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Effects of Intermolecular Interactions on ^{33}S Magnetic Shielding in Gaseous SF_6

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Density-dependent ^{33}S magnetic shielding has been measured for the first time. For pure gaseous SF_6 and its binary mixtures with Xe, CO_2 and NH_3 at 298 K, an increase in density linearly decreases the ^{33}S shielding constant of SF_6. This permits one to separate quantitatively the shielding contributions due to intermolecular interactions and the shielding parameter of an isolated SF_6 molecule. Spin−spin coupling in SF_6 ($^1J_{SF}$) has also been measured but only for gaseous samples of high densities. It was observed that the $^1J_{SF}$ coupling constant increases for more dense samples and that the increase is even more pronounced in liquid solutions. All of the new results can be used for an improved verification of ab initio calculations of sulfur shielding and spin−spin coupling in the SF_6 molecule because the new ^{33}S NMR measurements reveal the magnitudes of appropriate intermolecular effects.

Introduction

The nuclear magnetic shielding of a nucleus in a molecule is affected by both intermolecular interactions and intramolecular motion. In the gas phase, these effects are observed as a dependence of the shielding constant [$\sigma(T,\rho)$] on density and temperature

$$\sigma(T) = \sigma_o(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + ... \qquad (1)$$

where $\sigma_o(T)$ is the shielding for an isolated molecule and the higher terms [$\sigma_1(T)$, $\sigma_2(T)$, ...] are dependent on the density ρ and describe the intermolecular interactions in gases[1]. For most gaseous compounds at constant temperature, the shielding $\sigma(T)$ varies linearly with density[2] if the pressure of the gas does not exceed 40 atm. In such a case, $\sigma_2(T)$ and the higher-order coefficients in eq 1 can be safely ignored, and the remaining parameters, i.e., $\sigma_o(T)$ and $\sigma_1(T)$, can be precisely determined. Density-dependent shielding has been successfully measured for a large number of gaseous systems[3−5] but mostly for nuclei with no electric quadrupole moments. Recently, similar results have also been published for ^{17}O magnetic shielding.[6]

Sulfur-33 has a natural abundance of 0.76%, a nuclear spin number of $^3/_2$, and a relatively large quadrupole moment [−0.064 b, where 1 b (barn) = 10^{-28} m^2].[7] In numerous chemical compounds it leads to weak and very broad ^{33}S NMR signals. Wasylishen et al.[8] have shown that a molecule of sulfur hexafluoride (SF_6) has exceptional properties, as its octahedral symmetry almost completely reduces the electric field gradient at the sulfur nucleus and its ^{33}S half-width line is less than 1 Hz in the liquid state. A seven-line multiplet [$^1J(^{33}S, ^{19}F) = 251.8(2)$ Hz] was reported in this latter paper.[8]

In the gas phase, the ^{33}S NMR signal of SF_6 is extremely weak because of its low density, so heteronuclear decoupling and polarization transfer from the fluorine nuclei to sulfur are jointly required to observe the natural-abundance ^{33}S spectra in a reasonable time. Such a method has permitted us to observe precisely the ^{33}S NMR chemical shift for SF_6 in the gas phase as a function of density. In this study, we report for the first time the density-dependent ^{33}S nuclear shielding of pure gaseous SF_6 and its binary mixtures with xenon (Xe), carbon dioxide (CO_2), and ammonia (NH_3). Our results allow for a determination of the ^{33}S shielding constant of SF_6 free of intermolecular effects, e.g., extrapolated to the zero-density limit, and the influence of intermolecular interactions on the shielding in SF_6 in selected gaseous solvents. We also present new measurements of the spin−spin coupling between the ^{19}F and ^{33}S nuclei for pure SF_6 and for the solute gas in several liquid solvents. The preliminary results show the range of intermolecular effects in the latter coupling constant in SF_6, and therefore, the value of $^1J_{SF}$ can be found with better accuracy.

