Temperature dependence of ^{77}Se, ^{125}Te, and ^{19}F shielding and M-induced ^{19}F isotope shifts in MF_6 molecules

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The high resolution NMR spectra of ^{77}Se, ^{125}Te, and ^{19}F nuclei in SF_6, SeF_6, TeF_6, and WF_6 molecules are measured as functions of density and temperature in the pure liquid and in the dilute gas. The ^{19}F chemical shifts between the isotopomers of these molecules are observed in all but WF_6, and the $^{m'}MF_6$–$^{m}MF_6$ shifts exhibit a strict proportionality to the mass factor $(m'-m)/m'$.

INTRODUCTION

The ^{19}F shielding and its anisotropy in SF_6, SeF_6, and TeF_6 have been measured[1] and that of WF_6 has been estimated.[2] In this paper we study the temperature dependence of the ^{19}F shielding. We also find the isotope shifts in the ^{19}F signal due to the various isotopes of S(32,34), Se(74–82), and Te(122–130), and the temperature dependence of ^{77}Se and ^{125}Te chemical shifts in these molecules. The recent interest in these molecules is largely due to their high symmetry which makes them very good candidates for introduction of realistic models for stretching and bending anharmonicity[3] for comparison against electron diffraction studies of hot molecules.[4,5] NMR shifts with temperature are sensitive to these anharmonicities. The ^{19}F shielding in SF_6 in the zero-pressure limit[6] and its temperature dependence was previously interpreted by using a simple model for calculating the mean S–F bond length,[7,8] a model which successfully accounted for the electron diffraction data at high temperatures (298–1000 K).[5] The simultaneous availability of the temperature coefficient of chemical shifts and the isotope shifts in the M and X spectra of MX_6 molecules provides a test of anharmonic models. Unlike electron diffraction, NMR does not measure mean bond displacements and mean square amplitudes directly. On the other hand, the precision and accuracy of NMR measurements are superior to those of electron diffraction. Furthermore, by measuring temperature shifts and isotope shifts of both nuclei in the bond, it is possible to have a reasonable test of the anharmonic force field.

EXPERIMENTAL RESULTS

The experimental procedures are described in earlier work.[9] For each molecule (SeF_6, TeF_6, WF_6) the resonance frequencies are measured as a function of temperature in several pure gas samples of known densities. Data were taken at 75.3 and 188.4 MHz for ^{19}F, 38.2 MHz for ^{77}Se, and

TABLE I. Density coefficient of the chemical shift in dilute gas and in the liquid.

	$\sigma_1 = \lim_{\rho\to 0} (\partial\sigma/\partial\rho)_T$[a] ppm/amagat ^{19}F	$(\sigma_{LIQ} - \sigma_{VAP})$[a] at 300 K ppm		Effective σ_1[a,b] ppm/amagat		Polarizability[e] α 10^{-24} cm^{-3}
		^{19}F	M[c]	^{19}F	M[c]	
SF_6[d]	$-0.0156 + 2.13\times 10^{-2}(T-300)$ $T = 280$–390 K					6.505
SeF_6	$-0.0316 + 1.1\times 10^{-2}(T-300)$ $T = 320$–380 K	-4.8	-1.38	$-0.020 + 5.9\times 10^{-2}(T-300)$ $T = 250$–310 K	-0.007	7.73
TeF_6	$-0.0365 + 2.2\times 10^{-2}(T-300)$ $T = 320$–380 K	-5.4	-2.0	$-0.022 + 5.3\times 10^{-2}(T-300)$ $T = 240$–320 K	-0.01	9.00
WF_6	$-0.0374 + 8.6\times 10^{-2}(T-300)$ $T = 360$–380 K	-7.4		$-0.025 + 3.6\times 10^{-2}(T-300)$ $T = 300$–330 K		

[a] Corrected for bulk susceptibility. Measured in samples of density 3 to 30 amagat.
[b] Calculated using liquid denstities from Ref. 17, and vapor densities from Ref. 18.
[c] M nuclei observed were ^{77}Se and ^{125}Te.
[d] Reference 6.
[e] Reference 19.

