ref. [24]. [f] See text.

Used in eqs. (2)–(4) this gives $C_{av}=3.91$ kHz, which is well within the error estimates of Ozier's molecular beam results. We therefore use Ozier's value $C_{av}=3.88\pm0.23$ kHz. $C_d=C_\parallel-C_\perp$ is reported as 9.0 ± 3.5 kHz from the same MBMR spectrum. With this value, $C^2_{eff}(^1H)=22.25\pm2.25$ kHz^2. We can also calculate a value of $C_\parallel-C_\perp$ from the theoretical anisotropy in ^1H shielding in SiH_4, $\Delta\sigma=7.82$ ppm [26]. Using eq. (7) with $g(^1H)=5.58536$ and the rotational constant $B=8.5712\times10^7$ kHz [21] yields $C_\parallel-C_\perp=4.1$ kHz for ^1H in SiH_4. This value proves to be too small, since our data are most consistent with $C_\parallel-C_\perp=9.9$ kHz, which indicates that the anisotropy in the proton shielding should be closer to 19 ppm.

An accurate value of C_{av} has been measured (also by MBMR) for ^{19}F in SiF_4, 2.42 ± 0.08 kHz [22,24]. Using eqs. (2)–(4), this translates to $\sigma_0(^{19}F, SiF_4)=370$ ppm, which is in good agreement with the value 363.2 ± 6 ppm measured in the zero pressure limit and based on the absolute shielding in HF [27]. Only an upper limit for C_d has been determined ($\leqslant3$ kHz) [22]. Thus, we use $C^2_{eff}(^{19}F)$ obtained from the T_1 minimum in low density SiF_4 gas, $C^2_{eff}(^{19}F)=6.30\pm0.22$ kHz^2 [19]. This corresponds to $C_d=2.22$ kHz. The value of r_0 derived from electron diffraction data on SiF_4 is 1.54 Å [23], from which the rotational constant B is 4.206×10^6 kHz.

There is a very minor contribution to the relaxation of ^1H and ^{19}F from intramolecular dipole–dipole (DD) interactions. By assuming that the collision cross sections for SR and DD relaxation are the same, we can calculate the ratio of T_1^{-1}(DD) to T_1^{-1}(SR), which for ^1H in SiH_4 is 3.3×10^{-2}, and for ^{19}F in SiF_4 is 2.8×10^{-3}. Since T_1^{-1}(obs.) is the sum of $T_1^{-1}(SR)+T_1^{-1}(DD)$, then for SiH_4, this corresponds to $T_1(^1H, SR)=1.033T_1(^1H, obs.)$. For SiF_4, this corresponds to $T_1(^{19}F, SR)\approx1.003\times T_1(^{19}F, obs.)$. Using the experimental results shown in table 1 in eq. (10), we obtain $C(^{29}Si)=\pm40.6\pm5$ kHz, in SiH_4. Similarly, $C(^{29}Si)=\pm1.997\pm0.05$ kHz, in SiF_4. Using $g_{Si}=-1.1106$ and the theoretical value for the free Si atom 874.1 ppm [10], choosing positive signs for $C(^{29}Si)$ in both molecules we calculate from eqs. (4) and (6) $\sigma_0(^{29}Si$ in $SiH_4)=482.3\pm48$ ppm and $\sigma_0(^{29}Si$ in $SiF_4)=481.6\pm12$ ppm. The large quoted uncertainties in the individual ^{29}Si absolute shieldings for SiH_4 and SiF_4 which are obtained by this method arise primarily from the quoted uncertainties in the C^2_{eff} of ^1H and ^{19}F. It now appears that the error estimates by Ozier et al. are too large. The T_1 experiments in SiH_4 and SiF_4 provide two completely independent determinations of very nearly the same point (separated by only 6.7 ppm) on the ^{29}Si shielding scale. The coincidence of these two truly independent results is remarkable. Since a large part of $C^2_{eff}(^1H$ or $^{19}F)$ is the isotropic average $C^2_{av}(^1H$ or $^{19}F)$ which is directly related to $\sigma_{av}(^1H$ or $^{19}F)$, the values are constrained to be consistent with the absolute shielding scales of both ^1H and ^{19}F and also the 6.7 ppm ^{29}Si shielding difference between SiH_4 and SiF_4. We find all these conditions are satisfied well within more realistic error estimates of ±10 ppm. We therefore report the following as our best values of ^{29}Si shielding in these molecules:

$$\sigma_0(^{29}Si, SiH_4)=475.3\pm10\ \text{ppm}\,,$$

$$\sigma_0(^{29}Si, SiF_4)=482.0\pm10\ \text{ppm}\,.$$

The spin–rotation constants for ^{29}Si appropriate for these values of σ_0 are

$$C(^{29}Si, SiH_4)=41.3\pm1\ \text{kHz}\,,$$

$$C(^{29}Si, SiF_4)=1.995\pm0.05\ \text{kHz}\,.$$

Finally, the measured ^{29}Si chemical shifts in SiH_4 and SiF_4 gas relative to neat liquid Me_4Si lead to

$$\sigma(^{29}Si, Me_4Si, \ell, \text{sph})=368.5\pm10\ \text{ppm}\,.$$

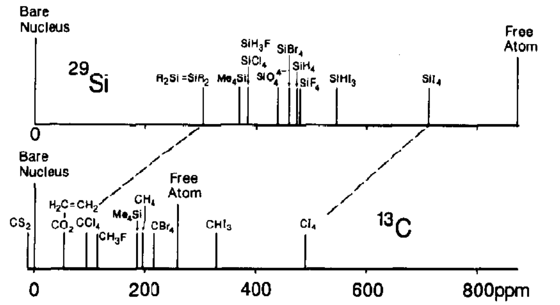

Fig. 1. Comparison of [13]C and [29]Si shielding in selected systems. Chemical shifts cited in refs. [7,28,29] have been converted to the absolute scale determined in this work, using Me_4Si(ℓ, sph) = 368.5 ppm.

In fig. 1 we compare the Si and C shielding scales. There is parallel behavior between analogous molecules in the two scales. The range of chemical shifts of Si is nearly the same as that of C, but their relationships to the diamagnetic shielding in the free atom relative to the bare nucleus are different. The parallel chemical shift behavior has been known for a long time, but the latter observation is only possible with a knowledge of the absolute scale.

Ab initio calculations of $\sigma_e(^{29}Si, SiH_4)$ yield 481.8 [26], 472.2 [4], and 499.5 ppm [2], which can be compared with our value $\sigma_0(SiH_4) = 475.3$ ppm. The calculated $\sigma_e(^{29}SiF_4) = 556$ ppm [3] is somewhat more shielded than our experimental $\sigma_0(SiF_4) = 482.0$ ppm. Our results allow us to calculate the paramagnetic term from eq. (4) which leads to an empirical value of $\sigma^p(^{29}Si) = -424.2$ ppm in SiH_4, to be compared with ab initio values −418.0 [26] and −427.7 ppm [4], and $\sigma^p(^{29}Si) = -611.7$ ppm in SiF_4, to be compared with the ab initio value −533 ppm [3]. Results of other ab initio calculations are shown in table 3. It appears that theory underestimates the paramagnetic shielding term in most [29]Si environments (except SiH_4) by about 75–115 ppm. Vibrational corrections which convert theoretical σ_e to experimental σ_0 values are expected to be too small to account for these discrepancies. Our estimates of vibrational corrections are based on theoretical derivatives of shielding $\sigma'(^{29}Si) = -17.1$ ppm $Å^{-1}$ and $\frac{1}{2}\sigma''(^{29}Si) = -113.4$ ppm $Å^{-2}$ in SiH_4 [2]. Mean bond displacements are estimated according to the method of ref. [32] from r_e values and the parameters of Herschbach and Laurie [33],

$$\langle \Delta r \rangle_{SiH} \approx 19.135 \times 10^{-3}\ Å \quad \text{at 300 K},$$

and from Cyvin's tables [34],

$$\langle (\Delta r)^2 \rangle_{SiH} \approx 7.8854 \times 10^{-3}\ Å^2 \quad \text{at 300 K}.$$

