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CONCURRENT ^{19}F AND ^{77}Se OR ^{19}F AND ^{125}Te NMR T_1 MEASUREMENTS FOR DETERMINATION OF ^{77}Se AND ^{125}Te ABSOLUTE SHIELDING SCALES

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^{77}Se and ^{125}Te absolute nuclear shieldings in SeF_6 and TeF_6 are determined from simultaneous T_1 measurements of ^{77}Se and ^{19}F (and ^{125}Te and ^{19}F) in the gas phase.

The nuclear shielding is a second-order molecular electronic property which provides a severe test of the accuracy of molecular quantum-mechanical calculations. While electric dipole polarizability and hyperpolarizabilities provide tests of the wavefunction at the outer regions, nuclear shielding is very sensitive, especially to contributions from high angular momentum functions, in the regions close to a particular nucleus.

Precise measurements of *differences* in shielding are easy to carry out in the liquid phase. In most NMR studies the resonance frequencies are measured and a chemical shift is defined as $\delta = (\nu_i - \nu_{\text{ref}})/\nu_{\text{ref}}$. From the relationship between the resonance frequency ν_i, the external magnetic field B_0, the magnetogyric ratio γ and the nuclear shielding σ_i,

$$\nu_i = (\gamma/2\pi)(1-\sigma_i)B_0,$$

we can write the chemical shifts in terms of the nuclear shielding

$$\delta = (\sigma_{\text{ref}} - \sigma_i)/(1-\sigma_{\text{ref}}) \approx \sigma_{\text{ref}} - \sigma_i \ .$$

Published δ values can be placed on a common scale if the chemical shifts between the references used to define δ are known.

Calculations of nuclear shielding can be compared with experiment in a relative sense, by taking differences between calculated σ values and comparing them with δ. A true assessment of calculated σ values can only be made if shielding values are known. In principle, to establish an absolute scale it is sufficient to find one molecule in which the shielding of a given nucleus is known. This has been done for ^{13}C using the CO molecule, for ^{31}P using PH_3, for ^{19}F using HF, for ^{17}O using CO, ^{15}N using NH_3 and ^{33}S using OCS [1–5]. In each case, molecular beam magnetic (or electric) resonance or high-resolution microwave spectroscopy provides the spin-rotation constant tensor of the nucleus in the molecule. When the gauge origin is chosen at the nucleus in question, there is a known relation between the spin-rotation constant and the paramagnetic part of the nuclear shielding. This permits calculation of the nuclear shielding if the diamagnetic part is also known [6]:

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

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

where

$$\sigma^{\text{SR}} = (m_{\text{p}}/2mg_k)\tfrac{1}{3}\sum_{\alpha=x,y,z} C_{\alpha\alpha}^{(k)}/B_\alpha \ ,$$

in which B_α are the rotational constants and $C_{\alpha\alpha}^{(k)}$ the spin-rotation tensor components of the kth nucleus along the inertial principal axes. For this choice of gauge origin it has been shown by Flygare that σ^{d} in a molecule can be approximated (to within a few ppm) by [7]

$$\sigma^{\mathrm{d}} = \sigma(\text{free atom}) + (e^2/3mc^2)\sum_{N'} Z_{N'}/r_{N'} \; .$$

Thus in this approximation

$$\sigma \approx \sigma^{\mathrm{SR}} + \sigma(\text{free atom}) \; .$$

To obtain the shielding we only need to measure $C_{\alpha\alpha}^{(k)}$ since the B_α are usually known.