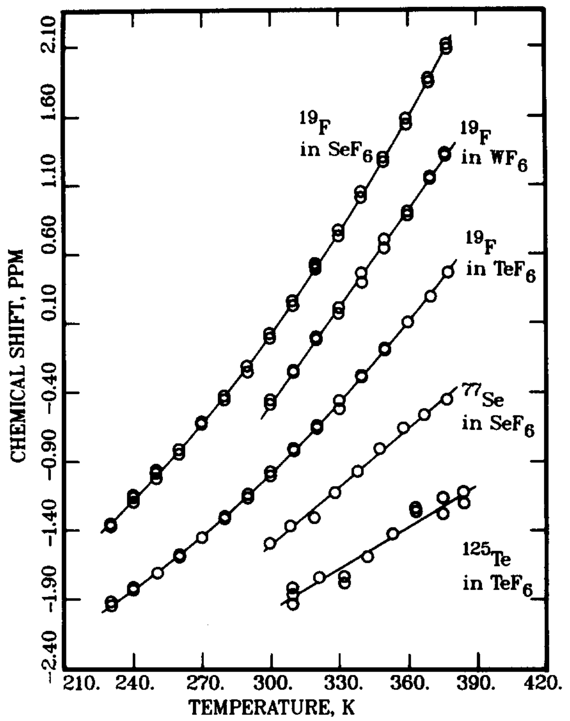

FIG. 1. Temperature dependence of the shielding in the zero pressure limit in gas samples of SeF_6, TeF_6, and WF_6, observed at 75.3 (^{19}F), 38.2 (^{77}Se), and 63.3 MHz (^{125}Te). The ordinate is "as is" for ^{19}F in SeF_6 only. The other plots have been displaced 0.5 ppm apart, for display.

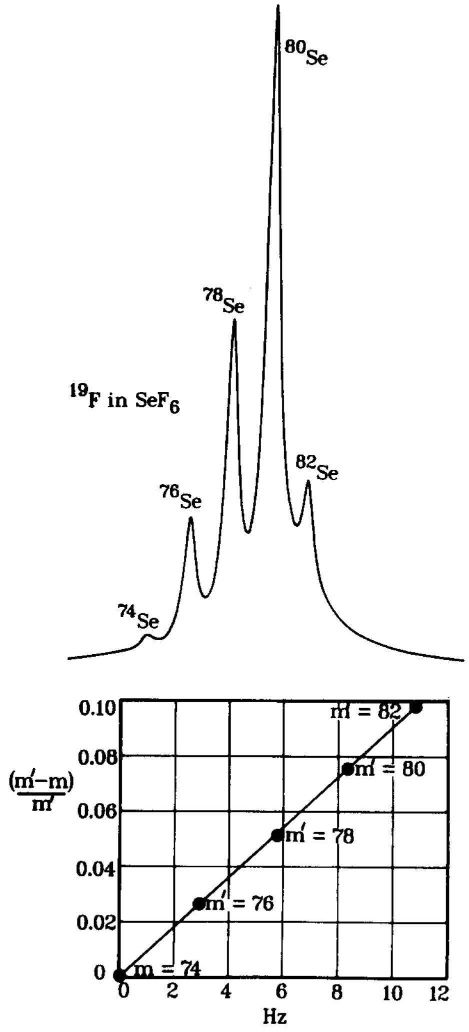

FIG. 2. ^{19}F spectrum in liquid SeF_6 at 300 K at 188.3 MHz, showing only the "center peak." ^{77}Se satellites are 1421 Hz apart (not shown). The intensities of the peaks for the isotopomers are consistent with the natural abundance of the Se isotopes. The isotope shifts between $^{m'}SeF_6$ and $^{m}SeF_6$ are plotted for $m = 74$.

25.3 and 63.3 MHz for ^{125}Te, using Bruker WP-80 and IBM WP-200 NMR spectrometers. The shifts in the nuclear resonance frequencies (NMR chemical shifts) are direct measures of the change in the nuclear magnetic shielding, $\sigma(T,\rho)$ in the gas phase. We obtain both $\sigma_0(T) - \sigma_0(300)$ and $\sigma_1(T)$ in