Experimental Section

Gas samples were prepared by condensation of the pure gases from the calibrated part of a vacuum line into 8.1-mm-o.d. (6.1-mm-i.d.) glass tubes (approximately 5.5 cm long), which were then sealed. The volumes of the sample tubes and the vacuum line were measured using mercury. Sulfur hexafluoride (99.75%, Aldrich), xenon (99.9%, Messer, Duisburg, Germany), carbon dioxide (99.8%, Aldrich), and anhydrous ammonia (99.99%, Aldrich) from lecture bottles were used without further purification to prepare samples. In the gaseous mixtures, the solute gas (SF_6) was kept at a low constant pressure (∼1.0 atm) and mixed with various quantities of the gaseous solvents Xe, CO_2, and NH_3 (approximately 1−15 atm). Samples containing liquid solvents were prepared in 5-mm-o.d. (3.3-mm-i.d.) glass tubes that were slightly longer (up to 9 cm), where the level of the liquid phase was 5.5 cm high. Liquid solvents were carefully dehydrated and degassed before SF_6 was added. The sealed gas samples were fitted into standard 10-mm-o.d. thin-walled NMR tubes (Wilmad 513-PP) filled with liquid DMSO-d_6 in the annular space. DMSO-d_6 was used for the lock system and as the external reference standard. Later, the chemical shifts were expressed relative to external 2 M aqueous Cs_2SO_4 solution. Three to five spectra were recorded for each sample to avoid

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accidental errors and to increase the precision of the measurements.

The spectra were measured on a Varian Unity Plus 500 spectrometer at 38.420 MHz using a 10-mm VT BB probe tunable in the range of 15−50 MHz. All measurements were carried out at a constant temperature of 298 K. The 4000−35 000 scans were coherently added to obtain a S/N ratio above 10. A relaxation delay of 0.5 s and an acquisition time of 1 s were used in all measurements. The 5000 FID complex points were zero-filled to 8192 time domain complex points and multiplied by a 2−10-Hz exponential line-broadening function prior to Fourier transformation. The refocused $^{33}S\{^{19}F\}$ INEPT sequence and heteronuclear decoupling were used to strengthen the weak SF_6 signal at low concentrations. Polarization transfer from ^{19}F to ^{33}S was accomplished according to the method proposed by Morris et al.[9]

$$\pi/2(^{19}\mathrm{F})_x - \Delta_1/2 - \pi(^{33}\mathrm{S})_x\,\pi(^{19}\mathrm{F})_x - \Delta_1/2 - \pi/2(^{19}\mathrm{F})_y\,\pi/2(^{33}\mathrm{S})_x - \Delta_2/2 - \pi(^{33}\mathrm{S})_x\,\pi(^{19}\mathrm{F})_x - \Delta_2/2 - \mathrm{FID}\,(^{33}\mathrm{S}) \quad (2)$$

To achieve the appropriate transfer amplitude, the delay Δ_1 should be optimized for maximum excitation of single quantum coherences of low-γ spin, i.e., for the spin $I = n/2$ to the first maximum of the function $\sin(\pi J\Delta_1)\cos^{n-1}(\pi J\Delta_1)$ (cf. Nanz et al.[10]). In the case of ^{33}S nuclei with $I = {}^3/_2$, Δ_1 was set to $0.196/{}^1J_{SF} = 0.78$ ms. Similarly, the optimal refocusing delay Δ_2, which is necessary for application of heteronuclear decoupling during acquisition, should be set to the first extreme of $\sin(\pi J\Delta_2)\cos^{m-1}(\pi J\Delta_2)$[11] for m equivalent spin-$^1/_2$ nuclei, which, in the case of $m = 6$ in SF_6, gives $\Delta_2 = 0.134/{}^1J_{SF} = 0.53$ ms. To evaluate the $^1J_{SF}$ coupling constant, the refocusing delay and ^{19}F decoupling were omitted.

Additionally, for measurements of the $^1J_{SF}$ coupling constant, 2D heteronuclear $^{33}S/^{19}F$ NMR spectra were recorded for the first time. As in the application of the INEPT technique to excite exclusively single-quantum ^{33}S coherence (selected by standard two-step phase cycling of both ^{33}S $\pi/2$ pulses), the constant delay for $^{33}S-^{19}F$ coupling evolution was set to $0.196/{}^1J_{SF} = 0.78$ ms.[10] A sample 2D spectrum is shown in Figure 1.