Spin-rotation constants of any two nuclei in the same molecule can be related to one another provided that both nuclei relax entirely by the spin-rotation mechanism. In the gas phase, in the exchange narrowing limit, there is a single characteristic correlation time τ identical for both nuclei,

$$\tau = (\rho \bar{v} \sigma_J)^{-1}$$

according to Gordon's theory. Here ρ is the gas density, $\bar{v}$ the mean relative velocity of the molecules, and σ_J the cross section for changes in the molecular rotational angular momentum, characteristic of the "molecule–collision partner" pair and the temperature [8]. The nuclear spin relaxation time characteristic of this mechanism is given by [8]

$$(1/T_1)_{\mathrm{SR}} = \tfrac{2}{3}\langle J^2 \rangle C_{\mathrm{eff}}^2 \tau \; .$$

So that for two nuclei k and k' in the same molecule,

$$T_1(k)/T_1(k') = C_{\mathrm{eff}}^2(k')/C_{\mathrm{eff}}^2(k) \; .$$

For linear molecules $C_{\mathrm{eff}}^2 = C_\perp^2$. For spherical tops [9]

$$\begin{aligned} C_{\mathrm{eff}}^2 &= C_{\mathrm{av}}^2 + \tfrac{4}{45}(\Delta C)^2 \\ &= [\tfrac{1}{3}(2C_\perp + C_\parallel)]^2 + \tfrac{4}{45}(C_\parallel - C_\perp)^2 . \end{aligned}$$

A nucleus in the center of a spherical top is a favorable choice since all $C_{\alpha\alpha}^{(k)}$ are equal by symmetry and only C_{av}^2 enters into the relaxation expression. If both nuclei k and k' relax entirely by spin rotation, and if C_{eff}^2 is known for one nucleus, e.g., ^{19}F in SeF_6 or TeF_6 [10], then C_{av} for the central nucleus (and thus the shielding) can be obtained from the measured ratio of relaxation times in the gas phase. This is supported by our empirical observations in CH_4 in various buffer gases, in which the ratio of measured ^{13}C and ^{1}H relaxation times in the gas phase is independent of buffer gas, temperature, or density, and is within experimental error of the inverse ratio of C_{eff}^2 values from molecular beam data [11]. These molecular beam data, in turn, are consistent with the ^{13}C shielding scale (based on $C_\perp$ in CO) and the ^{1}H shielding scale (based on γ of the H atom).

It is also possible to determine C_{eff}^2 from the density dependence of T_1 in the region of the minimum [12]. However, for most systems, the minimum T_1 occurs at such low densities that such measurements are feasible only for ^{1}H and ^{19}F nuclei which have the highest NMR sensitivity, and which also have well-established shielding scales based on spin-rotation constants from molecular beam and high-resolution microwave measurements.

In this note we establish the ^{77}Se and ^{125}Te shielding scales by concurrent measurement of the ^{19}F and ^{77}Se (or ^{125}Te) spin relaxation times in SeF_6 (or TeF_6) molecules in the dilute gas phase. This method has not been used before although in a related method, ^{207}Pb and ^{119}Sn shielding scales were proposed using the T_1 of quadrupolar nuclei such as ^{35}Cl on the same molecule to calculate C_{eff}^2 of Sn or Pb by using relaxation theory in liquids to define the ratio of correlation times for quadrupolar and spin-rotation relaxation [13]. We have made the concurrent T_1 measurements in the liquid phase and show that the ratio of T_1 values differ from those found in the gas. We compare the Se and Te shielding scales with that of ^{33}S.

The sample is a sealed glass tube containing SeF_6 (or TeF_6) gas at 330 K. To minimize the sources of error, T_1 measurements are carried out under identical conditions, i.e., in the same sample in the same probe and at the same time. The "observe" channel of an IBM WP 200SY NMR spectrometer is tuned to either ^{77}Se (38.2 MHz) or ^{125}Te (63.3 MHz) using a broadband probe. The decoupling channel of this probe has been modified so that it can be tuned to ^{19}F (188.4 MHz) as well as to ^{1}H. The 90° pulse widths in both channels are determined under acquisition conditions, with the temperature controlled to better than $\pm 0.1°$. Inversion recovery experiments are set up in both channels with appropriate sets of delay times for the nuclei. Any systematic drift in spectrometer conditions during the long data acqui-