$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)\rho + \cdots \tag{1}$$

by separating out the density dependent part of the chemical shifts. The values obtained for $\sigma_1(T) = \lim_{\rho \to 0} (\partial\sigma/\partial\rho)_T$ (the second virial coefficient of nuclear shielding), shown in Table I, are typical of ^{19}F shielding and correlate roughly with the polarizability of the molecules. Analogous information can be obtained from the gas-to-liquid shift, which is obtained by observing both the vapor and liquid signals in a sample. $(\sigma_{LIQ} - \sigma_{VAP})/(\rho_{LIQ} - \rho_{VAP})$ gives an effective σ_1 value which is 60%–70% of the $\sigma_1(T)$ obtained from $\lim_{\rho \to 0} (\partial\sigma/\partial\rho)_T$ in dilute gas samples. It has been previously noted that the gas-to-liquid shifts give density coefficients of the chemical shift that are smaller in magnitude than dilute gas samples do.[10] The contribution to σ of the many-body terms which are not shown in Eq. (1) is opposite in sign to the binary term $\sigma_1(T)\rho$, so that the density coefficient in the liquid phase is smaller. Where sensitivity of the observed nucleus is low, gas-to-liquid shifts are the only sources of σ_1 information. Comparison of these two sources such as those in Table I shows the magnitudes of the errors associated with the use of gas-to-liquid shifts when $\lim_{\rho \to 0} (\partial\sigma/\partial\rho)_T$ cannot easily be obtained.

TABLE II. Temperature dependence of nuclear shielding in the zero pressure limit. $\sigma_0(T) - \sigma_0(300\text{ K}) = a_1(T-300) + a_2(T-300)^2$.

		a_1(ppm deg^{-1})	a_2(ppm deg^{-2})	T(K)
^{19}F	SF_6^{a}	-1.207×10^{-2}	-2.68×10^{-5}	280–380
	SeF_6	-2.29×10^{-2}	-5.0×10^{-5}	230–380
	TeF_6	-1.61×10^{-2}	-3.48×10^{-5}	230–380
	WF_6	-2.33×10^{-2}		300–380
^{77}Se	SeF_6	-1.40×10^{-2}		300–380
^{125}Te	TeF_6	-1.03×10^{-2}		310–380

[a] Reference 6.

The temperature dependence of the ^{19}F chemical shifts at the zero-pressure limit are obtained by removing the empirically determined density-dependent contributions from each data point. The residuals are shown in Fig. 1 and these can be described by the quadratic functions

$$\sigma_0(T) - \sigma_0(300) = a_1(T-300) + a_2(T-300)^2$$

shown in Table II.

The ^{77}Se and ^{125}Te chemical shifts are also temperature dependent in the zero-density limit, as shown in Fig. 1. For these central nuclei the temperature coefficients of the chemical shifts in the liquid phase are smaller than might be expected from their large chemical shift ranges. This is in marked contrast to ^{77}Se in H_2Se. The gas-to-liquid shift in the latter system is very large: $\sigma_{\text{LIQ}} - \sigma_{\text{VAP}} = -120$ ppm at 300 K, and the temperature dependence of the ^{77}Se signal in liquid H_2Se is fairly sizable too, about -0.25 ppm/deg.[11] For SeF_6, the ^{77}Se gas-to-liquid shift is -1.38 ppm at 300 K and for ^{125}Te in TeF_6 it is -2.0 ppm at 300 K. The temperature dependence of the ^{77}Se and ^{125}Te signals in the liquid SeF_6 and TeF_6 are -0.002 ppm/deg (280–320 K) and -0.002 ppm/deg (270–310 K), respectively. While the bent H_2Se structure leaves the two lone pairs of the Se atom exposed to intermediate interactions, the central ^{77}Se and ^{125}Te nuclei in SeF_6 and TeF_6 suffer much smaller intermolecular effects, of the order of -0.01 ppm amagat^{-1}. All these numbers have been corrected for bulk susceptibility effects.

The central ^{19}F signals in liquid SeF_6 and TeF_6 corresponding to the molecules containing zero spin Se and Te nuclei are shown in Figs. 2 and 3. The spectral resolution allows the determination of the ^{19}F chemical shifts of individual isotopomers of SF_6, SeF_6, and TeF_6, with the relative intensities of the peaks corresponding to the natural abundances of the various isotopes of Se and Te. The isotope shifts were measured relative to the molecule containing the most abundant isotope and then converted relative to the lowest mass isotopomer in Table III. The isotope shifts shown in Figs. 2 and 3 are plotted against the mass factor $(m' - m)/m'$ for $m = 74$ in SeF_6 and $m = 122$ in TeF_6. The perfectly linear relationships found here are similar to that obtained for ^{77}Se isotope shifts in $R_1{}^{77}\text{Se}^{m'/m}\text{SeR}_2$.[12,13] The isotope shift in SF_6 was also observed and is the same as previously reported.[14] $^1\Delta^{19}\text{F}(^{34/32}\text{S}) = \sigma(^{19}\text{F in } ^{32}\text{SF}_6) - \sigma(^{19}\text{F in } ^{34}\text{SF}_6) = -0.053$ ppm.