Results and Discussion

The ^{33}S magnetic shielding in gaseous sulfur hexafluoride (SF_6) was found to be density-dependent. In the present study, this effect was observed for pure SF_6 and three binary mixtures of SF_6 with xenon (Xe), carbon dioxide (CO_2), and ammonia (NH_3) as the gaseous solvents. At low density and constant temperature (298 K), the ^{33}S shielding in pure SF_6 slightly increases as the SF_6 density becomes larger. The dependence on density is linear, and according to eq 1, it implies a positive σ_1 coefficient (cf. $\sigma_1 = \sigma_{1AA}$ in Table 1). However, the σ_1 term consists of two contributions

$$\sigma_1(T) = (\sigma_1)_b + [\sigma_1(T)]_{int} \quad (3)$$

where $(\sigma_1)_b$ is the bulk susceptibility effect equal to $-(4\pi/3)\chi_M$ for a cylindrical sample parallel to the external magnetic field. The second term in eq 3 is exclusively due to intermolecular interactions, and its value is negative for pure SF_6 [cf. $\sigma_{1(A-A)}$ in Table 1]. This is consistent with numerous results for other nuclei, which show that intermolecular interactions have mostly a net deshielding effect on the nucleus in a molecule. Moreover, the linear dependence on density permits the precise determination of the shielding of an isolated molecule [$\sigma_0(298)$] when the results of NMR measurements are extrapolated to the zero-density limit. In this work, the ^{33}S shielding constant for SF_6 was measured relative to 2 M aqueous Cs_2SO_4 solution as the external reference standard, and its value, as shown in Table 1, is equal to 175.90(1) ppm. As seen, this sulfur shielding can be determined with high accuracy, and it is significant. The absolute ^{33}S shielding tensor of SF_6 can already be calculated using advanced ab initio methods,[12] as has been done for OCS.[13] The octahedral symmetry of the SF_6 molecule permits such calculations to be performed together with rovibrational corrections. The new scale of ^{33}S magnetic shielding can be based exclusively on accurate theoretical results, as has been done for ^{17}O shielding.[14] Then, the present $\sigma_0(298)$ parameter for SF_6 can be used as an excellent reference standard for further experimental applications in ^{33}S NMR spectroscopy. It is worth noting that some ab initio calculations of sulfur shielding in SF_6 have already been performed at the coupled Hartree−Fock (CHF) level. Using the IGLO (individual gauge for localized orbitals) method, Schindler obtained 408.7 and 388.6 ppm as the ^{33}S shielding constant of SF_6 for two different basis sets.[15]

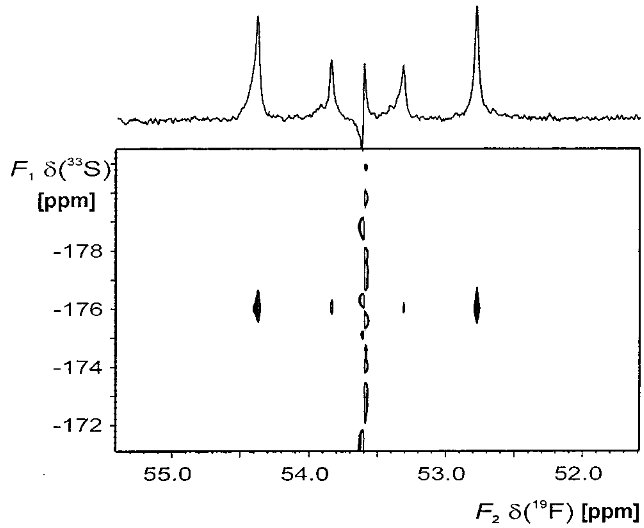

Figure 1. Expansion of a heteronuclear $^{33}S/^{19}F$ NMR correlation spectrum of gaseous SF_6 at high pressure (approximately 20 atm). The 2D spectrum was obtained by the application of the refocused $^{33}S-^{19}F$ HMQC technique. Sixteen scans were coherently added for each state TPPI data set for 180 t_1 increments. The maximum t_1 and t_2 times were 90 and 512 ms, respectively. A relaxation delay of 0.1 s was used. The data matrix containing 180 × 2048 complex points in t_1 and t_2 was zero-filled to 512 × 4096 complex points and apodized by a cosine function in both time domains prior to Fourier transformation.