Table 1
Spin relaxation times (s) and standard deviations

	SeF_6 (gas)	SeF_6 (liq.)	TeF_6 (gas)	TeF_6 (liq.)
$T_1(^{19}F)$	7.81×10^{-2} (0.5%)	0.780 (0.7%)	0.132 (1.2%)	2.49 (0.5%)
$T_1(^{77}Se)$	6.54×10^{-2} (2%)	0.814 (0.8%)		
$T_1(^{125}Te)$			7.54×10^{-3} (2.3%)	0.160 (1%)
$T_1(^{19}F)/T_1(^{77}Se)$	1.19	0.96		
$T_1(^{19}F)/T_1(^{125}Te)$			17.5	15.6

sition period is converted to pseudo random errors by cycling, in which 1/8 of the total number of transients are taken and stored for each delay time for one nucleus and then the other. This constitutes one cycle. The next cycle goes through the delay list for one nucleus and then the other, acquiring the next eight, and so on. Thus, the ^{19}F T_1 experiment and the ^{77}Se (or ^{125}Te) T_1 experiment are done in the same sample *essentially simultaneously*. As a further check, one additional ^{19}F T_1 experiment is done before the beginning and another after the end of the entire acquisition period. The T_1 experiments were also conducted in the same way in samples of SeF_6 liquid and TeF_6 liquid at 296.2 K.

The experimental results are shown in table 1. The molecular and nuclear parameters used in the calculations are given in table 2. The free atom values used here are corrected for relativistic effects using interpolated values from relativistic calculations [16,17]. Only the magnitude of C can be obtained from our experiments (table 3). The signs are assigned on the basis of the σ values obtained. Defined with the gauge origin at the nucleus in question, σ^p is usually negative for most heavy nuclei. For SeF_6 the two possible values of σ^p which can be calculated from C are 1559.7 or −2160.7 ppm, from which we choose the latter i.e. $C(^{77}Se)$ is negative. For TeF_6 the two possible values of σ^p are 2570 or −3070 ppm and we

Table 2
Molecular and nuclear parameters used

	SeF_6	TeF_6	Ref.
r_0 (Å)	1.688	1.811	[14,15]
B_0 (MHz)	2.357×10^3	1.964×10^3	
g	1.0650 (^{77}Se)	−1.7648 (^{125}Te)	
$C_{av}(^{19}F)$ (kHz)	-4.46 ± 0.10	-2.44 ± 0.07	[10]
$\Delta C(^{19}F)$ (kHz)	4.47 ± 0.17	2.07 ± 0.17	[10]
σ(free atom) (ppm) [a]	3298 (Se)	6580 (Te)	

[a] Non-relativistic values of 2998 and 5362 ppm [16] for Se and Te were corrected for relativistic effects (estimated to be 300 and 1220 ppm respectively [17]).

Table 3
Calculated values for the M nucleus in MF_6

	^{77}Se in SeF_6	^{125}Te in TeF_6
C (kHz)	-5.086 ± 0.175	10.53 ± 0.49
est. error	3.5%	4.6%
σ^{SR}_{av} (ppm)	-1860 ± 64	-2790 ± 130
σ^{p}_{av} (ppm)	-2161 ± 64	-3070 ± 130
σ_{av} (ppm)	1438 ± 64 [a]	3790 ± 130 [a]

[a] Error does not include the uncertainty in the theoretical value of σ(free atom).

choose the latter, which with a negative $g(^{125}Te)$ implies that $C(^{125}Te)$ is positive. Although the relationship between σ^p and C is exact only for the rigid isolated molecule at its equilibrium configuration, we have used rovibrationally averaged values at room temperature for all quantities. The errors in σ associated with this are smaller than the rovibrational corrections to shielding (-8 and -9 ppm respectively for ^{77}Se and ^{125}Te in SeF_6 and TeF_6 [18]) since the vibrational corrections to C and σ^p tend to slightly increase the magnitudes of both.

Using the shielding values for ^{77}Se in $SeF_6(g)$ and ^{125}Te in $TeF_6(g)$ and the known gas-to-liquid shifts for SeF_6 and TeF_6 [18] we find the shielding for the reference liquids $\sigma(Me_2Se, \ell) = 2069$ ppm and $\sigma(Me_2Te, \ell) = 4333$ ppm. The ^{77}Se and ^{125}Te chemical shifts of selected systems [19,20] are shown in figs. 1 and 2. Incidentally, the large temperature dependence of the ^{77}Se shielding in $Me_2Se(\ell)$ makes it a less desirable reference than $SeF_6(\ell)$.