TABLE III. ^{19}F isotope shifts induced by S, Se, and Te isotopes.

	m'	$^1\Delta\ ^{19}\text{F}(^{m'/m}\text{M})$ ppm
$^{m'}SeF_6$	74	0
	76	−0.0154
	77	a
	78	−0.0301
	80	−0.0442
	82	−0.0576
$^{m'}TeF_6$	122	0
	123	−0.0012
	125	−0.0054
	126	−0.0088
	128	−0.0116
	130	−0.0148
$^{m'}SF_6$	32	0
	34	−0.053

[a] The $^1\Delta\ ^{19}\text{F}(^{80/77}\text{Se})$ has previously been reported as -0.021 ± 0.004 [T. Birchall, S. L. Crossley, and R. J. Gillespie, J. Chem. Phys. **41**, 2760 (1964)] which agrees with our results.

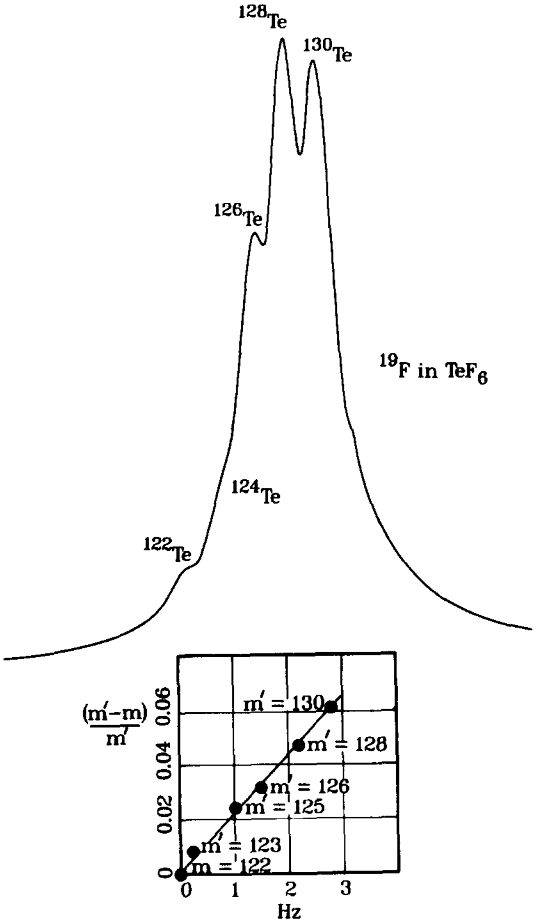

FIG. 3. ^{19}F spectrum in liquid TeF_6 at 300 K at 188.4 MHz showing the center peak. ^{123}Te and ^{125}Te satellites are 3082 and 3717 Hz apart (not shown). The isotope shifts are measured relative to $^{130}TeF_6$ and converted to shifts relative to $^{122}TeF_6$ for purposes of plotting vs $(m' - m)/m'$ with $m = 122$.

Finally, we compare the temperature coefficients of shielding $[d\sigma_0(T)/dT]$ of various binary fluorides at 300 K in Fig. 4. In general trend of increasing magnitude of the temperature coefficients with more deshielded ^{19}F environments in C–F bonds (fluoromethanes) has been reported.[15] In Fig. 4(a) we find a broadly similar trend when comparing different M–F bonds, despite the large differences in symme-