TABLE 1: ^{33}S Magnetic Shielding in Pure Gaseous SF_6 and Its Binary Mixtures with Xenon, Carbon Dioxide, and Ammonia at 298 K

	solute (A)		gas solvent (B)	
parameter	SF_6	Xe	CO_2	NH_3
σ_0 (ppm)[a]	175.90(1)			
σ_{1XY} (ppm L mol^{-1})[b]	0.052(7)	−0.034(20)	−0.030(22)	−0.165(9)
$(\sigma_{1Y})_b$ (ppm L mol^{-1})[b,c]	0.184	0.191	0.087	0.068
$\sigma_{1(X-Y)}$ (ppm L mol^{-1})[b,d]	−0.132(7)	-0.225(20)	-0.117(22)	−0.233(9)
$\sigma_{1(X-Y)}$ (ppm mL g^{-1})[b,d]	−0.90(5)	−1.71(16)	−2.65(51)	−13.69(6)

[a] Relative to 2 M aqueous Cs_2SO_4 solution as the external reference standard. [b] X = Y = A for pure SF_6 and X = A, Y = B for binary mixtures. [c] $(\sigma_{1Y})_b = -(4\pi/3)\chi_M$, where χ_M is the molar susceptibility of the solvent gas (Y).[25] [d] $\sigma_{1(X-Y)} = \sigma_{1XY} - (\sigma_{1Y})_b$.

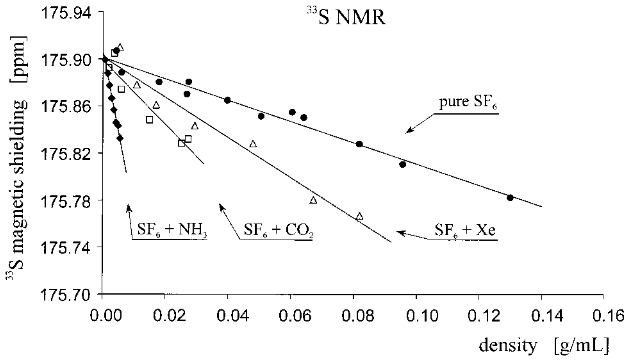

Figure 2. Density dependence of ^{33}S magnetic shielding in pure gaseous SF_6 and its binary mixtures with xenon, carbon dioxide, and ammonia relative to the sulfur-33 shielding in 2 M aqueous Cs_2SO_4 solution at 298 K. Densities refer to SF_6 for the neat solute gas and to the gaseous solvents (NH_3, CO_2, and Xe) in the binary mixtures where the density of SF_6 was kept low and approximately constant [$\rho(SF_6) =$ 0.006−0.007 g/mL].

At the CHF level of approximation, these results seem acceptable, but the CHF method does not include electron correlation, and for this reason, the latter theoretical results for SF_6 cannot be particularly accurate. Meanwhile, the ^{33}S shielding scale is based on the spin-rotation constant for OCS measured by molecular-beam experiments and Flygare's procedure.[16−19] This gives the absolute ^{33}S shielding in OCS equal to 843(12) in Wasylishen's original scale[8] or to the more reliable value of 817(12) ppm if the diamagnetic contribution of the shielding is better estimated.[13] Application of the present ^{33}S shielding scale remains limited because the appropriate $\sigma_0(T)$ parameter for OCS has never been measured. A linear OCS molecule gives poor ^{33}S measurements in the gas phase, as its NMR signal is weak, broad and strongly dependent on intermolecular interactions (cf. the large ^{33}S gas-to-liquid shift of OCS).[20] The absolute sulfur shielding of SF_6 can therefore be estimated as equal to 373 ppm (or 399 ppm in Wasylishen's original scale[8]) according to the existing experimental results. More advanced calculations of ^{33}S nuclear magnetic shielding in SF_6 are badly needed for improvement of the sulfur shielding scale.

For a binary mixture of gas A with gas B as the solvent, the density-dependent shielding in eq 1 can be rewritten as[1]

$$\sigma(T) = \sigma_o(T) + \sigma_{AA}(T)\rho_A + \sigma_{AB}(T)\rho_B + ... \qquad (4)$$