The Se and Te shielding scales are compared to ^{33}S [3] in fig. 3. We note parallel behaviour of SF_6, SeF_6, TeF_6 relative to the bare nucleus and free atom. The similarities between the Se and Te chemical shifts have been previously noted, a linear relationship between $\delta(Se)$ and $\delta(Te)$ in analogous compounds with a slope of 1.8 has been found [21]. This is reflected in fig. 3, although the factor which relates the respective shielding may be closer to 2.0. S and Se shifts in analogous compounds have also been compared [3]. We note in fig. 3 that the factor which

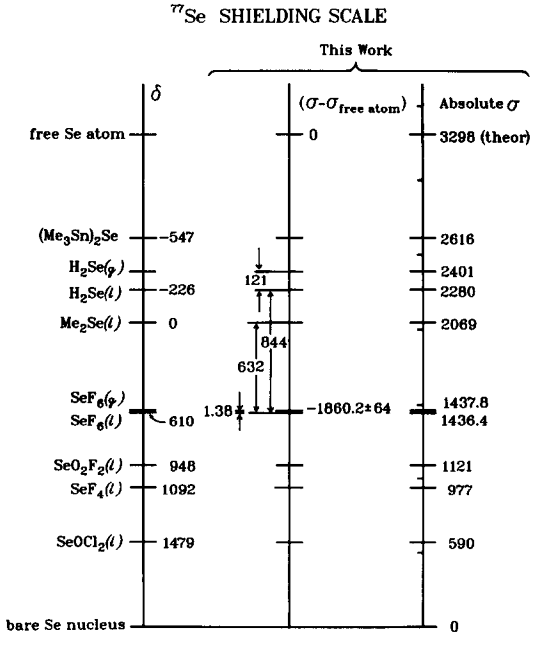

Fig. 1. ^{77}Se shielding scale. Chemical shifts (δ) are from ref. [19].

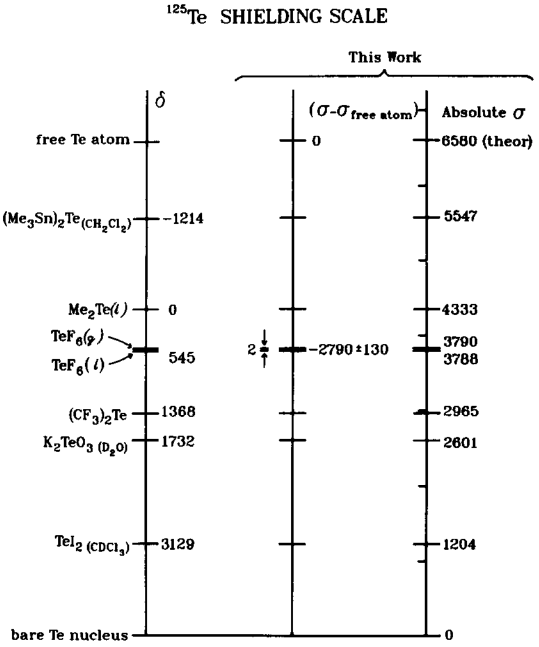

Fig. 2. ^{125}Te shielding scale. Chemical shifts (δ) are from refs. [19,20].

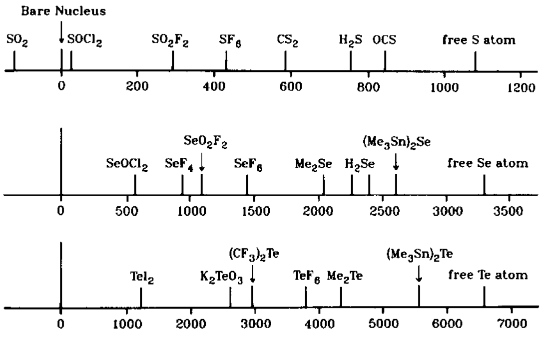

Fig. 3. Comparison of S, Se and Te shielding in selected systems. Chemical shifts from refs. [19,20] have been converted to the absolute scale dtermined in this work. The ^{33}S shielding scale is from ref. [3].

relates the shielding is close to 3.0.