Table 3
Comparison with ab initio theoretical calculations of [29]Si shielding, all in ppm

Molecule A	$\delta = \sigma(Me_4Si, ℓ, sph) - \sigma(A)$	$\sigma(A) - \sigma(\text{free atom})$	Absolute shielding [a]	Theor. σ_e
SiH_4	−106.8 [b] −91.9 [c]	−398.8 [b]	475.3 [b]	499.5 [g] 481.8 [h] 472.2 [i]
SiF_4	−113.5 [b] −112.9 [d] −113.6 [e]	−392.1 [b]	482 [b]	556 [j]
SiF_5^-				619 [j]
SiF_6^{2-}	−187.0 [e]		555.5 670	668 [j]
SiO_4^{4-}	−71 [f]		439.5	529.5 [j]
Me_4Si(ℓ, sph)	0		368.5 [b]	

[a] Based on our value $\sigma_0(SiF_4) = 482 \pm 10$ ppm, and the δ values in column 2.
[b] This work. [c] Ref. [30]. [d] Ref. [28].
[e] Ref. [29]. SiF_6^{2-} based on $\sigma((NH_4)_2SiF_6$, satd. aq.$) - \sigma(SiF_4$, 30 atm gas$) = +74.3$ ppm.
[f] For the monomeric species in an aqueous solution of potassium silicate [31].
[g] Ref. [2]. [h] Ref. [26]. [i] Ref. [4]. [j] Ref. [3].

These lead to

$$\sigma_0(300\,\mathrm{K}) - \sigma_e \approx -4.9\ \mathrm{ppm}$$

for ^{29}Si in SiH_4 (and −0.3 ppm for ^1H in this molecule). The vibrational corrections for ^{29}Si in SiF_4 are probably comparable ($\sigma'(^{29}Si)$ is expected to have a larger magnitude and $\langle \Delta r \rangle$ is smaller), and are also too small to account for the 74 ppm difference between the ab initio σ_e value and our experimentally derived σ_0 value. Except for ref. [2], the shielding calculations cited in table 3 use a common gauge origin. Use of local origins in shielding calculations generally tend to improve agreement with experiment (see for example the review in ref. [1], and could very well improve the theoretical value of ^{29}Si shielding in SiF_4 by 50–100 ppm.

We have found that the two completely independent determinations of the Si shielding scale in this work are in agreement with the ^1H absolute shielding scale, the ^{19}F absolute shielding scale and also the Si chemical shift between SiH_4 and SiF_4 to better than ±10 ppm. The ^{19}F shielding scale is well established, with several independent determinations based on the spin–rotation constants in a number of small molecules agreeing with the chemical shifts in the zero-pressure limit. The ^1H shielding scale is also well established on the basis of hydrogen atomic beam data. It is satisfying to find that the Si shielding scale is consistent with these.