where ρ_A and ρ_B are the densities of A and B, respectively. According to eq 3, the coefficients $\sigma_{AA}(T)$ and $\sigma_{AB}(T)$ contain the bulk susceptibility corrections [$(\sigma_A)_b$, $(\sigma_B)_b$] and the $[\sigma_1(T)]_{int}$ terms taking account of intermolecular interactions during binary collisions of A−A and A−B molecules [$\sigma_{1(A-A)}(T)$ and $\sigma_{1(A-B)}(T)$, respectively]. In this study, the density of A (SF_6) in gaseous solutions was kept low and constant. The results of our ^{33}S shielding measurements are displayed in Figure 2, where the linear dependence on gas density (ρ_A or ρ_B) is clearly visible. However, the intermolecular effects are fairly modest, and it was necessary to change the units of density for better presentation of our results in Figure 2. The shielding data for SF_6 alone are available from observation of the pure solute gas. This has enabled us to determine all of the $\sigma_{AB}(298)$ and $\sigma_{1(A-B)}(298)$ shielding parameters with satisfactory precision, their values being given in Table 1. For the first time, it is possible to monitor precisely the influence of intermolecular interactions on the ^{33}S magnetic shielding in gases. It is worth comparing the magnitude of these effects with similar data available from previous ^{19}F NMR studies for SF_6 and its gaseous solutions. The sulfur $\sigma_{1(A-A)}(298)$ parameter is equal to −0.134(7) ppm L mol^{-1} (cf. Table 1), whereas the fluorine $\sigma_{1(A-A)}$ term is more significant, being −0.358(15) ppm L mol^{-1} at 303 K according to Mohanty et al.[21] or −0.397 ppm L mol^{-1} at 300 K according to Jameson et al. (as estimated from the original data accounting for the bulk susceptibility effect and the change of units).[22] Here, small differences in temperature are negligible when the cited results are compared. The observation can be extended to over the $\sigma_{1(A-B)}$ parameter if xenon is used as the gas solvent. The sulfur $\sigma_{1(A-B)}(298)$ parameter is less negative than the fluorine $\sigma_{1(A-B)}(303)$ parameter, being −0.223(20) and −489(16) ppm L mol^{-1},[21] respectively. It is obvious that the external fluorine nuclei in SF_6 are more exposed and more sensitive to interactions with other molecules than the sulfur nucleus. However, any simple explanation based on the geometrical structure of SF_6 molecule (e.g., the solute site factor[23]) can not provide an adequate description of intermolecular effects in nuclear magnetic shielding. An intermolecular shielding surface is needed to provide appropriate insights into the latter effects. The intermolecular shielding surface can be calculated by ab initio methods, but this requires enormous computational work, and for large molecules such as SF_6, such a procedure is still not viable in practice.

TABLE 2: $^1J_{SF}$ Spin−Spin Coupling Constant (Hz) for SF_6 from ^{33}S NMR Spectra at 298 K

SF_6 sample	^1J ($^{33}S-^{19}F$)
gaseous, ∼20 atm	250.1(4)
supercritical fluid[a]	251.4(2)
liquid	251.6(2), 251.8(2)[b]
in CS_2	253.1(2)
in n-C_5H_{12}, n-C_6H_{14}, C_6F_6, $[(CH_3)_3Si]_2O$, and CH_3CN	253.4(2)
in $(CH_3)_2CO$	253.8(2)
in CCl_4 and c-C_6H_{12}	254.0(2)
in C_6H_6 and $(CH_3)_2SO$	255.2(2)
in CH_3I	255.7(2)

[a] From ^{19}F NMR spectrum at 333 K and ∼44 atm. [b] At 295 K.[8]

Our present ^{33}S NMR study reveals that the spin−spin coupling between the ^{19}F and ^{33}S nuclei in SF_6 is also density-dependent, which signifies the modification of $^1J_{SF}$ by intermolecular interactions. However, in this case, the precision of the ^{33}S NMR measurements for gaseous samples has not been satisfactory enough to give the $^1J_{SF}$ spin−spin coupling constant free from intermolecular interactions. One can only presume that the $^1J_{SF}$ value extrapolated to the zero-density limit is probably below 250.0 Hz. Table 2 presents the results showing the increase of the $^1J_{SF}$ parameter when SF_6 samples are changed from gas to supercritical fluid and pure liquid. The increase is even larger when a small amount of SF_6 is dissolved in other liquids. It is worth noting that the $^1J_{SF}$ spin−spin coupling constant of an octahedral SF_6 molecule is not really constant; rather, its variations in liquid solvents easily exceed 5 Hz and do not correlate with permittivity (dielectric constant). The same increase in $^1J_{SF}$ (3.3 Hz) is observed for hydrocarbons such as n-pentane and n-hexane (ϵ = 1.84 and 1.87, respectively) as for acetonitrile (ϵ = 36.64), and the same effect (5.1 Hz) is observed for benzene (ϵ = 2.28) as for DMSO (ϵ = 47.24). For this reason, the change in $^1J_{SF}$ spin−spin coupling cannot be due to the different permittivities of the media, as has been suggested for other systems.[24]