Table 1 shows that $T_1(^{19}F)/T_1(^{77}Se)$ in the liquid phase is significantly different from that in the gas phase. The same is true for TeF_6. In both cases the measured ratio in the liquid is smaller than in the gas. It is known that $\sigma^F(\ell) < \sigma^F(g)$ for all molecules, also for TeF_6 and SeF_6. We have measured the gas-to-liquid shift for SeF_6, $\sigma^F(SeF_6, \ell) - \sigma^F(SeF_6, g) = -4.8$ ppm and $\sigma^{Se}(SeF_6, \ell) - \sigma^{Se}(SeF_6, g) = -1.38$ ppm [18]. If we assume that all of the shielding change in going from gas to liquid is in the paramagnetic term, the 4.8 ppm change in σ^F amounts to a 0.03 kHz change in C^F. On the other hand, 1.38 ppm change in σ^{Se} amounts to a 0.0038 kHz change in C^{Se}. The ratio $C^2_{eff}(^{77}Se)/C^2_{eff}(^{19}F)$ changes to 1.18 , which is indeed somewhat smaller than the 1.19 observed in the gas but not as small as the observed ratio in the liquid, 0.96. A similar calculation based on the observed $\sigma^F(TeF_6, \ell) - \sigma^F(TeF_6, g) = -5.4$ ppm and $\sigma^{Te}(TeF_6, \ell) - \sigma^{Te}(TeF_6, g) = -2.0$ ppm leads to a 0.03 kHz and 0.0075 kHz change in C^F and C^{Te}, giving a T_1 ratio of 17.1, somewhat smaller than the 17.5 observed in the gas, but not as small as 15.6 observed in the liquid. Therefore, the T_1 ratio in the liquid phase is different from that in the gas phase for reasons other than medium effects on the magnitudes of the spin-rotation constants. Two possible reasons may be:

(a) Spin rotation is no longer the only mechanism which should be considered in the liquid phase. Any contribution to T_1 from other mechanisms (such as dipole–dipole or anisotropic chemical shift) would make the T_1 ratio change from $C^2_{eff}(^{77}Se)/C^2_{eff}(^{19}F)$ to a smaller value, based on the γ and $\Delta\sigma$ values for ^{19}F being greater than for ^{77}Se.

(b) The spin rotation mechanism in the liquid phase is different from that in the gas phase. Unlike the dilute gas for which Gordon's theory has been demonstrated to work extremely well, liquid phase relaxation theory is still in the developing stages. In the liquid the correlation time τ may not necessarily be the same for both the ^{19}F and the ^{77}Se nuclei. Therefore, it is not appropriate to use liquid phase relaxation times for an accurate determination of spin rotation constants.

The conclusions are as follows:

In favorable systems, simultaneous measurements of T_1 of two spin-1/2 nuclei in the same molecule in the gas phase provides a means of determining the nuclear shielding scale of the second nucleus from that of the first. This method can be applied when the spin-rotation tensor of the first nucleus is independently known or can be calculated from its known shielding tensor. The latter can be obtained by measurement of the chemical shift anisotropy and the isotropic absolute shielding based on some primary reference (such as ^1H in H atom, ^{13}C in CO, ^{15}N in NH_3, ^{17}O in CO, ^{19}F in HF, ^{31}P in PH_3 or ^{33}S in OCS). In a linear molecule only the isotropic shielding is necessary since $\sigma_\parallel$ is entirely diamagnetic. For spherical tops the $(\Delta C)^2$ term is 4/45 times as small as the C^2_{av} term, so that even when ΔC and $\Delta\sigma$ are unknown an estimate may be adequate. An appropriate molecule in which two nuclei relax nearly exclusively by spin rotation in the gas phase effectively provides a bridge between the shielding scales in these nuclei.

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