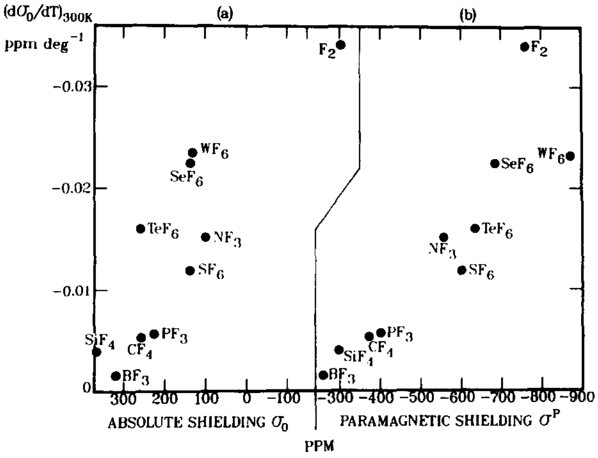

FIG. 4. Correlation of temperature coefficients of chemical shifts with (a) the absolute ^{19}F shielding and with (b) the paramagnetic term in the ^{19}F shielding (absolute shielding from Refs. 20 and 1, temperature coefficients from this work and Refs. 6 and 21, paramagnetic shielding from Refs. 1, 22, and 23 or calculated from absolute shielding from Ref. 20, this work, and diamagnetic shielding from Ref. 22).

try of the F environments. In the series of related molecules SF_6, SeF_6, and TeF_6, the $d\sigma_0/dT$ values for ^{19}F do not seem to change systematically with absolute shielding. These values do correlate with the paramagnetic term in the shielding, however. In Fig. 4(b) we see that an improved correlation is obtained with the paramagnetic contribution to shielding, which supports our earlier conclusions on the dependence of $d\sigma_0/dT$ on σ^p.[16]

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[1] S. K. Garg, J. A. Ripmeester, and D. W. Davidson, J. Magn. Reson. **39**, 317 (1980).

[2] I. Ursu, M. Bogdan, P. Fitori, A. Darabont, and D. E. Demco, Mol. Phys. **56**, 297 (1985).

[3] J. F. Stanton and L. S. Bartell, J. Phys. Chem. **89**, 2544 (1985).

[4] M. H. Kelley and M. Fink, J. Chem. Phys. **77**, 1813 (1982).

[5] S. R. Goates and L. S. Bartell, J. Chem. Phys. **77**, 1866, 1874 (1982).

[6] C. J. Jameson, A. K. Jameson, and S. M. Cohen, J. Chem. Phys. **67**, 2771 (1977).

[7] L. S. Bartell, J. Chem. Phys. **70**, 4581 (1979).

[8] C. J. Jameson, Mol. Phys. **40**, 999 (1980).

[9] C. J. Jameson, A. K. Jameson, and D. Oppusunggu, J. Chem. Phys. **81**, 1198, 2571 (1984).

[10] C. J. Jameson, A. K. Jameson, and D. Oppusunggu, J. Chem. Phys. **81**, 85, 2571 (1984); C. J. Jameson and A. K. Jameson, J. Magn. Reson. **62**, 209 (1985).

[11] H. J. Osten (unpublished results).

[12] C. J. Jameson and H. J. Osten, J. Chem. Phys. **81**, 4293 (1984).

[13] W. Gombler, J. Magn. Reson. **53**, 69 (1983).

[14] R. J. Gillespie and J. W. Quail, J. Chem. Phys. **39**, 2555 (1963).

[15] C. J. Jameson, Mol. Phys. **54**, 73 (1985).

[16] C. J. Jameson and H. J. Osten, Ann. Rep. NMR Spectrosc. **17**, 1 (1986).

[17] *Gmelin Handbook* (Springer, Berlin, 1984), including Se Supplement Vol. B2; V. V. Malyshev, Teplofiz. Vys. Temp. **14**, 47 (1976) (Engl. transl. pp. 41–47); **11**, 1010 (1973) (Engl. pp. 901–905).

[18] J. K. Shou and C. E. Hamrin, J. Chem. Eng. Data **16**, 37 (1971); *Landolt Börnstein Series 6* (Springer, Berlin, 1967), Vol. IV, 4a; D. Meixner, A. Heintz, and R. N. Lichtenthaler, Ber. Bunsenges. Phys. Chem. **82**, 220 (1978).

[19] Landolt-Börnstein, *Zahlenwerte und Funktionen* (Springer, Berlin, 1962), Vol. II, 8.

[20] C. J. Jameson, A. K. Jameson, and P. M. Burrell, J. Chem. Phys. **73**, 6013 (1980).

[21] A. K. Jameson, K. Schuett, C. J. Jameson, S. M. Cohen, and H. Parker, J. Chem. Phys. **67**, 2821 (1977).

[22] J. Mason, J. Chem. Soc. Dalton Trans. **1975**, 1426.

[23] D. W. Davidson, S. K. Garg, C. I. Ratcliffe, J. S. Tse, and S. R. Gough, Can. J. Chem. **62**, 1229 (1984).