Conclusions

Modern NMR techniques allow for the observation of weak ^{33}S signals in the gas phase. We have used this opportunity to observe density-dependent ^{33}S shielding in SF$_6$ for the first time. It is shown that the SF$_6$ molecule exhibits a unique ^{33}S NMR spectrum, which permits the sulfur shielding to be measured with high accuracy. Here, the appropriate $\sigma_0(298)$ parameter, representing shielding at the zero-density limit, is obtained with satisfactory accuracy and can be used as the origin of a future improved ^{33}S shielding scale. Generally, the intermolecular effects on ^{33}S shielding in SF$_6$ are modest and might be important for further applications. SF$_6$ is a fairly inert gas, and its ^{33}S signal decoupled from the ^{19}F nuclei can be easily used as the internal reference standard for other ^{33}S NMR measurements. The spin−spin coupling constant in SF$_6$ is also found to be dependent on intermolecular interactions, but quantitative measurements of $^1J_{SF}$ as a function of density are beyond our NMR capabilities. Altogether, our experimental study provides insight into the magnitude of intermolecular effects in ^{33}S shielding and spin−spin coupling in SF$_6$, and this knowledge might prove helpful for advanced ab initio calculations in this field.

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References and Notes

(1) Raynes, W. T.; Buckingham, A. D.; Bernstein, H. J. *J. Chem. Phys.* **1962**, *36*, 3481.

(2) Jameson, C. J. *Bull. Magn. Reson.* **1980**, *3*, 3.

(3) Govil, G. *Appl. Spectrosc. Rev.* **1973**, *7*, 47.

(4) Jackowski, K.; Raynes, W. T. *Mol. Phys.* **1977**, *34*, 465.

(5) Jameson, C. J. *Chem. Rev.* **1991**, *91*, 1375.

(6) Makulski, W.; Jackowski, K. *Chem. Phys. Lett.*, **2001,** *341*, 369.

(7) *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; p 625.

(8) Wasylishen, R. E.; Connor, C.; Friedrich, J. O. *Can. J. Chem.* **1984**, *62*, 981.

(9) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760.

(10) Nanz, D.; von Philipsborn, W. *J. Magn. Reson.* **1991**, *92*, 560.

(11) Pegg, D. T.; Doddrell, D. M.; Brooks, W. M.; Bendall, M. R. *J. Magn. Reson.* **1981**, *44*, 32.

(12) Helgaker, T.; Jaszuński, M.; Ruud, K. *Chem. Rev.* **1999**, *99*, 293.

(13) Jackowski, K.; Jaszuński, M.; Makulski, W.; Vaara, J. *J. Magn. Reson.* **1998**, *135*, 444.

(14) Sundholm, D.; Gauss, J.; Schäfer, A. *J. Chem. Phys.* **1996**, *105*, 11051.

(15) Schindler, M. *J. Chem. Phys.* **1988**, *88*, 7638.

(16) Flygare, W. H. *J. Chem. Phys.* **1964**, *41*, 793.

(17) Flygare, W. H.; Goodsman, J. *J. Chem. Phys.* **1968**, *49*, 3122.

(18) Gierke, T. D.; Flygare, W. H. *J. Am. Chem. Soc.* **1972**, *94*, 7277.

(19) Flygare, W. H. *Chem. Rev.* **1974**, *74*, 653.

(20) Jackowski, K. *J. Mol. Struct.* **2001**, *563−564*, 159.

(21) Mohanty, S.; Bernstein, H. J. *J. Chem. Phys.* **1971**, *54*, 2254.

(22) Jameson, C. H.; Jameson, A. K.; Cohen, S. M. *J. Chem. Phys.* **1977**, *67*, 2771.

(23) Rummens, F. H. A. *NMR Basic Principles and Progress* **1975**, *10*, 46.

(24) Åstrand, P.-O.; Mikkelsen, K. V.; Jørgensen, P.; Ruud, K.; Helgaker, T. *J. Chem. Phys.* **1998**, *108*, 2528.

(25) Angus, W. R.; Favède, J.; Hoarau, J.; Pacault, A. *Zahlenwerte und Funktionen*; Landolt-Börnstein Series; Hellwege, K. H., Hellwege, A. M., Eds.; Springer-Verlag: Berlin, 1967; Band II, Teil 10.