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[1] C.J. Jameson, Nucl. Magn. Reson. 16 (1987) 1.
[2] D.B. Chesnut and C.K. Foley, J. Chem. Phys. 85 (1986) 2814;
D.B. Chesnut, Chem. Phys. 110 (1986) 415.
[3] J.A. Tossell and P. Lazzeretti, J. Chem. Phys. 84 (1986) 369.
[4] P. Lazzeretti and R. Zanasi, J. Chem. Phys. 72 (1980) 6768.
[5] G. Fronzoni and V. Galasso, Chem. Phys. 103 (1986) 29.
[6] R. Wolff, R. Radeglia and J. Sauer, J. Mol. Struct. THEOCHEM 139 (1986) 113.
[7] K.W. Zilm, D.M. Grant, J. Michl, M.J. Fink and R. West, Organometallics 2 (1983) 193.
[8] E. Lippmaa, M. Magi, A. Samoson, G. Engelhardt and A.R. Grimmer, J. Am. Chem. Soc. 102 (1980) 4889;
G. Engelhardt and R. Radeglia, Chem. Phys. Letters 108 (1984) 271;
R. Radeglia and G. Engelhardt, Chem. Phys. Letters 114 (1985) 28;
A.R. Grimmer and R. Radeglia, Chem. Phys. Letters 106 (1984) 262.
[9] W.D. Phillips, W.E. Cooke and D. Kleppner, Phys. Rev. Letters 35 (1975) 1614;
T. Myint, D. Kleppner, N.F. Ramsey and H.G. Robinson, Phys. Rev. Letters 17 (1966) 405;
P.F. Winkler, D. Kleppner, T. Myint and F.G. Walther, Phys. Rev. A 5 (1972) 83.
[10] G. Malli and C. Froese, Intern. J. Quantum Chem. Symp. 1 (1967) 95.
[11] H. Krüger, O. Lutz, A. Schwenk and G. Stricker, Z. Physik 266 (1974) 233.
[12] J. Kodweiss, O. Lutz, W. Messner, K.R. Mohn, A. Nolle, B. Stutz and D. Zepf, J. Magn. Reson. 43 (1981) 495.
[13] O. Lutz and G. Stricker, Phys. Letters A 35 (1971) 397.
[14] W.H. Flygare, J. Chem. Phys. 41 (1964) 793.
[15] A.K. Jameson and C.J. Jameson, Chem. Phys. Letters 134 (1987) 461.
[16] T.D. Gierke and W.H. Flygare, J. Am. Chem. Soc. 94 (1972) 7277.
[17] C.J. Jameson and A.K. Jameson, Chem. Phys. Letters 135 (1987) 254.
[18] R.G. Gordon, J. Chem. Phys. 44 (1966) 228.
[19] J.A. Courtney and R.L. Armstrong, Can. J. Phys. 50 (1972) 1252.
[20] R.R. Sharp, J. Chem. Phys. 60 (1974) 1149; 57 (1972) 5321;
R.M. Hawk and R.R. Sharp, J. Chem. Phys. 60 (1974) 1009.
[21] I. Ozier, R.M. Lees and M.C.L. Gerry, Can. J. Phys. 54 (1976) 1094.
[22] I. Ozier, L.M. Crapo and S.S. Lee, Phys. Rev. 172 (1968) 63.
[23] S.R. Goates and L.S. Bartell, J. Chem. Phys. 77 (1982) 1866;
L.E. Sutton, ed., Interatomic distances, Supplement (Chem. Soc., London, 1965).
[24] I. Ozier, S.S. Lee and N.F. Ramsey, J. Chem. Phys. 65 (1976) 3985.
[25] W.T. Raynes, Nucl. Magn. Reson. 7 (1978) 1.
[26] R. Höller and H. Lischka, Mol. Phys. 41 (1980) 1041.
[27] C.J. Jameson, A.K. Jameson and P.M. Burrell, J. Chem. Phys. 73 (1980) 6013.
[28] H. Marsmann, Basic Princ. Progr. NMR 17 (1981) 65.
[29] R.B. Johannesen, F.E. Brinckmann and T.D. Coyle, J. Phys. Chem. 72 (1968) 660.
[30] U. Niemann and H.C. Marsmann, Z. Naturforsch. 30b (1975) 202.
[31] R.K. Harris, C.T.G. Knight and W.E. Hull, J. Am. Chem. Soc. 103 (1981) 1577.
[32] C.J. Jameson and H.J. Osten, J. Chem. Phys. 81 (1984) 4300.
[33] D.R. Herschbach and V.W. Laurie, J. Chem. Phys. 35 (1961) 458.
[34] S.J. Cyvin, Molecular vibrations and mean square amplitudes (Elsevier, Amsterdam, 1968).